Highly distributed copper nanoparticles on carbon supports for methanol steam reforming

Dissertation
zur Erlangung des Doktorgrades
der Naturwissenschaften

vorgelegt der Fakultät für Chemie
der Ruhr-Universität Bochum
von

Nelli Muratova
aus
Almaty – Kasakstan

Bochum 2007
Referent: Prof. Dr. F. Schüth
Korreferent: Prof. Dr. M. Muhler
Tag der mündlichen Prüfung: 30.07.2007
Acknowledgments

First of all, I wish to thank Prof. Ferdi Schüth for giving me the opportunity to work in his group where I was able to greatly develop myself on both a professional and personal level. I am deeply grateful to him for all the motivation, advice and competent direction he provided for me. The catalysis seminars allowed me to extend my knowledge about the interesting and at the same time difficult topics, which would have been challenging to study alone. Besides the interesting dissertation theme, I gained much from the freedom I was given.

I would like to thank Massimilianno Comotti, Christian Baltes and Sascha Vukojević for the opportunity to work with them on such an exciting topic, stimulating discussions, for support and fruitful scientific collaboration over the past years. Dr. Inga Ritzkopf, Dr. Alberto Martinez-Joaristi, Nikita Ardentov and Dr. An-Hui Lu for initial help in my work and the fruitful discussions; Dr. Wolfgang Schmidt and Dr. Claudia Weidenthaler for sharing so many productive working hours. An important part of my actual knowledge about sorption and XRD has been strongly influenced by Dr. Schmidt. Dr. Weidenthaler advised me on XRD, and on how to work with huge the amounts of published knowledge. In addition, I would like to thank Christian Baltes for measuring the copper surface area.

I would like to thank as well Mr. Bernd Spliethof for the beautiful TEM-images; Mr. Axel Dreier likewise for the great TEM-images and Ms. Roswitha Barabasch for her invaluable help in the search for literature; the entire staff from the MPI für Kohlenforschung, because from many more or less hidden positions they have greatly contributed to excellent working conditions.
I wish to thank Dr. Elena-Lorena Salabaş for her warm welcome when I entered Prof. Schüth’s group and for her friendship which has developed during the past few years.

A very special thanks goes also to my other friends, and all former or present colleagues at the MPI, Mülheim, who participated actively during my years of study in Germany, and for the nice and communicative working atmosphere we had.

Finally, I wish to thank my family and my dear husband for their great support, understanding and endless patience.
1. Introduction

1.1. Motivation and Strategy

2. State of the art

2.1. Hydrogen production from methanol

2.1.1. Steam reforming of methanol

2.1.2. Catalysts for steam reforming of methanol

2.1.3. Relationship between bulk structure and activity of supported copper catalysts

2.1.4. Different metal oxides as promoters of the Cu/ZnO or Cu/ZnO/Al₂O₃ catalysts

2.2. Mesoporous materials

2.3. Synthesis of copper nanoparticles

2.4. Formation methods of small particles located within pore structures

3. Experimental

3.1. Materials preparation

3.1.1. Synthesis of SBA-15

3.1.2. Synthesis of CMK-3 or CMK-5 type carbons

3.1.3. Hydrogen peroxide treatment

3.1.4. Copper and zinc introduction in systems

3.2. Characterisation techniques

3.2.1. TEM (EDX)

3.2.2. Sorption

3.2.3. XRD
3.2.4. TPR……………………………………………………………………49
3.2.5. N₂O decomposition………………………………………………...49
3.3. Catalytic activity measurements……………………………………51
3.3.1. Description of methanol steam reforming apparatus set-up………..51
3.3.2. IR calibration, measurement……………………………………....53
3.3.3. Gas Chromatography……………………………………………54

4. Results and discussion

4.1. The carbon based Cu/CMK-3, Cu/CMK-5, Cu/Kugelkohle catalytic systems (TEM, XRD, TPR and sorption measurements)…………………..56
4.1.1. Influence of different copper precursors on catalytic activity……….57
4.1.1.1. Copper supported on hydrophobic CMK-5..........................58
4.1.1.2. Copper supported on hydrophilic CMK-5……………………....62
4.1.1.2.1. Effect of H₂O₂ treatment.............................................62
4.1.1.2.2. Impregnation with copper...........................................67
4.1.2. Influence of different pore sizes of CMK-5..............................72
4.1.2.1. Temperature programmed reduction.................................76
4.1.2.2. Influence on the synthesis route of the Cu/CMK-5 samples.................................................................79
4.1.3 Cu/CMK-3, Cu/Kugelkohle catalytic systems................................83
4.1.3.1. Specific surface area analysis of copper impregnated CMK-5, CMK-3 and Kugelkohle carbons..............................................87
4.1.3.2. Temperature programmed reduction..................................89
4.1.3.3. Adsorption measurements..............................................94
4.1.3.4. XRD measurements of copper particles supported on different mesoporous carbon.........................................................101
4.1.4. Cu/CMK-5, Cu/CMK-3 and Cu/Kugelkohle catalytic systems. Effect of copper loading on catalytic activity.....................................104

4.2. Influence of ZnO on catalytic activity of Cu/CMK-3, Cu/CMK-5, Cu/Kugelkohle.................................................................111
4.2.1. Specific surface analysis of copper and zinc impregnated CMK-5, CMK-3 carbons and Kugelkohle.............................................115
4.2.2. CO formation........................................................................116
4.2.3. Adsorption measurements..................................................117
Kurzzusammenfassung


Trotz der Abwesenheit von ZnO konnte eine beachtenswert hohe katalytische Aktivität der Kupfer-Nanopartikel bei der Dampfreformierung von Methanol beobachtet werden. Maximale Wasserstoffausbeuten von bis zu 97%, der vom industriellen Cu/ZnO/Al$_2$O$_3$ Katalysator bekannten, konnten mit Hilfe der Cu/Kohle-Katalysatoren erreicht werden. Sämtliche getesteten Katalysatoren zeigten nach einem Einsatz von 12h einen Aktivitätsabfall von weniger als 10%.
In einem nächsten Schritt wurde dem Cu/Kohle-System Zn als ein weiteres Element zugefügt, um dessen möglichen Einfluss beurteilen zu können. Im Vergleich zum reinen Cu/Kohle-System zeigten sämtliche Zn-haltigen Proben eine Abnahme der Wasserstoffproduktion. Eine Veränderung der CO-Bildung konnte hingegen nicht beobachtet werden. Folglich scheint das Zink einen negativen Effekt auf die Cu/Kohle-Katalysatoren zu haben. Die Rolle des Zinks im aktiven Katalysator ist aufgrund der Wechselwirkung mit dem Kupfer experimentell schwer nachzuvollziehen und bedarf weiterer mechanistischer Untersuchungen, die nicht im Rahmen dieser Arbeit durchgeführt werden können.
Abstract

The aim of this work is to study the catalytic properties and the role of copper in the steam reforming of methanol. This evaluation is quite difficult in the case of the well known commercial Cu/ZnO/Al₂O₃ catalysts since different phenomena overlap, and different active phases are likely to be present. Therefore, a material in which copper would only slightly interact with the support would be very suitable. Thus, production of hydrogen by methanol steam reforming has been studied over a series of Cu/carbon catalysts prepared by incipient wetness impregnation of ordered mesoporous carbons (CMK-5 and CMK-3) and activated carbon (Kugelkohle) supports. Catalytic activity was compared to that of a commercial Cu/ZnO/Al₂O₃ catalyst. Samples were characterised by X-ray diffraction, N₂-physisorption, transmission electron microscopy and temperature programmed reduction techniques. A copper loading up to 22 wt.-% was achieved, with particle sizes below 5 nm for the activated carbon and CMK-5 support, and 10 nm for the CMK-3 support, respectively. Carbon supported copper nanoparticles have shown remarkably high catalytic activity in the steam reforming of methanol despite the absence of ZnO. Maximum hydrogen yields of up to 97% of those achieved over an industrial Cu/ZnO/Al₂O₃ catalyst system were observed over the Cu/carbon catalysts. All catalysts have only shown a drop of activity of less than 10% after 12 h on stream, while no particle growth after the catalytic reaction was observed.

As a further investigative step zinc was added to the copper/carbon systems in order to establish the possible influence of this element on the activity of the resultant catalytic system. A decrease of the overall hydrogen production for all zinc containing catalysts in comparison with Cu/carbon materials was observed. There was no observed difference in CO formation over the Cu/ZnO loaded materials and Cu/carbon systems. Thus, zinc seems to have a negative effect on the catalytic performances of the Cu/carbon systems. However, a clear explanation of the role of this element in the working catalyst cannot be given so far.
Chapter 1

1.1. Motivation and Strategy

Hydrogen fuel cell systems are an extremely effective and environmentally friendly tool for the production of electric power due to the direct use of electrons resulting from a simple chemical reaction that forms only water from hydrogen and oxygen. [1] Hydrogen is one of the most promising energy carriers for the future. The lack of a hydrogen refueling infrastructure, combined with the complexity of storage and handling of the hydrogen, are the main drawbacks of applying direct hydrogen on-board storage. Furthermore, the weight of the hydrogen tank on board a vessel is 5-6 times greater than the weight of a tank for gasoline or diesel. [2] An alternative would be a direct methanol fuel cell (DMFC) which converts methanol directly to electricity, [3] or the on board hydrogen production from methanol. Processes for hydrogen production from methanol are steam reforming, [4-7] decomposition, [8,9] partial oxidation [10,11] and combined reforming (oxidative steam reforming). [12] In all the considered reactions, methanol steam reforming offers the highest hydrogen yield (75 vol.-%) and lowest CO concentrations. Furthermore, methanol steam reforming can be operated at mild conditions, e.g. atmospheric pressure and low temperature.

Until now copper-based materials are most frequently used for methanol steam reforming reactions. The traditional compositions of the commercially available copper-based steam reforming catalysts are variations of Cu/ZnO/Al₂O₃. [13,14] However, the commercial Cu/ZnO/Al₂O₃ catalyst does not fulfill the requirements satisfactorily, especially with respect to the long-term stability and desired low CO formation. In
particular, CO represents a poison for the Pt electrode of a fuel cell, where the maximum allowed concentration of this molecule is ca. 10 ppm. [15]

Steam reforming of methanol, synthesis of methanol and methanol decomposition have many features in common; essentially the copper is one of the active components catalysing these processes. From in situ studies of model Cu/ZnO systems, it is known that Cu$^0$-species represent the relevant active sites, which are dispersed in form of nanoparticles on the ZnO matrix. [16-18] However, the exact structure of the active species as well as the role of copper in working catalysts remains presently unknown, because most physicochemical studies cannot be undertaken under realistic reaction conditions. Thus, the literature is full of contradictory information about the most important parameters governing this reaction.

Recently, it was shown that colloidal copper nanoparticles have remarkably high catalytic activity in a quasi-homogeneous methanol synthesis reaction in absence of any solid support. [19] Based on this, we decided to study the influence of isolated Cu nanoparticles and Cu/ZnO particles in the methanol steam reforming reaction. One of the possible ways to protect Cu particles from agglomeration is to place them into a confined environment, which is usually present in ordered porous materials. The highest activity in steam reforming of methanol was observed for particles of 4-5 nm size up to 10 nm, [5,19] thus, from the available porous materials, mesoporous ones are preferred. CMK-5 ordered mesoporous carbon seems to be a good candidate for this purpose due to its narrow pore size distribution, fascinating regular structure and high surface area. [20] Furthermore, Cu placed on a carbon support is not in contact with any phases which could influence its activity. In comparison with ordered mesoporous silica, such as SBA-15, CMK-5 is hydrothermally stable, which is an important requirement to be fulfilled for the studied reaction. Moreover, the synthesis procedure for CMK-5, in comparison with other types of carbons, allows variation of the mesopores size, and thus via nanoparticle confinement to study the influence
of particle size on the reaction. In order to investigate the possible effect of the support on the Cu particle size, two other mesoporous carbons, CMK-3 and Kugelkohle, were used in this work.

The aim of this work is to provide the answers to the following questions:

- How to introduce copper in porous carbon support?
- Does the support have an influence on the copper size distribution?
- How does the reaction rate depend on the amount of copper?
- What is the role of zinc in methanol steam reforming, and how to introduce zinc in the Cu/Carbon systems?

With these aims, copper catalysts will be prepared by wetness impregnation of carbon with copper nitrate dissolved in ethanol, water, acetone, THF or with aqueous solution of copper acetyl acetonate, and will be tested in methanol steam reforming. Furthermore, morphology and other properties of the prepared samples will be studied by combining several techniques, such as X-ray diffraction, N\textsubscript{2}-physisorption, temperature programmed reduction and transmission electron microscopy. In addition, comparison will be made between samples obtained on various supports: CMK-5 with different pore diameters, CMK-3 and Kugelkohle. The influence of copper loading will be analyzed as well. In order to make the studied system more similar to the industrial catalyst Cu/ZnO/Al\textsubscript{2}O\textsubscript{3}, zinc will be introduced into the series of Cu/carbon materials. Thus, the effect of zinc on the system can be evaluated.
Chapter 2

State of the art

2.1. Hydrogen production from methanol

The advantages of using methanol as a hydrogen source are that steam reforming is operated at atmospheric pressure, low temperature and low amount of generated CO. Moreover, it has a high hydrogen/carbon ratio and contains no carbon–carbon bonds, thus reducing the risk of coke formation and catalyst fouling. Additionally, there are many sources for the production of methanol, such as natural gas, oil, coal, and biomass. Methanol is the fourth most produced chemical commodity after sulfuric acid, ammonia and ethylene, with a production in excess of 25 million tons. [21,22] Another advantage of using methanol as a hydrogen source is its start-up energy requirement. The start-up energy is the necessary energy to bring the fuel processor system from ambient temperature to an operating temperature where fuel cell quality hydrogen can be produced. The most obvious method for the generation of heat for the fuel processor operation is the combustion of the on-board fuel that is used to generate the hydrogen-rich fuel cell feed. To further compare the effect of fuels on starting up the fuel processor, the start-up energy as a function of fuel has been modeled. [23] The start-up energy was calculated for the fuels gasoline, natural gas, ethanol, methanol and dimethylether (DME) (Fig. 2.1). Due to the fact that methanol and DME have much lower autothermal reformer temperatures, and do not require water gas shift reactors they have much lower start-up energy requirements for the startup of their associated fuel processors in comparison with gasoline, methane and ethanol.
A compact fuel cell power generation system equipped with a micro hydrogen production system is expected to be able to be used as a power source for a wide variety of electronic devices. It is typical to apply such a system to portable devices, such as laptop, palmtop computers or portable telephones.

There are three process alternatives for production of hydrogen via the conversion of methanol:

1. Decomposition: \[ \text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO} \quad \Delta H_0 = 128 \text{ kJ mol}^{-1} \]
2. Partial oxidation: \[ \text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{H}_2 + \text{CO}_2 \quad \Delta H_0 = -155 \text{ kJ mol}^{-1} \]
3. Steam reforming: \[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2 \quad \Delta H_0 = 131 \text{ kJ mol}^{-1} \]

The decomposition reaction is the simplest process from a chemical point of view as methanol is solely used as feedstock. [24] However, the reaction is extremely endothermic which means that it requires additional energy to proceed. Furthermore, the decomposition results in a product as gas containing up to 67% hydrogen and 33% carbon monoxide. [8,9] The CO clean-up system is regarded to be the most complicated and expensive part of the fuel cell. Due to these drawbacks, the decomposition of methanol has been found to be unsuitable for fuel cell applications.
In contrast to the decomposition reaction, partial oxidation is a fast and exothermic reaction. The exothermic behaviour of this reaction has two consequences i.e., an additional energy supply for the reaction is not necessary, but due to the fast increase of temperature in the reactor hot spots can form, which can cause the deactivation of the oxidation catalyst through sintering of the metal particles. [25] The reaction pathway for production of hydrogen by partial oxidation of methanol is quite complicated. A number of different routes may contribute to conversion of methanol with oxygen and/or steam. Some of these are presented in Fig. 2.2, which shows the reaction network for different stoichiometries. [14] Hydrogen and carbon dioxide are the main products, while water and carbon monoxide are the only by-products formed in significant amounts. [10] Hydrogen concentration up to 67% in a product stream can be achieved when methanol is partially oxidized with pure oxygen in the feed.

**Fig. 2.2.** Reaction pathways for conversion of methanol with oxygen and/or steam at different stoichiometries [14].

Due to the absence of oxygen, the composition of the product gas from steam reforming of methanol is less complicated than that from partial oxidation. Without oxygen
present, the risk of surface oxidation is diminished and the active $\text{Cu}^0$ surface can be maintained.

The reformed gas contains hydrogen, carbon dioxide, unconverted methanol and water. Carbon monoxide is the only observable by-product, detected in small quantities when methanol is almost completely converted. Methanol steam reforming is considered to be the most favourable process of hydrogen production in comparison to the decomposition and partial oxidation of methanol. The reason for that is the ability to produce gas with high hydrogen concentration (75%) and high selectivity for carbon dioxide. As an additional energy supply one can use the heat of the exhaust gas. Another alternative to produce hydrogen from methanol is the combination of the partial oxidation with steam reforming. The advantage of this process is that the heat required for the reaction can be supplied by the reaction itself (autothermal reaction). However, the concentration of hydrogen in the product gas and methanol conversion are lower than in the methanol steam reforming. [26]

2.1.1. Steam reforming of methanol

The general reaction conditions of methanol steam reforming are as follows:

- reaction temperature: 250-300 °C
- pressure: 1 bar
- 1:1 to 1:1.3 molar ratio of methanol to water

The main products of methanol steam reforming are hydrogen and carbon dioxide; in addition, a small amount of carbon monoxide is produced in this process (up to 2 volume % in dry product stream when using a copper based catalyst). CO produced in the steam reforming reaction is a poison for the proton-exchange membrane (PEM) fuel cells, which are currently used, and as a result much attention has been focused on the mechanism of CO formation during the reaction. The reaction network for methanol steam reforming can be described by the following equations:
The methanol steam reforming reaction [eq. (1)] can formally be considered as a combination of water gas shift [eq. (2)] and methanol decomposition [eq. (3)] processes. Amphlett et al. [27] noted that carbon monoxide production is less than that predicted from the equilibrium composition. Peppley et al. [28,29] found that the methanol decomposition reaction is much slower than the steam reforming reaction. Furthermore, when water is added to the feed, methanol decomposes at lower temperatures. [8] It was shown by Breen et al. [25] that CO₂ and H₂ are the primary products of the reaction, with CO being formed at higher temperatures by the reverse water-gas shift reaction. It was indicated as well that CO was not formed at low contact times and that its concentration only became significant when the methanol was almost consumed at higher contact times. [6,25] The results from kinetic measurements provided evidence for a consecutive reaction scheme in which methanol and water react first to produce carbon dioxide and hydrogen [eq. (1)]. Then carbon dioxide and hydrogen react via the reverse water gas shift reaction [eq. (2)] to produce CO. [30] There was no evidence of the occurrence of the methanol decomposition reaction [eq. (3)]. Breen and Takahashi et al. [31] observed a small quantity of methyl formate with no formation of formic acid as an intermediate, and thus proposed the following reaction sequence for the catalyst:

\[
2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCHO} + 2\text{H}_2 \quad (4)
\]

\[
\text{CH}_3\text{OCHO} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{CH}_3\text{OH} \quad (5)
\]

\[
\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \quad (6)
\]

Jiang et al. [21,32] carried out a detailed kinetic analysis of the steam reforming reaction and found that the reaction over a Cu/ZnO/Al₂O₃ catalyst could also be explained by eq. (4)
– (6), they suggested that the carbon monoxide observed in the product stream is produced *via* the decomposition of methyl formate.

**2.1.2. Catalysts for steam reforming of methanol**

Methanol steam reforming is a heterogeneously catalyzed process with gaseous reactants and a solid catalyst. The catalysts used in this reaction are commonly based on copper and promoted with various metal oxides. The promoted copper catalysts are normally fixed on solid supports. The catalyst support has the function of increasing the surface area of the active component and also stabilizing the catalyst under reaction conditions, i.e., protecting against sintering of the metal particles. According to the stability of the metals proposed by Hughes, [33] copper is very susceptible to thermal sintering. Therefore, copper based catalysts typically contain one or more oxides that improve the stability, mainly by physically separating the copper crystallites. The steam reforming reaction \( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 \) can be regarded as the reversed methanol synthesis reaction. For the synthesis of methanol typically \( \text{CO}/\text{CO}_2/\text{H}_2 \) is used as the feed stock. Nevertheless, on the copper surface the \( \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \) reaction proceeds, while in the gas phase the reverse water-gas shift reaction, producing \( \text{CO}_2 \) from \( \text{H}_2\text{O} \) and \( \text{CO} \), takes place. [19] Therefore, it must be considered, that optimum catalysts for the methanol synthesis do not necessarily produce hydrogen to the same extent. The Cu/ZnO system has been studied extensively after reduction and under the reaction conditions of methanol synthesis. [34,35] However, the active Cu phase in the working catalyst is not fully elucidated yet.

Previously, differences in the reduction kinetics of CuO/ZnO were mainly studied by conventional temperature-programmed reduction (TPR) methods. [25,36] Nevertheless, these methods do not measure the structural evolution of the catalyst during reduction (*e.g.*, evolution of different bulk phases). Fierro *et al.* [37] studied the reduction of CuO/ZnO with
different Cu/Zn ratios and found a promoting effect of ZnO on the reducibility of CuO. Lower temperature reducibility is an indication of high copper distribution. Another function of ZnO is to hold the Cu crystallites in a dispersed state and thus maintaining a high surface area. [38,39] In contrast to this, several authors postulate that ZnO plays an active role either by stabilizing active Cu\(^{1+}\) species in the ZnO matrix or by creating synergetic effects with metallic copper sites. [40,41] Porta et al. [42] described an intermediary Cu\(_2\)O phase, however, the detection of Cu\(_2\)O is based on \textit{ex situ} investigations, which may not represent the “real” state of the Cu phase under reduction conditions. Some authors have proposed that the activity of the catalyst is influenced by the morphology and the structural disorder of the copper particles, or by incorporation of copper into ZnO. [43-46] The presence of Cu–Zn alloys was also recently suggested by Nakamura and co-workers. [41,46] It was shown, by \textit{in situ} extended X-ray absorption fine structure (EXAFS) studies under different reaction conditions, that the large changes in coordination numbers are not accompanied by large changes in the Cu–Cu distances. In fact, in all cases the Cu–Cu bond lengths are quite constant (2.56±0.03 Å) and agree well with the Cu–Cu bond length in metallic copper (\(R_{\text{Cu-Cu}}=2.55\) Å). The bond length for the copper-zinc samples was larger (2.66±0.03 Å). In some cases, results support a model were metallic copper is the active phase since the catalyst activity was only related to the copper metal surface area. [47] Copper-based catalysts for methanol synthesis/reforming can be divided into three groups: the binary systems Cu/Al\(_2\)O\(_3\) (I) and Cu/ZnO (II), and the ternary Cu/ZnO/Al\(_2\)O\(_3\) (III). [48-50] Classically prepared materials show a linear correlation between the copper surface area and synthesis activity, which increases from I to III. It was shown by Kurtz et al. [50] that a decrease in the catalytic activity is particularly pronounced for the Al\(_2\)O\(_3\)-free Cu/ZnO catalyst; Al\(_2\)O\(_3\) can be considered as a stabilizer for the Cu crystallites, preventing the Cu particles from sintering. Moreover, Al\(_2\)O\(_3\) was found to be a structural promoter for Cu/ZnO catalysts and the Cu/ZnO/Al\(_2\)O\(_3\) catalysts turned out to be far more active than the binary Cu/ZnO
catalysts. Addition of Zn to a co-precipitated Cu-Al$_2$O$_3$ sample and the deposition–precipitation into zinc oxide with a high specific surface area clearly underlines the importance of metal-substrate interactions, leading to highly active CuZnO$_x$ species under industrially relevant reaction conditions. A linear correlation was observed not only for the Cu/ZnO/Al$_2$O$_3$ catalysts but also Cu/MgO, Cu/Al$_2$O$_3$, Cu/MnO, and Cu/SiO$_2$. [49] The linearity of the relationship confirms the general assumption that a higher specific Cu surface area leads to a higher catalytic activity for each catalytic system. The influence of the precursor structure, which is apparently preserved in the calcined CuO/ZnO precursor, can lead to an enhanced reduction rate through the beneficial interaction of various types of defects leading to an increased reactivity of the solid phase. Those defects may be introduced during calcination of the hydroxycarbonate precursor at mild decomposition temperatures, affording a high density of defects in the oxide. [42,51] It should be noted as well that differences in catalytic activity can be achieved depending on the synthetic method of the Cu/ZnO catalyst. It was established by Agrell et al. [52] that catalysts derived from oxalate precursors prepared in microemulsions were more active for methanol conversion at low temperatures than those prepared by conventional carbonate co-precipitation in aqueous solution. The difference in catalytic behaviour was ascribed to a possible partial embedding of Cu in the ZnO phase in the microemulsion catalysts. However, in methanol steam reforming, this catalyst had reverse performance with lower hydrogen production on a catalyst prepared by a microemulsion in comparison with one made by conventional co-precipitation. [52] It is clear that not only catalyst composition, but also catalyst morphology play an important role in determining the catalytic behaviour.
2.1.3. Relationship between bulk structure and activity of supported copper catalysts

For Cu/ZnO catalysts (5% Cu), changes of the copper crystallite morphology have been concluded from in situ EXAFS investigation and were confirmed later on with in situ TEM investigations. [18,34,43,45] It was found, that depending on the oxygen partial pressure, copper particles tend to change their morphology from a disc-like to a more spherical shape and, therefore, the total copper surface area is affected. If, for example, water is added to the gas atmosphere, [46] the adsorption of these molecules on the different Cu facets is believed to be the driving force for the surface reconstruction. The transfer of these observations to other systems was only partly shown for Cu/SiO$_2$. In principle, the ability of the support to form oxygen vacancies was suggested to be an important prerequisite. For Cu/ZnO catalysts with higher copper concentrations Günter et al. [53] found, that the observed microstructural changes of copper and zinc oxide correlate with the methanol steam reforming activity. In the proposed model the increase in activity after oxygen addition (to methanol and water) cycles is explained with the depletion of Zn in the Cu lattice and the resulting larger domains of structural disorder (e.g. strain). It has been reported for Cu/Al$_2$O$_3$ and Cu/ZnO catalysts, that after a certain activation time, the catalysts became active for methanol steam reforming [54,55] and that the activity resulted from a partial re-oxidation of previously reduced copper metal to Cu$_2$O. Depending on the methanol – water ratio the amount of Cu$_2$O formed was different.

Nevertheless, CuO/ZnO/Al$_2$O$_3$ catalysts have poor long term stability. One of the main factors which causes the decay of the catalyst activity with time on stream is the sintering of the metal particles, which results in a decrease of the surface area of the active phase. In order to solve these problems, high CO formation and poor long-term stability, many strategies concerning the improvement of the catalyst properties have been followed i.e. synthesis of other metal based catalysts (Ce, Fe, Pd), synthesis of copper based catalysts...
promoted with different metal oxides, and synthesis of copper based catalysts with various preparation methods.

2.1.4. Different metal oxides as promoters of Cu/ZnO or Cu/ZnO/Al₂O₃ catalysts.

In earlier investigations about CuZnAl(Zr) oxide catalysts, it was noticed that the substitution of Zr improves the catalytic performance in terms of methanol conversion and H₂ production rate. Velu and Suziki [56] proved that a substitution of Zr for Al in the CuZnAl(Zr) oxide catalysts improved the catalytic performance because of an enhancement in copper reducibility and metal dispersion as a result of the formation of a "\( \text{Cu}^{2+}–\text{O}–\text{Zr}^{4+}–\text{O}– \)" solid solution at the surface of the catalyst. The presence of zirconium in these catalyst systems brings about a synergistic interaction with the copper species. The catalytic behavior and the role of different components of Cu/Zn/Al and Cu/Zn/Zr/Al metal oxide systems were discussed by a number of authors. [15,25,56,57] ZrO₂ is known to possess oxygen ion vacancies, which causes a geometric effect that can influence the dispersion and alter the morphology of the supported copper metal particles. [58] Venu et al. [57] assumed that the catalyst containing Zr exhibits the highest copper surface areas and copper dispersion, and the smallest copper particle size compared to those without Zr (Al-containing analogous). Breen et al. [25] reported a study of the catalytic behaviour over Cu/Zn and Cu/Zr catalysts for steam reforming of methanol. The results showed that both, Cu/Zn and Cu/Zr catalysts, are active for the methanol steam reforming reaction. In addition, the Cu/Zn catalyst is found to be more active than Cu/Zr with respect to the hydrogen production per kg catalyst. However, this does not mean that Cu/Zr is less active than Cu/Zn when the comparison to the methanol conversion per copper surface area is taken into account. At the same copper content in both catalysts (70% molar ratio of Cu), the Cu/Zr catalyst has a significantly lower copper surface area (3.7 m²g⁻¹) than the Cu/Zn (34.5
Furthermore, it was shown that the addition of zinc to the Cu/Zr catalyst resulted in catalysts with considerably higher copper dispersions than those of the Cu/Zr catalysts. Zinc additions also improved the activity over a wide temperature range from 143 to 345 °C. These investigations point out that zinc plays a key role in the improvement of the copper dispersion, which relates to the activity. The influence of alumina on the performance of the catalyst has also been observed. The stability of the catalyst was increased by adding alumina to the Cu/Zn/Zr materials. It was assumed that the stability is due to the stabilization of the active amorphous zirconia phase. This result reveals indirectly that the amorphous zirconium phase is responsible for the catalyst stability. The activity of the catalyst was also increased by adding alumina. The increase in the activity was found to be correlated with an increase in both the copper and total (BET) surface area. The study of the activity in correlation with the reducibility of the catalyst using TPR analysis showed that the most active catalysts had reduction peaks at the lowest temperature. Among the catalysts (Cu/ZnO, Cu/ZnO/Al₂O₃, Cu/ZnO/ZrO₂/Al₂O₃) tested, [59,60] the Cu/ZnO/ZrO₂/Al₂O₃ catalyst exhibits the highest methanol conversion and the lowest CO concentration in the outlet gas.

Addition of small amounts of chromate to the leaching liquor significantly enhanced the Cu surface area and BET surface area of skeletal Cu. [61] However, higher concentrations of chromate caused significant decreases of the ratio of Cu surface area to BET surface area.

The addition of Cs to a Cu/Al₂O₃ catalyst increases its activity and stability for hydrogen production from methanol steam reforming. The results of X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) [62] showed that the presence of Cs oxide prevents copper oxide crystallites from sintering and the reduction into metallic Cu proceeded at lower temperature.
The presence of CeO$_x$ was not only effective in enhancing the copper dispersion in the Cu/ZnO catalyst [63] but Ce$_2$O$_3$ is such a strong reducing reagent that it can decompose water into oxygen and hydrogen. [64] Therefore, water can be activated by the reduced ceria. It was noted by Men et al. [65] that production of CO$_2$ consumes one surface oxygen and accordingly one oxygen has to migrate to the copper–ceria interface to regenerate the depleted copper surface oxygen. Therefore, the oxygen vacancy is restored by the oxygen migration on ceria, i.e. oxygen reverse spillover. Furthermore, the dependence of the catalytic activity on the Cu/Ce ratio showed clearly an increase in catalytic activity with the decrease of the copper loading. The postulated reaction mechanism [65] involves several distinct steps: (1) the adsorption of methanol and water at the Cu/CeO$_2$ interface; (2) the surface reaction and gaseous product desorption; (3) the migration of surface oxygen from CeO$_2$ to the reduced Cu (oxygen reverse spillover); (4) the regeneration of partially oxidized copper and oxygen vacancies.

A promoting effect was found by adding iron. Tsai et al. [66] showed that the quasicrystalline alloy Al-Cu-Fe has similar activity, expressed by the production of H$_2$ of 235 l/kg min at 573 K, as the commercial catalyst. The excellent activities for the reactions were explained by copper oxide particles existing at the surfaces of the quasicrystal. [66] The surface energy of Cu is smaller than that of Fe and this would be the driving force for a surface diffusion process which drives Cu from the inside of Fe to the surface of Fe. However, the measurements of physicochemical properties of the plated Cu-Fe/Zn catalyst [67] suggest in contrast that the zinc, mixed in the plated layer, moved from the bulk to the surface of the plated layer by oxidation.

It is well known that 8A group noble metals, such as Pd, are active in methanol transformation reactions as well. [68,69] However, their catalytic functions for methanol conversion differ drastically from that of Cu. For instance, Pd exhibits poor selectivity for methanol steam reforming, producing mostly the decomposition products (hydrogen and
carbon monoxide). This behavior can be explained based on surface science studies. It was revealed via these investigations [68] that the structures of aldehydes adsorbed on 1B metals (Cu and Ag) are strongly different from those on 8A group metals (Rh, Ru, Pt, Pd). They adsorb preferentially in $\eta^1$(O)-structure on 1B metals, while on the 8A group they exist as $\eta^2$(C,O)-aldehydes (Fig. 2.3).

![Fig. 2.3. Adsorption of aldehydes on metals 1B group (Au, Cu) (a) and on metals 8A group (Rh, Ru, Pt, Pd) (b) [69]](image)

The $\eta^1$(O)-HCHO species preserves the molecular identity of HCHO and it simply desorbs without decomposition in temperature desorption experiments. In contrast, the C-C and C-H bonds are rapidly ruptured for $\eta^2$(C,O)-aldehyde species. Hence, it is highly probable that the difference in the original catalytic functions of copper and 8A group metals for the steam reforming and the dehydrogenation of methanol can be ascribed to the difference in the structures of HCHO intermediates formed on these metals. The only catalyst which has been found to give a reasonable activity and selectivity for steam reforming is Pd/ZnO. [69] Tomishige et al. also [70] reported that methanol decomposition mainly proceeded even in the presence of steam over Pd/C catalyst, whereas methanol steam reforming proceeded in the presence of steam over Zn–Pd/C catalyst. The comparison between Pd/C and Zn–Pd/C strongly suggested that more highly dispersed Pd–Zn alloy particles are formed over Zn–Pd/C. Recently Iwasa et al. [71] carried out steam reforming of methanol with various ZnO-supported group 8–10 metal catalysts in the absence and presence of oxygen. In the absence of oxygen, supported Pd and Pt catalysts produce
hydrogen and carbon dioxide in a 3:1 molar ratio, indicating that the steam reforming of methanol proceeds with high selectivity. By contrast, over the other supported group 8–10 metals such as Fe, Co, and Ni, hydrogen and carbon monoxide are produced in a nearly 2:1 molar ratio, which shows that the decomposition of methanol occurs selectively. Nevertheless, no real benefits could be identified for the Pd/Zn alloy in comparison with Cu/ZnO catalyst. Pd is a quite expensive metal and is not interesting for the fuel processor of fuel cells.

Thus, steam reforming of methanol is a heterogeneously catalyzed process based on copper. However, reaction mechanisms, as well as active phases and structural changes of the catalysts are still under debate, and are dependent on the catalyst composition and reaction conditions. However, the positive effect of a large specific copper surface area has been established and often confirmed. Furthermore, several authors have observed a linear correlation between the copper surface area and reaction rate.

In principle, high-surface-area materials can be created by two different means: Either the bulk material is finely divided to achieve a higher specific surface area, or the bulk material is made porous. [72] Introduction of porosity to various materials can be achieved by impregnation of activated carbon with concentrated solutions of metal salts, followed by burning the carbon material. This method allows the synthesis of various different metal oxides. [73] Nonetheless, the presence of copper in such systems leads to a vigorous combustion of carbon at lower temperature, and significantly decreases the surface area in the resulting material.

2.2. Mesoporous materials.

According to the classification by the IUPAC, porous solids can be arranged into three main categories, depending on their pore size (diameter, $d$), in micro- ($d < 2$ nm), meso- ($2$ nm $< d < 50$ nm), and macroporous materials ($d > 50$ nm). [74] Some illustrative examples
are given in Fig. 2.4. The most famous members of the microporous materials are zeolites. In spite of the great amount of work dedicated to zeolites [75-78] and related materials with controlled porosity, obtained by self-assembly (polymers...) or colloidal (latex beads) templating, crystalline molecular sieves, the dimensions and accessibility of pores are still restrained to the sub-nanometer scale. This limits the application of these pore systems to the processing of small molecules.

Since the highest activity in steam reforming of methanol was observed for particle sizes from 4-5 nm up to 10 nm, [6] in the following the focus will be on mesoporous materials. Using supramolecular assemblies (micellar aggregates, rather than molecular species) as templating agents, a new family of mesoporous silica and aluminosilicate compounds (M41S) was prepared, which were first developed by a research group at Mobil Oil. [80,81] Originally, mesoporous silicas were classified into three groups depending on their structure: a hexagonal (MCM-41), a cubic (MCM-48), and a lamellar phase (MCM-50). Similar to MCM-41, FSM-41 mesoporous silica with cylindrical pores was synthesized. [79] MCM-41-type materials are characterized by a regular hexagonal arrangement of
cylindrical pores, presenting a sharp pore distribution. The M41S family was synthesized from different silica sources (such as TEOS, Ludox colloidal silica, fumed silica, sodium silicate), a cationic surfactant (C\textsubscript{16}TMABr), a base (NaOH, TMAOH), and water. [82] From a general point of view, the formation mechanism of mesostructured phases, based on the specific electrostatic interaction between an inorganic precursor (\(I\)) and the surfactant polar head (\(S\)) was formalized by Huo et al. [83] The reaction path involving cationic surfactants and negatively charged silica species is called the \(S^+I^-\) path. Analogously, the \(S^-I^+\), \(S^+X^-I^+\) (where \(X^-\) is a counteranion), and \(S^-M^+I^-\) (where \(M^+\) is a metallic cation) paths were established. The pore structure and dimension of the mesoporous silica materials could be controlled by varying the experimental conditions, such as the ratio of the silica precursor to the surfactant and the chain length of the surfactant. The development of the M41S family triggered the synthesis of many mesoporous silica materials, having diverse pore structures using various organic structure-directing agents, including neutral amine surfactants, [84] alkyl(PEO) surfactants. [85] Recently, hexagonal micelle-templated silicas (MTS) with large surface area (700–900 m\(^2\) g\(^{-1}\)), large pore size (5 to 9 nm) and thick walls (3.5 to 5.3 nm) called SBA-15 have been reported by Zhao et al. [86,87] In these materials, silica is structured by triblock copolymers, e.g. (EO)\textsubscript{20}(PO)\textsubscript{70}(EO)\textsubscript{20} (Pluronic P\textsubscript{123}), in acidic conditions. Syntheses are performed in a temperature range from 35 to 100 °C and provide solids with high thermal and hydrothermal stability. These materials represent an interesting alternative to large pore MCM-41, the pore size of which is restricted to 3 to 7 nm and which features walls not thicker than 1 nm. [81] Thin walls are responsible for the low mechanical stability of these MCM-41 materials, the elasticity limits of which increase with the square of the ratio between the wall thickness and the pore opening. [88] Ordered mesoporous material is considered to be an ideal host for nanoparticles due to its large surface area and well-defined pore structure. Various metallic and semiconductor nanoparticles or nanowires have been prepared with MCM-41 or SBA-15 as the host [89-
As it was already mentioned above, SBA-15 was successfully impregnated by a copper solution, creating copper particles up to 10 nm in size. [89]

### 2.3. Synthesis of copper nanoparticles

Transition metals such as gold, platinum, silver, copper and nickel exhibit high catalytic activities for many chemical reactions. [94] There are many simple procedures for the fabrication of gold [95-97] and platinum [97-100] nanoparticles using various reducing agents coupled with a metal salt. Unlike these noble metals, copper nanoparticles can be easily oxidized to form copper oxide during the course of fabrication. Copper colloids e.g., which are used in the Schüth laboratory [19] and produced by anhydrous reduction with aluminium alkyles (H. Bönnemann et al. [101]), are stable only in inert and dry atmosphere. These oxidation problems can be overcome to some extent by using reverse micelles [102,103] (M.P. Pileni et al. [104]), or microemulsions using water-in-oil or gels, [105,106] as well as radiation techniques. [73,107] Many of these procedures are complicated and involve multiple solvent systems.

Chemical vapor deposition is a good way to control the nanoparticles’ growth and particle spreading, but should be restricted only to thin silica films or silica particles (not monolithic samples), to prevent uneven distribution of the metal compounds within the material. Another limitation of chemical vapor deposition is that to prevent the formation of excessively large or uneven particles, some additional restrictions should be applied. For example, Hyeon and coworkers [108] synthesized Cu nanoparticles from the thermal decomposition of commercially available copper acetylacetonate in oleylamine. Particles obtained by this method are smaller than 12 nm. It has been shown by Kauppinen et al. [109] that crystalline, nanometer-sized copper and copper oxide particles with sizes from 6 to 30 nm can also be produced by thermal vapor decomposition of a metal–organic precursor, Cu(acac)₂, at relatively low temperatures (up to 705 °C). The product of the
decomposition reaction depends on the precursor vapor pressure: copper particles were formed at vapor pressures higher than 10 Pa, copper (I) oxide at pressures lower than 1 Pa, and a mixture of the metal and its oxide at intermediate vapor pressures. Recently, silica spheres coated with copper nanoparticles (5–17 nm), coverage (40–80%) through supercritical fluid chemical deposition were achieved. [110] The coating process was based on the reduction of metal precursors with hydrogen in a supercritical CO$_2$/isopropanol mixture in a temperature range between 100 and 150 °C at 24 MPa. However, the parameters affecting the overall deposition are not well understood, which leads to difficulties when attempting to reproduce the copper nanoparticle surface on different substrates. [74] Luong’s [111] strategy for Cu nanoparticle deposition on carbon nanotubes was to use of Nafion, a perfluorosulfonated and negatively charged polymer to solubilize and disperse the single-wall carbon nanotubes. Due to the charge interactions, it was then possible to deposit the Cu nanoparticles into the Nafion modified carbon nanotubes. AFM analysis indicated a high and homogeneous dispersion of spherical Cu nanoparticles with a size of 6.0 ± 1.8 nm.

Recently, it has been made possible to fabricate monodispers nanostructured metal catalysts by using a new method of laser electro dispersion. [112] In this method liquid metallic drops of sub-micron size are ejected from the melted target surface. Particles are further forced into the substrate by the electric field applied to the substrate holder. The electric field also provided the means for particle size selection: it prevented the larger droplets from hitting upon the substrate. Amorphous Cu nanoparticles produced by this technique have spherical shape, their outer diameter is 5 nm and the size dispersion is lower than 10%. As a support, surface-oxidized silicon substrates were used.

All methods listed above are quite specific and require individual equipment. The problem with synthesizing copper nanoparticles by more simple methods is their high susceptibility to agglomeration.
Chemisorption-hydrolysis has been revealed as an adequate method to prepare nanodispersed copper catalysts supported on oxidic acidic supports. [113] The high surface area of SiO$_2$-Al$_2$O$_3$ used as support allows the high dispersion at high copper content with uniform spreading of the CuO$_x$ particles. Cu loading was varied from 0.23 to 12.4 wt %. For catalytic applications, the most essential characteristics are an interpenetrating pore structure of the mesoporous solids and formation of small particles located within the pores. Such particles offer a huge surface area and superior catalytic properties in a variety of catalytic reactions.

Another method to synthesize small particles is introducing the metal in porous material. This method is very simple and allows synthesis of well-reproducible materials. As can be seen above, a variety of available methods allow synthesis of nanoparticles in mesoporous solids using various approaches. One should choose the method of synthesis taking into consideration the requirements towards particle characteristics generally determined by the possible application of such materials.

### 2.4. Formation methods of small particles located within pore structures

Several general ways for functionalization of mesoporous solids with inorganic materials have been described. [114] In the following, some of the interesting methods will be described, taking into consideration their advantages and disadvantages from the viewpoint of particle growth control, and influence on the material properties.

#### 2.4.1. Addition of metal compounds to the precursor solution

A very simple synthetic method is addition of inorganic compounds (metal salts or alkoxides) in the precursor solution. In this way a modifying metal is introduced in the mesoporous material body (but not necessarily placed in the pores) and particles form during calcination. [115] Normally, to avoid a negative influence of the additive on the
ordering of mesoporous oxides, metal compound loading is kept low. However, a narrow particle size distribution is difficult to achieve during uncontrolled particle growth within the silica body during calcination. Moreover, a significant fraction of the nanoparticles is embedded in silica (or other mesoporous material) walls. Thus, this method of preparing nanoparticles within mesoporous solids for catalytic applications has a number of disadvantages which make it inferior in comparison with to other methods.

### 2.4.2 Templating over metal-containing frameworks

This approach was first described by Bronstein et al. [114,115] When metal nanoparticles are located in block copolymer micelle cores [114] or in microgels [115] and these polymeric systems are used as templates for silica casting, both pore size and metal particle growth control can be governed by the template. Bronstein combines the use of spherical microgels as nanosized exotemplates for the synthesis of metal colloids [95] and endotemplates during casting the mesoporous sol-gel silicas, along with a block copolymer (polystyrene-block-poly(ethylene oxide), PS-b-PEO) template. After calcination the latter provides an interpenetrating mesopore structure and good access to macropores formed due to microgels. This method does not ensure a regular location of metal nanoparticles throughout the mesoporous solid, but this disadvantage is of no importance for catalytic applications. Using metal-particle-containing templates seems to be promising for robust control over nanoparticles growth in mesoporous solids. Cupric oxide (CuO) nanoparticles have been prepared in an amorphous SiO₂ matrix using a complex of Cu(II) with poly(vinyl alcohol) (CuPVA) as a template. [61] The authors report the formation of CuO particles within the porous silica after calcination. Moreover, copper oxide particles can be present both in the pores and in the silica body. The latter will reduce the particle surface area available for participation in catalytic reactions which the authors consider as being a suitable application.
2.4.3. Impregnation with metal compounds followed by reduction, thermolysis, or other treatment.

Straightforward impregnation of preformed mesoporous solids with solutions of the desired metal compound followed by reduction, thermal decomposition, UV-irradiation, or ultrasonic treatment of the metal-compound-containing material is extensively used in the preparation of mesoporous materials containing nanoparticles. Incorporation of described metal compounds normally occurs due to capillary forces. Since no noticeable chemical interaction of the mesoporous oxide walls with the metal compounds or the forming metal (metal compound) particles is involved in this case, control over particle formation can be realized only due to the limits imposed by the pore structure. [114] As this is the case, the conditions of impregnation and further treatment are crucial for the structure of the materials synthesized. When referring to “quality”, several material characteristics should be considered: (a) preservation of the mesoporous material’s ordered structure, (b) uniformity of particle distribution within the pores, (c) narrow particle size distribution, and (d) match of the particle size to pore size. To improve control over nanoparticle formation while using incipient wetness impregnation, some authors used consecutive impregnations (four to five times) with drying the material in between to ensure that the mesopores are completely filled with metal precursor. [116] In this case, the amount of precursor is fixed and determined by the pore size and volume. The recipe is well reproducible as the final particle size is controlled by the precursor amount and in some cases by the pore size. However, it is not yet entirely understood when nanowires and when nanoparticles are formed.

Copper particles (≈2 wt.-%) were successfully introduced with incipient-wetness impregnation of Cu(NO₃)₂ into the structure of tubular or particulate TiO₂. [89] Except high dispersion of copper species, nothing was mentioned about the copper particle size. The hexagonally packed structure of SBA-15 allowed Zhang et al. [79] to obtain highly
distributed copper particles with a copper loading up to 4.7 wt.-% by simple wetness impregnation of copper in a silica matrix. The particle diameter was controlled by the pore size of the silica template.

2.4.4. Chemical interaction of metal compounds with functional groups of mesoporous oxides

If the mesoporous oxide walls are functionalized, the chemical interaction with metal compounds is a strong driving force for the incorporation of metal species into the pores. A functional group can play a dual role: (a) being an anchor for metal compounds and/or (b) interacting with the surface of the growing nanoparticles. [114,115,117] Because metal particle formation does not influence the mesoporous structure it is possible to obtain metal nanoparticles much smaller than the pore size by this method. Presumably the metal nanoparticles are forced to nucleate in the micropore entries, but they are restricted to grow beyond their cavity.

However, application of ordered mesoporous silica is limited for the reason of low structural stability under hydrothermal conditions. [118,119] Mesoporous silicas with interconnected pore structures have been successfully used as templates for the synthesis of mesoporous carbon materials. Two groups [119,121] nearly at the same time employed MCM-48 (alumina) silica materials as the templates for the fabrication of mesoporous carbon. The carbon precursor, sucrose or in situ polymerized phenol resin, was incorporated into the 3D interconnected pores of the MCM-48 template; subsequent carbonization followed by the removal of the silica template resulted in the generation of mesoporous carbon materials having 3D interconnected pore structures. Judging by the low-angle XRD pattern, the resulting carbon was not a real negative replica of the MCM-48 silica template, because the replicated carbon underwent a structural transformation during the removal of the silica template. It was suggested that the cubic MCM-48 with the Ia3d structure was
converted to a new cubic \( I4_1/a \) structure. [122] Following the first report on the synthesis of ordered mesoporous carbons using MCM-48 as silica template, various mesoporous carbon materials with different pore structures were synthesized, using a variety of different mesoporous silica templates. [123] Templated synthesis of ordered carbons potentially offers an additional flexibility of making volume-templated and surface-templated carbons. [124-126] In the first case, the entire void space of the template is infiltrated with carbon, whereas in the second case, carbon is introduced as a film on the surface of the template. Of all the reported mesoporous carbons prepared by templating mesostructured silica materials, mesoporous carbons obtained from SBA-15 silica have attracted the most attention. Because of the well-ordered structure of SBA-15 silica (i.e. hexagonally ordered cylindrical nanochannels), the carbons obtained as inverse replicas are highly ordered. Two types of carbons derived from SBA-15 have been reported, CMK-3 and CMK-5. The structure of CMK-3 can be described as highly ordered hexagonal arrays of carbon nano-rods connected by means of carbon spacers. [127] When the SBA-15 channels are partially filled by the carbon precursor, a carbon termed as CMK-5 is obtained. Its structure consists of 2-D hexagonally ordered carbon nano-pipes. [125,128] The pore size distribution curve exhibited bimodal pores, corresponding to the inside diameter of the carbon cylinders (5.9 nm) and the pores formed between the adjacent cylinders (4.2 nm), respectively. [122] In our case hexagonally ordered mesoporous carbon as a support has several advantages such as very high surface area (in the range between 1400 – 2000 \( \text{cm}^2\text{g}^{-1} \)), stability under reaction conditions, and no connection of copper with metal or metal oxide. Furthermore, the pore structure of CMK-5 type carbon depends on the framework of SBA-15, and in this way it is possible to synthesize highly controlled ordered porous carbon with various diameters. In addition, carbon tubes might be used as membrane materials for batteries and fuel cells, anodes for lithium ion batteries, capacitors, and chemical filters. However, these technologies are unsuitable for use cars because the reactions are not capable of instant
scaling, which is required when a car starts, stops or accelerates. Additional systems could be coupled to the fuel cell to make this application practical, but this increases cost, weight and complexity. This benefit became more attractive in further applications of methanol. In this work it have been accomplished the synthesis of highly distributed copper particles and studied them in the steam reforming methanol.
Chapter 3

Experimental

3.1. Materials preparation

In this chapter convenient synthetic conditions are described, providing efficient and reproducible control of pore connectivity and pore wall thickness for the synthesis of high quality SBA-15 mesoporous silica as well as CMK-3 and CMK-5 type mesoporous carbons.

3.1.1. Synthesis of SBA-15

SBA-15 is a mesoporous silica composed of two-dimensional hexagonal arrays of channels that typically range from 5–9 nm in diameter. [86] It is commonly synthesized under strongly acidic conditions, using a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer named Pluronic P_{123} as a structure-directing agent. SBA-15 silicas were synthesized as reported by Zhao et al. [86,89] A 4.0 g sample of Pluronic \((\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}\) \text{P}_{123} was dissolved in 30 g of water and 120 g of 2 M HCl solution. The solution was stirred until the polymer had completely dissolved. Then the solution was placed at 40 °C under thermostatic conditions and 8.50 g of tetraethylorthosilicate (TEOS) was added. The resulting mixture was stirred for 4 h at this temperature and then kept at 60 °C, 80 °C, 100 °C or 140 °C for 24 h without stirring. The solid product was filtered, and dried without washing overnight at 90 °C. The samples will be referred to as SBA-15-\(n\), where \(n\) is the ageing temperature. SBA-15-80 and SBA-15-100 were subsequently calcined in air for 6 h at 550 °C. SBA-15-60 and SBA-15-140 were treated with sulfuric acid before calcination. The sulfuric acid treatment was carried out as reported by Yang et al. [90] To wash out the polymer template, 4.0 g of SBA-15 was mixed
with 250 g of ethanol and 2 g 0.1 M HCl, and stirred for 1.5-2 h at room temperature. The solid sample was filtered and dried for 2 h at 90 °C. Afterwards the powder was added to 500 mL 48 wt.- % H₂SO₄ solution and refluxed at 95 °C for 24 h. The product was recovered by washing with water, dried at 90 °C and subsequently calcined in air for 6 h at 200°C.

In a typical synthesis process proposed by Ryoo et al. [129] 3.46 g of P₁₂₃ was dissolved in 21.6 g of distilled water and 4.5 g of concentrated HCl (35%). To this mixture, 5.6 g of TEOS was quickly added with stirring at 35 °C. The mixture was stirred at 35 °C for 24 h, and subsequently heated for 24 h at 60 °C, 80 °C, 100 °C or 140 °C under static conditions. The solid product was then filtered and dried without washing at 90 °C. The sample nomenclature is the same as above (SBA-15-\(n\), where \(n\) is ageing temperature). SBA-15-80 and SBA-15-100 were subsequently calcined in air for 6 h at 550 °C. SBA-15-60 and SBA-15-140 were treated with sulfuric acid before calcination as described above.

All samples described below are synthesized by the Zhao method, unless otherwise indicated.

3.1.2. Synthesis of CMK-3 or CMK-5 type carbons

The recent discovery of ordered mesoporous materials provided a new generation of silica templates suitable for the synthesis of mesoporous carbons, possibly with ordered mesoporous structures. Ryoo et al. first realized this opportunity, [120] synthesizing ordered mesoporous carbon. 4 g of SBA-15, 0.25 g AlCl₃ and 500 g ethanol were mixed together for 2 h at room temperature. The solution was subsequently evaporated and the solid was calcined at 550 °C for 3 h. The total pore volume of the silica template was calculated by \(N₂\)-adsorption measurement. The aluminosilicate was infiltrated with the amount of furfuryl alcohol (\(C₅H₆O₂\), used as a carbon precursor) corresponding to the pore value in the case of CMK-5, and with an amount corresponding to 1.4 times the pore volume to synthesize
CMK-3 type carbon. The composite samples were left at room temperature for 2 h, and at 95 °C for 15 h. The SBA-15 containing the furfuryl alcohol (FA) was heated for carbonization at 80 °C for 1 h and then at 300 °C for 3 h, and finally at 850 °C for 2 h under vacuum, which resulted in the aluminosilicate catalyzed polymerization of the FA in the form of tubes less than 3.6 nm in diameter after.

Following a different synthesis procedure for CMK-3 and CMK-5 type carbon, proposed by Zhao, [156] oxalic acid was used as the catalyst for polymerization of furfuryl alcohol. The calculated pore volume of the silica template was impregnated with twice the amount of FA : mesitylene (TMB) in a ratio of 50:50 in the case of CMK-5 material and 70 : 30 to synthesize CMK-3 type carbon. Afterwards the samples were kept at 50 °C for 24 h and 90 °C for 24 h. Then the silica materials filled with FA were calcined at 800 °C under Ar. This procedure is one step shorter, since the samples are not calcined before impregnation with FA. Nevertheless, the carbonization does not have the preferential starting point at the walls and spontaneously begins in the whole volume of SBA-15. The composite material was then pelletized, fractioned and sieved (250-500 µm). The silica matrix was dissolved using NaOH or HF aqueous solutions. Afterwards, samples were washed with water until neutral pH was reached, and dried at 90 °C overnight.

3.1.3. Hydrogen peroxide treatment

The surface of the carbon was functionalized by treatment with 15% H₂O₂. [130] In a typical treatment, 400 mg of mesoporous carbon was spread on a filter paper. The material was then washed with an appropriate amount of 15% H₂O₂ solution (enough to completely impregnate the solid) and then connected to vacuum and dried. This treatment was repeated 10 times and usually 20 mL of solution were consumed.
3.1.4. Copper and zinc introduction in the systems

Copper was added to the carbon support by impregnation with a 4.5 M copper nitrate aqueous solution. Typically 300 mg of carbon were soaked with Cu(NO$_3$)$_2$ solution which was added in three portions of 0.1 mL each. The copper nanoparticles within the carbon were obtained by nitrate decomposition at 150 °C under a flow of N$_2$, followed by Cu$^{II}$ reduction at 250 °C under a 5% H$_2$/N$_2$ flow. The resulting samples had a final copper loading of 22 wt.-%. The samples are denoted Cu/CMK-5, Cu/CMK-3 and Cu/C (C produced with Kugelkohle (Blücher GmbH)) respectively.

Copper was also added to carbon by impregnation with nitrate salts dissolved in ethanol, acetone or tetrahydrofuran (THF) solution. For impregnation saturated solutions of copper nitrate were used. The maximum concentration of nitrate in acetone was 2.7 M, and 2.3M in both ethanol and THF. Copper acetylacetonate was also used as precursor. With this copper salt, a maximum concentration of 0.08 M could be achieved. Also these solutions were added to the carbon support in three portions.

Samples, where the concentration of copper was varied, were impregnated with differently concentrated copper nitrate aqueous solutions. For the study of the influence of the copper loading, CMK-5 material with 3.9 nm pore diameter and a pore volume of 1.55 cm$^3$/g was used. Typically, 65 mg of CMK-5 carbon was used, and 0.1 mL of copper nitrate solution with various concentrations (0.56 M – 4.5 M) was added. Afterwards, samples were reduced in 5% H$_2$/N$_2$ flow at 250 °C.

Zinc oxide was introduced in the copper/carbon systems by post synthesis treatment with 1.0 M zinc nitrate solution. Samples were impregnated in three steps by adding of total solution volumes corresponding to 70% of the original carbon pore volume. The resulting samples were subsequently heated to 150 °C. Some copper impregnated carbon materials were impregnated with zinc directly after drying at 90 °C. The Cu/ZnO nanoparticles within
the carbon were obtained by nitrate decomposition at 150 °C under a flow of N₂, followed by Cu²⁺ reduction at 250 °C under a 5% H₂/N₂ flow. The resulting samples had a final copper loading of 22 wt.-% and ZnO ≈5%.

Fig. 3.1 shows the scheme of the synthesis procedure. SBA-15 was used as a template for the synthesis of CMK-5 and CMK-3 type mesoporous carbon. After functionalizing the carbon surface, the materials were impregnated with copper nitrate solution. Subsequent reduction allowed highly distributed copper nanoparticles to be obtained.

Fig. 3.1. Synthesis of carbon supported copper nanoparticles
3.2. Characterization techniques

The synthesized systems are metallic nanoparticles highly distributed within or on the mesoporous carbons. Mesoporous materials are characterized by techniques including X-ray diffraction (XRD), electron diffraction (ED), small angle X-ray scattering (SAXS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), gas adsorption measurements, and thermogravimetry-differential thermal analysis. Techniques such as XRD, SAXS and high resolution TEM combined with EDX have been proved to be useful for the elucidation of the structure and thickness and sample composition. Gas adsorption measurements are used to determine surface area, pore size, and pore size distributions of template-free solids. For the characterization of copper nanoparticles TEM measurements, wide angle XRD and N$_2$O decomposition (or Reactive Frontal Chromatography (RFC)) as well as temperature programmed reduction (TPR) are commonly used. TEM analysis allows to get information about the size, shape and arrangement of the particles which make up the specimen, as well as their relationship to each other on the atomic scale. Frontal chromatography and N$_2$ adsorption allow the determination of the specific copper surface area and total surface areas of materials. The temperature of the reduction of copper as well as information about different copper species and special interaction with the surface can be obtained by the TPR technique.

3.2.1. TEM (EDX)

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. What can be seen with a light microscope is limited by the wavelength of light. TEMs use electrons as the “light source” and their much smaller wavelength make it possible to get a resolution a thousand times better than with a light microscope. A "light source" at the top of the microscope emits the
electrons that travel through the evacuated column of the microscope. Instead of glass lenses focusing the light as in the light microscope, the TEM uses electromagnetic lenses to focus the electrons into a very thin beam. The electron beam then travels through the specimen under investigation. Depending on the density of the material present, some of the electrons are scattered and disappear from the beam. At the bottom of the microscope the unscattered electrons hit a fluorescent screen, which gives rise to a "shadow image" of the specimen with its different parts displayed in varied darkness according to their density. The image can be studied directly by the operator or photographed with a camera.

In analytical TEMs the elemental composition of the specimen can be determined by analyzing its X-ray spectrum or the energy-loss spectrum of the transmitted electrons. During EDX analysis, the specimen is bombarded with an electron beam inside the transmission electron microscope. The bombarding electrons eject electrons from core levels of the sample atoms. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell, resulting in the emission of characteristic X-rays. By analysis of the X-ray energy the identity of the atom from which the X-ray was emitted can be established, thus allowing quantitative analysis of the sample composition.

TEM investigations were performed with a Hitachi HF-2000 microscope, equipped with a cold-field emission gun at a beam energy of 200 kV. The samples were deposited on lacey carbon coated nickel grids in an argon glove-box, and transported by means of an argon filled sample holder to the microscope without contact with air. The copper loading of the catalyst was determined by energy-dispersive X-ray analysis (EDX) performed on a HF-2000 (Hitachi) TEM instrument equipped with a ThermoNoran (Thermo Electron Corporation) X-ray detector.
3.2.2. Sorption

Adsorption is a process that occurs when a gas or liquid accumulates on the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Desorption is the reverse process. The term sorption encompasses both processes. Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent with pressure (if gas) or concentration (if liquid) of the adsorptive.

Various mathematical formulations have been suggested for sorption isotherms, based on different physical models. One of the first isotherms goes back to Freundlich and Küster (1894) and it is a purely empirical formula valid for gaseous adsorbates:

\[
\frac{x}{m} = kP^n \quad (3.1)
\]

where \(x\) is the adsorbed quantity, \(m\) is the mass of adsorbent, \(P\) is the pressure of adsorbate and \(k\) and \(n\) are empirical constants for each adsorbent-adsorptive pair at each temperature. The function has an asymptotic maximum. As the temperature increases, the adsorbed quantity rises more slowly and higher pressure is required to achieve the maximum.

In 1916, I. Langmuir published a new isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed molecules of adsorbate, only on the free surface of the adsorbent.
Langmuir suggests that adsorption takes place through this mechanism: $A_{(g)} + S \leftrightarrow AS$, where $A$ is a gas molecule and $S$ is an adsorption site. These four points are seldom true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, the mechanism is clearly not the same for the very first molecules and for the last to adsorb. The fourth condition is the most troublesome, as often more molecules can adsorb on the monolayer, but this problem is solved by the BET isotherm. In 1938 S. Brunauer, P. Emmett and E. Teller developed an isotherm that takes into account that possibility, “BET” consists of the first initials of their family names. The proposed mechanism is now:

$$
\begin{align*}
A_{(g)} + S &= AS \\
A_{(g)} + AS &= A_2S \\
A_{(g)} + A_2S &= A_3S \text{ and so on…}
\end{align*}
$$

![Fig. 3.2. Langmuir isotherm (solid line) and BET isotherm (dotted line)](image)

The resulting BET equation is expressed by (3.2):

$$
\frac{1}{v[(P_0/P) - 1]} = c\frac{P}{P_0} + \frac{1}{v_mC} \quad (3.2)
$$

$P$ and $P_0$ are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, $v$ is the adsorbed gas quantity (for example, in volume units), and $v_m$ is the monolayer adsorbed gas quantity. $c$ is the BET constant, which is expressed by (3.3):

$$
c = \frac{a_1b_2}{b_1a_2} \exp\left(\frac{E_1 - E_L}{RT}\right) \quad (3.3),
$$

From the nature of the constants $a_1$, $a_2$, $b_1$ and $b_2$ is evident that $a_1b_2/a_2b_1$ will not differ much from unity. [131]
$E_1$ is the heat of adsorption for the first layer, and $E_L$ is that for the second and higher layers and is equal to the heat of liquefaction. Eq. (3.2) is an adsorption isotherm and can be plotted as a straight line with $1/(\nu[(P_0/P)−1])$ on the y-axis and $P/P_0$ on the x-axis according to experimental results. This plot is called a BET plot. The linear relationship of this equation is typically maintained only in the range of $0.05<P/P_0<0.35$. The value of the slope and the y-intercept of the line are used to calculate the monolayer adsorbed gas quantity $\nu_m$ and the BET constant $c$. The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. A total surface area $S_{\text{total}}$ and a specific surface area $S$ are evaluated by the following equations:

$$S_{\text{total}} = \frac{(\nu_m N s)}{M} \quad (3.4)$$

$$S = \frac{S_{\text{total}}}{a} \quad (3.5)$$

$N$: Avogadro's number, $s$: adsorption cross section, $M$: molecular weight of adsorbate, $a$: weight of solid sample. Fig. 3.2. shows the difference between Langmuir isotherm and BET isotherm. The Langmuir isotherm is usually better for chemisorption, the BET isotherm works better for physisorption.

For nitrogen adsorption, a Nova Quantachrome device was used. Before analysis samples were activated under vacuum at 150 °C for 2h. Isotherms were recorded at -196 °C. $N_2$-physisorption was used in order to characterize the surface area and pore size distribution of the mesoporous materials before and after impregnation with copper. The Brunauer Emmett Teller (BET) [131] surface area was calculated from the adsorption data in the relative pressure interval from 0.04 to 0.2. Pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) [132] method from the adsorption branch. The total pore volume was estimated from the amount of nitrogen adsorbed at $p/p_0 \approx 0.99$. 
3.2.3. XRD

X-ray powder diffraction finds frequent use in materials science because sample preparation is relatively easy and the test itself is often rapid and non-destructive. The vast majority of engineering materials are crystalline, and even those which are not yield some useful information in diffraction experiments. The pattern of powder diffraction peaks can be used to quickly identify materials (pattern database), and changes in peak width can be used to determine crystal size, purity, and texture. Since all possible crystal orientations are measured simultaneously, the diffraction pattern is observed as a series of concentric rings of varying intensity. Materials that do not have long range order may also be studied by scattering methods that rely on elastic scattering of monochromatic X-rays.

- X-ray reflectivity is an analytical technique for determining thickness, roughness, and density of single layer and multilayer thin films.
- Wide angle X-ray scattering (WAXS), a technique concentrating on scattering angles 2θ typically between 10 and 90° is used for the determination of crystal structures.

Bragg's Law refers to the simple equation:

\[ n\lambda = 2d \sin \theta \] (3.6)

derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, \( \theta \)). The variable \( d \) is the distance between atomic layers in a crystal, and the variable \( \lambda \) is the wavelength of the incident X-ray beam, \( n \) is an integer. This observation is an example of X-ray wave interference, commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries.

The measurements were carried out on 2 different diffractometers:
1. Samples were analyzed with a STOE STADI P diffractometer equipped with a linear position sensitive detector in transmission geometry using Cu-K$_{\alpha 1}$ radiation allowing to measure 2 theta angles down to 1.0 °.

2. Samples were additionally analyzed on a STADI P diffractometer (Stoe) in the Bragg-Brentano (reflection) geometry. The step width was 0.02° at an acquisition time of 8 s per step.

3.2.4. TPR

Temperature programmed reduction (TPR) is usually used to find out the temperature of reducibility of the metal containing samples. Depending on size and shape, as well as the surroundings of the metal compound, the reduction temperature can be different. In TPR analysis hydrogen (or carbon monoxide) consumption is recorded with linearly increasing temperature.

TPR measurements were performed in a fixed bed reactor with an inner diameter of 5 mm. This experimental setup is equipped with two gas lines: a mixture of 5% H$_2$ (99.9995%) in N$_2$ and N$_2$. Quantitative determinations were carried out using the thermo conductive detector Hydros® 100 (Rosemount Inc.). Reduction experiments were conducted with 50 mg of freshly impregnated samples. In a typical run, the temperature was ramped with a heating rate equal to 5 °C/min up to 300 °C under hydrogen stream (5 vol % in N$_2$) using a total flow of 34 cm$^3$/min.

3.2.5. N$_2$O decomposition

N$_2$O decomposition (refers to Reactive Frontal Chromatography (RFC)) was used to determine the copper surface area. RFC was first introduced and described by Chinchen et al. [157,158] The method is based on decomposition of N$_2$O on exposed Cu atoms with formation of atomic oxygen and nitrogen in the gas phase. [158,159] The stoichiometry of
the copper surface atom with respect to adsorbed oxygen is assumed to be 2:1 (half monolayer coverage of oxygen).

\[
\begin{align*}
\text{CuO} + \text{H}_2 & \rightarrow \text{Cu} + \text{H}_2\text{O} \\
2 \text{Cu} + \text{N}_2\text{O} & \rightarrow \text{Cu}_2\text{O} + \text{N}_2 \\
\text{Cu}_2\text{O} + \text{H}_2 & \rightarrow 2 \text{Cu} + \text{H}_2\text{O}
\end{align*}
\]

The copper surface area was calculated assuming $1.47 \times 10^{19}$ copper atoms per m$^2$. [158]

The copper surface determination device, based on N$_2$O reactive frontal chromatography (RFC), has been established in our group as parallel detection method, enabling the characterization of 16 catalysts at the same time. [160]

The experimental setup consists of an Equinox 55 FTIR spectrometer (Bruker) which was operated in the continuous scan mode, allowing to record about 14 spectra per minute with a spectral resolution of 32 cm$^{-1}$. This time resolution is more than sufficient for reliable analysis. The external port of the spectrometer is used to pass the IR beam via an imaging optics through the gas cuvette which has been described elsewhere [161] onto the FPA detector which consists of an array of 64 x 64 pixels.

The samples to be analyzed are placed in the sample cartridges of a 16-channel parallel reactor made from brass, the principle of which has been described elsewhere. [162] Inlet gas is fed into the reactor via a common inlet, the outlet of each channel is passed through 1/16” capillaries with a length of approximately 150 cm to the inlets of the channels of the 16-channel gas cuvette.

The procedure for the analysis is closely related to the one used in conventional N$_2$O RFC determination of copper surface area: [160] 200 mg of each sample is placed in the sample cartridges of 15 channels, the remaining channel is filled with the same amount of fused silica powder (125-250 µm) as t=0 reference. After closing the reactor lid, the catalysts are first reduced by passing 200 ml/min of a gas mixture containing 5% H$_2$ in nitrogen at 300 °C for 3h. The final temperature is reached with a ramp of 5 °C/min. After 3
h at reduction temperature, the gas is switched to pure nitrogen and the reactor is cooled down to 40 °C. Then the gas is switched to 1% N\textsubscript{2}O in helium at a flow of 40 ml/min in each channel. At the same time, recording of IR-spectra is started. All spectra are calculated against a background corresponding to the cuvette filled with nitrogen. The amount of N\textsubscript{2}O reacted is calculated from the breakthrough curves, the flow and the N\textsubscript{2}O concentration in the gas.

3.3. Catalytic activity measurements

The catalytic activity experiments were carried out at 1.1 bar in a stainless steel plug flow reactor (\(\varnothing\) 6 mm) placed inside a furnace. The temperature was measured by a K-type thermocouple in the catalyst bed. 100 mg of sieved catalyst (250-500 µm) mixed with 100 mg of sieved silica (250-500 µm) were exposed to a total flow of 260 cm³/min containing 11.7% methanol. The molar water to methanol ratio was 1:1 and nitrogen was added as a balance. Prior to the catalytic experiment, the catalyst was reduced in situ by exposing the material to 4% hydrogen in nitrogen at 200 cm³/min, increasing the temperature with a rate of 5 °C/min to 250 °C and keeping it isothermal for 1 h.

On-line analysis of the reaction products was performed using a Thermo Nicolet FT-IR-spectrometer (CH\textsubscript{3}OH, H\textsubscript{2}O, CO and CO\textsubscript{2}) and a CE Instruments GC 8000 gas chromatograph (H\textsubscript{2} and N\textsubscript{2}) equipped with TCD and FID detectors. The carrier gas for GC was Ar and the GC was equipped with a 0.32 mm Carboxen 1010 column from Supelco for the separation of permanent gases (N\textsubscript{2}, H\textsubscript{2}, CO and CO\textsubscript{2}). Samples were taken every 20 min.

3.3.1. Description of methanol steam reforming apparatus set-up

Fig. 3.3 shows the set-up used for studying the catalytic activity of copper/carbon in the steam reforming of methanol. The evaporators are filled with glass beads of 125-250 µm
in size in order to increase contact of the carrier gas with liquid. The amount of liquid fed is controlled by a pump. Into the reactor enters a mixture made of evaporated distilled water and methanol (98.5 % purity, Fluka), nitrogen (4.0, Messer Griesheim GmbH) which is passed through the catalyst layer with a rate of 260 ml/min. Methanol conversion was measured in a temperature range between 250 °C and 300 °C. Afterwards, the reacted mixture goes to the IR spectrometer. The line connecting reactor and IR instrument was heated to 130 °C to avoid condensation of residual water and methanol. In order to increase condensation of residual methanol and water, two cooling vessels, filled with glass beads of a size of 0.5-1 mm, are located before the gas chromatograph.

**Fig. 3.3.** Experimental set-up for methanol steam reforming

a) gas flask, b) pressure reducer, c) mass flow pressure controller, d) turn on/off screw, e) pump, f) evaporator, g) reactor, h) temperature regulator, i) FTIR-spectrometer, j) computer for IR data collection k) manometer, l) cooling vessels, m) exhaust, n) gas chromatograph (GC), o) computer for GC data collection.
The presence of liquid is undesirable for GCs equipped with silica packed columns, so the line connecting IR and GC contains condensation vessels at temperatures of 2°C and -78°C. Thus, after these cooling traps only the gases CO, CO₂, H₂ and N₂ reach the GC instrument.

3.3.2. IR calibration, measurement

Infrared spectroscopy is an analytical method based on absorption of IR radiation by a sample. Different frequencies are absorbed by different stretching and bending vibrations of molecules or solids. The infrared portion of the electromagnetic spectrum is divided into three regions: the near-, mid- and far- infrared, named for their relation to the visible spectrum. The far-infrared, (approx. 400-10 cm⁻¹) lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid- infrared (approx. 4000-400 cm⁻¹) may be used to study the fundamental vibrations and associated rotational-vibrational structure, whilst the higher energy near-IR (14000-4000 cm⁻¹) can excite overtone or harmonic vibrations. Infrared spectroscopy works because chemical bonds have specific frequencies at which they vibrate corresponding to specific energy levels. The resonant frequencies or vibrational frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, eventually by the associated vibronic coupling. In order for a vibrational mode in a molecule to be IR active, it must be associated with changes in the permanent dipole. The resonant frequencies can be in a first approximations related to the strength of the bond, and the mass of the atoms at either end of it. Thus, the frequency of the vibrations can be associated with a particular bond type. Simple diatomic molecules have only one bond, which may stretch. More complex molecules may have many bonds, and vibrations can be conjugated, leading to infrared absorptions at characteristic frequencies that may be related to chemical groups.
Quantitative analysis of CO, CO$_2$, CH$_3$OH, and H$_2$O was achieved by analysis of the estimation of the specific bands of the components of the mixture at three different wavelengths for each compound (Table 3.1). Each component in gas mixture was measured four times during one analysis. For all component concentration was calculated corresponding calibration curves.

**Table 3.1.** The wavelengths of analyses for different compounds.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Wavelengths, cm$^{-1}$</th>
<th>Wavelengths, cm$^{-1}$</th>
<th>Wavelengths, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>3904.48</td>
<td>1869.04</td>
<td>4000-3790</td>
</tr>
<tr>
<td>Methanol</td>
<td>2843.74</td>
<td>1345.14</td>
<td>3150-2700</td>
</tr>
<tr>
<td>CO</td>
<td>2332.10</td>
<td>2293.52</td>
<td>2400-2280</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2175.94</td>
<td>2111.23</td>
<td>2240-215</td>
</tr>
</tbody>
</table>

*See appendix for calculation of concentration.*

**3.3.3. Gas Chromatography**

In general, chromatography methods exploit the differences in partitioning behavior between a mobile phase and a stationary phase to separate the components in a mixture. The components of a mixture may interact with the stationary phase based on charge, relative solubility or adsorption. Gas chromatography (GC) is a type of chromatography in which the mobile phase is a carrier gas, usually an inert gas such as helium or nitrogen, or sometimes hydrogen; the stationary phase is a microscopic layer of liquid or polymer inside a glass or metal tubing, or packed silica particles on an inert solid support, called a column. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time). Other parameters
that can be used to alter the order or time of retention are the carrier gas flow rate, and the temperature.

A number of detectors are used in gas chromatography. The most common are the flame ionization detector (FID) and the thermal conductivity detector (TCD). Both are sensitive to a wide range of components, and both work over a wide range of concentrations. While TCDs are essentially universal and can be used to detect any component other than the carrier gas (as long as their thermal conductivities are different to that of the carrier gas, at the detector temperature), FIDs are sensitive primarily to hydrocarbons, and are more sensitive to them than TCD. Both detectors are also quite robust. Since TCD is non-destructive, it can be operated in-series before an FID (destructive), thus providing complementary detection of the same eluents.

The GC equipped with a sampling valve, controlled by computer, was synchronized with the IR analysis. Thus, every 20 minutes one chromatographic measurement of H₂ and N₂ was carried out. The peak of nitrogen comes at 2 minutes and hydrogen at 2.5 minutes. The quantities of these two gases were calculated from corresponding calibration curves, correlating the peak area and the concentration of the component in the gas mixture. The sensitivity of the equipped detector was not sufficient to analyze CO and CO₂, however, the amount of CO and CO₂ were measured before by IR analysis. As mentioned above, the gas mixture flows passing through IR and GC are different due to condensation of the liquid compounds. Therefore, taking into account this difference the concentration of hydrogen in the complete gas mixture was recalculated. *The details of these calculations are described in the appendix.*
Chapter 4

Results and discussion

4.1. The carbon based Cu/CMK-3, Cu/CMK-5 and Cu/Kugelkohle catalytic systems (*TEM, XRD, TPR and sorption measurements*)

Ordered mesoporous material is considered as an ideal host for nanoparticles due to its large surface area and well-defined pore structure. More importantly, the pore size of ordered mesoporous material can be tuned within the nanometer range, and the pore surface can be functionalized with various organic groups. We can make use of such properties to effectively confine metal or metal oxide particles into nano-channels of mesoporous material. Mesoporous carbon supports have several advantages making them useful for the study of the methanol steam reforming reaction. Compared to mesoporous silica, carbon shows better stability under hydrothermal conditions. [118] It is possible to obtain copper particles with narrow size distribution on carbon supports, and study the correlation between particle size and catalytic activity. We used CMK-5 and CMK-3 type carbon as well as Kugelkohle to achieve highly distributed copper nanoparticles on a catalytically inert support. CMK-5 ordered mesoporous carbon can be described as a hexagonally packed array of carbon nanotubes. It has a number of variable properties, such as very high surface area and bimodal porosity. [124] CMK-5 material has well organized and easily controlled pore structure. Furthermore, because CMK-5 type carbon has the highest pore volume and surface area, but is less stable and more sensitive to different types of treatment, [129] in comparison with other studied carbons, this carbon was used as a model system for the
optimization of synthesis parameters. Metallic copper catalyzes carbon combustion already at low (down to 200 °C) temperature [73] in rather ill controllable manner, and thus on the CMK-5 structure this effect will become more obvious. When no zinc oxide is present in the catalyst composition, the catalytic activity of only copper can be studied.

### 4.1.1. Influence of different copper precursors

The synthesis procedure involved several steps: the carbon was impregnated with a copper containing solution, usually in only one step of incipient wetness impregnation; afterwards the material was calcined under inert and/or reducing atmosphere. One of the important tasks of the catalyst synthesis is to obtain a high copper loading within the carbon support. The impregnation solutions as well as copper precursors were varied. An overview of the different synthesized material is shown in Fig. 4.1. Carbon is typically hydrophobic, so when carbon is used without any special treatment it has a “hydrophobic” surface (Fig. 4.1 a).

---

**Fig. 4.1.** Overview of the synthesized materials
In order to functionalize the carbon surface by adding certain hydrophilic groups, some samples were treated with hydrogen peroxide. The “hydrophilic” carbon was denoted as CMK-5* (Fig. 4.1 b).

4.1.1.1. Copper supported on hydrophobic CMK-5.

To incorporate copper into the structure of carbon, different solutions of copper nitrate, such as ethanol, acetone, THF and water, were used. Since the amount of impregnated copper was limited by the carbon pore volume, the most concentrated solution was always used. Copper nitrate was chosen from the various copper salts due to its highest solubility and low temperature of decomposition. Copper nitrate decomposes at 130 °C, whereas for decomposition of copper sulfate and copper chloride it is necessary to heat the system up to a temperature of 600 °C. Other copper precursors, such as copper acetate and copper acetyl acetonate, have much lower solubility in water.

![Bar graph showing hydrogen yield from methanol steam reforming in the temperature range between 250 °C and 300 °C over Cu impregnated CMK-5 supports with hydrophobic surface in dependence of the solvent for the copper precursor.]

Fig. 4.2. Hydrogen yield from methanol steam reforming in the temperature range between 250 °C and 300 °C over Cu impregnated CMK-5 supports with hydrophobic surface in dependence of the solvent for the copper precursor.
Thus, hydrophobic carbon was impregnated by copper nitrate dissolved in ethanol, water, THF and acetone (Fig. 4.1 a). Hydrogen yield in the temperature range between 250 °C and 300 °C in methanol steam reforming over these samples is shown in Fig. 4.2. Poor activity up to only 6% maximum hydrogen yield was observed for copper on carbon with a hydrophobic surface. Since a dependence between structural properties of catalyst and its activity was expected, the samples were analyzed by TEM. The TEM image of a sample obtained from ethanol wetness impregnation of CMK-5 after calcination at 250 °C under argon is presented in Fig. 4.3. Due to the fact that in ethanol it was possible to reach a concentration of copper nitrate of 2.0 M, the final product had 10.0 wt.-% copper loading.

![TEM image of CMK-5 carbon impregnated with an ethanol solution of copper nitrate. Copper loading is 10 wt.-%.](image)

**Fig. 4.3.** TEM image of CMK-5 carbon impregnated with an ethanol solution of copper nitrate. Copper loading is 10 wt.-%.

Large domains of copper particles up to 80 nm in size were observed on the surface of the material. It seems that copper does not move into the tube structure and agglomerates on the surface with the formation of large particles. These particles have a low specific copper surface area, so this material was not active in methanol steam reforming. On the second
sample, CMK-5 impregnated with an aqueous solution of copper nitrate, no hydrogen was observed at all. The result of the impregnation with copper nitrate dissolved in water and subsequent calcination at 250 °C under Ar is shown in Fig. 4.4. The water solution obviously cannot penetrate the porous structure of the carbon due to the hydrophobic properties of the support, but the copper is also not deposited on the surface, in contrast to the sample made with ethanol solution. Copper nitrate dissolved in water does not wet the carbon surface, and thus the domains of copper oxide are formed as a completely separated phase. In contrast to water solution, THF as well as acetone are hydrophobic, so these solutions should more easily wet the surface of the carbon.

![Fig. 4.4. TEM image of CMK-5 carbon impregnated with water solution of copper nitrate. Copper loading is 22 wt.-%.

As can be seen in Fig. 4.5, copper particles are highly distributed on the surface of the carbon after impregnation from THF. However, it can also be seen, that the distribution of copper on the surface of the carbon is not the same in different parts of the sample. This observation was also proved by EDX analysis (data not shown). Copper was detected in
some parts of the sample by EDX, while in other parts no copper was found. The hydrogen yield over Cu-THF impregnated catalyst was higher than for the other samples, but also did not exceed 6%. Two reasons may account for this behavior: (a) the amount of copper available for the reaction is not sufficient for good catalytic performance and/or (b) particles have no links to the surface of the carbon in the sample; they may easily move under the reaction conditions, and therefore agglomerate. The TEM studies of this sample after the reaction test indicate particle growth and partial destruction of the hexagonally packed structure of the CMK-5 support.

![TEM image of CMK-5 carbon impregnated with THF solution of copper nitrate. Copper loading is 10 wt.-%.](image)

**Fig. 4.5.** TEM image of CMK-5 carbon impregnated with THF solution of copper nitrate. Copper loading is 10 wt.-%.

As shown in Fig. 4.5, particles with a diameter up to 15 nm are found, which is larger than the pore size of the CMK-5 material (3-5 nm); these particles are obviously located on the carbon surface. Thus, it is not possible to control the particle size by using THF as a solution for the impregnation of copper on mesoporous carbon. The last sample of this series was prepared by impregnation of the hydrophobic carbon CMK-5 with copper nitrate.
dissolved in acetone. The catalytic activity of the Cu-acetone impregnated sample was lower than for Cu-THF, and as it could be expected this sample did not have a homogeneous distribution of copper particles (Fig. 4.6). In spite of the presence of some small (6-10 nm) particles of copper, their number was lower in comparison with large copper agglomerates. Based on these results it can be concluded that the carbon support with unfunctionalized surface is not suitable for achievement of high copper dispersion.

![Fig. 4.6. TEM image of CMK-5 carbon impregnated with acetone solution of copper nitrate. Copper loading is 10 wt.-%.

4.1.1.2. Copper supported on hydrophilic CMK-5.

4.1.1.2.1. Effect of $H_2O_2$ treatment.

In order to improve the copper dispersion, the surface of a porous carbon material was modified to create surface functional groups which increase the hydrophilic (acid or base) properties and facilitate the interaction with guest species. Porous carbon with oxygen or nitrogen containing functional groups can be directly synthesized via a pyrolysis process, by using oxygen or nitrogen rich precursors. [133] However, the most frequently used method
to generate surface oxygen is oxidative treatment. This may include gas phase reactions (air or oxygen plasma) or liquid phase reactions (NaOCl, H$_2$O$_2$, HNO$_3$, or H$_2$SO$_4$ solutions). [134,135] Oxidation through partial gasification usually results in substantial carbon loss and causes changes in surface area and pore size distribution.

Nitric acid treatment produces the highest concentration of surface oxygen groups, especially carboxylic acid groups. Sodium hypochlorite and H$_2$O$_2$ as milder oxidizing agents rather favor phenol groups instead of lactones and carboxylic acid groups. The structure of a porous carbon usually remains almost unchanged after H$_2$O$_2$ treatment. [136,137] In order to explore the possibility of modifying the surface of such carbon types, we applied the milder oxidizing agent H$_2$O$_2$ with the goal to introduce oxygen-containing groups and thus to improve the hydrophilicity, while maintaining the pore structure. However, CMK-5 carbon loses its ordered structure after treatment with H$_2$O$_2$ (30 wt.-%) at room temperature, even after a few minutes of treatment. As shown in Fig. 4.7, the original CMK-5 carbon shows well-resolved (100), (110), and (200) reflections, indicating that the samples have an ordered structure with 2-D hexagonal symmetry. The lower intensity of the (100) reflection in comparison to that of the (110) reflection can be attributed to the diffraction interference between the pipe walls and the spacers interconnecting adjacent pipes. [138] Peak intensity relates to the ordering of the samples. In our case, the order decreases continuously with increasing concentration of H$_2$O$_2$. After treatment with 30 % H$_2$O$_2$, the well resolved characteristic reflections indicating hexagonal ordering disappear, regardless of the CMK-5 type carbon wall thickness, indicating the loss of structural order under the treatment conditions. The previous studies provided in our group showed that CMK-3 type carbon has higher stability than CMK-5 at the same condition (data unpublished). CMK-3 even after several hours’ treatment with 30% H$_2$O$_2$ has still resolved XRD reflection, indicating the retention of the original ordered structure. As mentioned above, CMK-5 and CMK-3 carbons have different structure; specifically CMK-5 carbon consists of hollow tubes while
CMK-3 has fully filled tubes (rods). Since CMK-3 is stable even after harsher treatment, the dissolution of interconnections between pipes can be excluded as the reason for the disordering of the CMK-5 structure.

Fig. 4.7. XRD patterns of CMK-5 type carbon treated with hydrogen peroxide (15-30%) in comparison with CMK-5 as made.

Thus, the XRD patterns (Fig. 4.7) show that the ordered structure of CMK-5 disappears after treatment with 30% H₂O₂. Evidently, H₂O₂ reacts with CMK-5 carbon walls, leading to substantial damage of the carbon structure. The experiments were repeated many times, always with the same result. Thus, H₂O₂ strongly reacts with the CMK-5 carbon, with cleavage of part of the C–C bonds, leading to structural collapse. It is different compared to the reaction between conventional activated carbon and H₂O₂, where the
structure and textural properties of the activated carbon are almost completely unchanged. [136,137]

**Fig. 4.8.** The XRD patterns of CMK-5 type carbon treated with 15% hydrogen peroxide several times in comparison with CMK-5 as made.

The aggressive action of H₂O₂ on the carbon structure depends on the concentration of the H₂O₂ solution. Treatment at concentrations below 22 % leaves the CMK-5 structure intact (Fig. 4.7) although peak intensities are reduced. 15wt.-% of hydrogen peroxide did not destroy the hexagonally ordered carbon structure even after repeating the treatment several times (Fig. 4.8). After the first treatment with 15% H₂O₂, the absolute peak intensity decreased, but the (100), (110) and (200) reflections were still well-resolved even for a sample, which was oxidatively treated three times. From the XRD results, one can conclude that CMK-5 carbon is completely destroyed only after treatment with 30% H₂O₂, however, 15% hydrogen peroxide treatment is sufficiently gentle, so that the CMK-5 material maintains a substantial part of its structural order even after three oxidative treatment steps.
Table 4.1 gives data on changes of the CMK-5 texture, such as pore volume and specific surface area, after treatment with 15% H$_2$O$_2$.

**Table 4.1.** Influence of H$_2$O$_2$ treatment on textural properties such as pore diameter, pore volume and specific surface area of CMK-5 carbon.

<table>
<thead>
<tr>
<th>H$_2$O$_2^a$, times</th>
<th>Surface area (BET), m$^2$/g</th>
<th>Volume, cm$^3$/g</th>
<th>D$_{adsorb}$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>1416</td>
<td>1.77</td>
<td>2.2</td>
</tr>
<tr>
<td>1</td>
<td>1501</td>
<td>1.87</td>
<td>3.2</td>
</tr>
<tr>
<td>-</td>
<td>1725</td>
<td>1.48</td>
<td>2.1</td>
</tr>
<tr>
<td>3</td>
<td>1711</td>
<td>1.43</td>
<td>3.3</td>
</tr>
</tbody>
</table>

$^a$The data were obtained for two different starting materials

The specific surface area and pore volume are not significantly different even after hydrogen peroxide treatment was repeated three times, whereas the diameter of the CMK-5 pores increased by 1 nm already after the first treatment. Fig. 4.9 shows that the hysteresis loop of the CMK-5, treated three times with 15% H$_2$O$_2$, moved to the higher pressure region in comparison with the original CMK-5. Thus, the loss of the structural order of the CMK-5 type carbon after treatment with 30% H$_2$O$_2$ is related to partial dissolution of its walls.
4.1.1.2.2. Impregnation with copper

In order to produce steam reforming catalysts, the ordered carbon treated with 15% H₂O₂ solution (denoted as CMK-5*) was impregnated with an ethanolic or aqueous solution of copper nitrate and an aqueous solution of copper acetyl acetonate (Fig. 4.1 b). The hydrogen yield achieved over these samples is shown in Fig. 4.10. Samples prepared by impregnation of partially hydrophilic CMK-5* with ethanolic and aqueous copper nitrate solution showed higher hydrogen yield than those based on carbon without a previous oxidation step. It is obvious that the samples made with carbon supports after hydrogen peroxide treatment have different surface properties. Large copper particles up to 20 nm in size are as before present on the CMK-5* surface impregnated with Cu from ethanol (Fig. 4.11). However, the agglomeration tendency of copper oxide appears to be much smaller than was observed for Cu-ethanol impregnated CMK-5 (copper particle size of 80 nm), which had not been previously oxidized (Fig. 4.3).
Fig. 4.10. Hydrogen yield in methanol steam reforming in the temperature range between 250 °C and 300 °C over Cu impregnated CMK-5* supports with hydrophilic surface in dependence of the solvent for the copper precursor.

Fig. 4.11. TEM image of CMK-5* carbon impregnated with ethanolic solution of copper nitrate. Copper loading is 10 wt.-%.
The highest activity was observed for CMK-5* impregnated with an aqueous solution of copper nitrate. Since copper nitrate has the highest solubility in water, this sample had also the highest copper loading in comparison with all other samples synthesized with other solvents. Fig. 4.12 shows that some small particles with a diameter of 5 nm are present in the sample, as well as particles with a size of 20 nm.

![TEM image of CMK-5* carbon impregnated with aqueous solution of copper nitrate. Copper loading is 22 wt.-%](image)

**Fig. 4.12.** TEM image of CMK-5* carbon impregnated with aqueous solution of copper nitrate. Copper loading is 22 wt.-%.

The TEM image of the CMK-5* sample prepared by impregnation with copper acetylacetonate aqueous solution is shown in Fig. 4.13. The copper particles present in this sample are small and homogeneously distributed in the carbon matrix. However, the solubility of Cu(acac)$_2$ in water was quite poor, and after five impregnation steps the copper loading was lower than 2 wt.-% in the obtained sample. The hydrogen yield was below the detection limit, probably due to the low copper content. The functionalization approach itself was successful and a high dispersion of copper oxide was achieved (Fig. 4.13). However, the sample with 2 wt.-% copper was not active in methanol steam reforming, and the highest
performance was achieved by the sample with a copper loading of 22 wt.-%. However, this sample has a broad distribution of copper particle sizes. As already mentioned, copper is able to catalyze the combustion of the carbon. [73] The carbon support in our case can be oxidized by the presence of NO\textsubscript{X} species formed from the decomposition of copper nitrate.

![TEM image of CMK-5* carbon impregnated with aqueous solution of copper acetyl acetate. Copper loading is \( \sim 2 \) wt.-%.

**Fig. 4.13.** TEM image of CMK-5* carbon impregnated with aqueous solution of copper acetyl acetate. Copper loading is \( \sim 2 \) wt.-%.

In order to reduce destruction of the carbon structure during calcination, a mixture of 5\% H\textsubscript{2} in Ar instead of pure argon was used during calcination. The obtained samples were air sensitive due to the small size of the metallic copper particles. These small particles had a narrow size distribution extending up to 5 nm. (Fig. 4.14). It was thus possible to synthesize copper particles within the CMK-5* hexagonally ordered mesoporous carbon starting from CMK-5 only with a partially oxidized surface. Therefore, the subsequent work was focused on samples which had been prepared after preoxidation of the CMK-5. Thus, all CMK-5 samples discussed further are the CMK-5 treated with H\textsubscript{2}O\textsubscript{2}, i.e. CMK-5*. 
**Fig. 4.14.** TEM image of CMK-5* carbon impregnated with aqueous solution of copper nitrate and reduced in 5% H\textsubscript{2} in Ar. Copper loading is 22 wt.-%
4.1.2. Influence of different pore sizes of CMK-5

The proper selection of the SBA-15 template allows one to tailor both the external and internal diameter of the carbon pipes in CMK-5. [138] In CMK-3, on the other hand, it is quite difficult to obtain samples with appreciably different mesopore diameters, mainly due to the fact that the wall thickness of the SBA-15 template is not easy to tailor. The external and internal pipe diameters of CMK-5 type carbon were varied by using SBA-15 templates with appropriate pore diameters. The common procedure to obtain different pore sizes of SBA-15 is to use different temperatures during the ageing stage (usually between 60 °C and 140 °C). Due to the fact that SBA-15-60 and SBA-15-140, synthesized at ageing temperatures of 60 °C and 140 °C, respectively, are produced on the border of the temperature range in which SBA-15 can be obtained, the resulting structures have lower ordering compared with SBA-15 synthesized at 80 and 100 °C. To facilitate the ordering of these mesoporous silica templates SBA-15-60 and SBA-15-140, the samples were treated with sulfuric acid. The action of the sulfuric acid during this treatment is not yet well understood. [139,140]

**Table 4.2.** The textural parameters of CMK-5 synthesized using different SBA-15 templates

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Surface area (BET), m²/g</th>
<th>D_{adsorb}, nm</th>
<th>Volume, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMK-5-80</td>
<td>1540</td>
<td>2.5</td>
<td>1.10</td>
</tr>
<tr>
<td>CMK-5-60</td>
<td>1436</td>
<td>3.3</td>
<td>1.56</td>
</tr>
<tr>
<td>CMK-5-140</td>
<td>1173</td>
<td>3.9</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Nevertheless, this procedure allows partial or complete removal of the template polymer by acid action, and the silica structure is exposed to lower stress during calcination. The
polymer is more easily removed from the silica due to acidic treatment, so it is not necessary to calcine samples afterwards at high temperature. Samples treated with sulfuric acid were calcined afterwards at lower (200 °C) temperature, so the pore size of SBA-15-60 was more or less similar as for SBA-15-100 and larger than for SBA-15-80. Using these SBA-15 samples, hexagonally ordered carbons of the CMK-5 type with pore sizes between 2.5-3.9 nm in diameter were obtained (Table 4.2). In order to remove polymer by calcination, high temperature (560 °C for 6 h) is required, but this treatment results in pores shrinkage. Therefore, SBA-15-100 and SBA-15-80 were not treated with sulfuric acid, because the pore size of both SBA-15s would increase after sulfuric acid treatment and the variation of CMK-5 pore sizes would have been smaller (between 3.3 and 3.9 nm). Pore size control is an important issue in ordered carbon synthesis. Samples were denoted CMK-5-n to indicate samples of CMK-5, which had been synthesized using SBA-15-n as a template.

Fig. 4.15. Isotherms of CMK-5 samples synthesized using the hard templates SBA-15, which had been produced at different aging temperatures in the range between 60 and 140 °C.
Nitrogen adsorption isotherms for these CMK-5 samples are shown in Fig. 4.15. All samples exhibit relatively high adsorption at low pressures, which indicates the presence of micropores. Nitrogen adsorption isotherms for these samples exhibit well-pronounced hysteresis loops that can be attributed to the capillary condensation and evaporation from the mesoporous interiors of the carbon pipes and pores created after silica had been removed. The relative pressure at which the capillary condensation step is observed and, consequently, the primary mesopore diameter [138,141] decreases for composites from CMK-5-80 to CMK-5-140 (for CMK-5-140, the step is poorly pronounced), as could be expected from the unit-cell size for these carbons. CMK-5-60, corresponding to SBA-15-60, has a larger pore diameter than CMK-5-80 carbon (Fig. 4.15). Thus, CMK-5 with three different pore sizes of 2.5, 3.3 and 3.9 were produced. In Table 4.2 it is shown, that the specific surface area decreases with increasing pore diameter of the CMK-5 material. These were the parent samples for the introduction of the copper nanoparticles. When metallic particles are deposited into ordered mesoporous supports, two cases often occur: deposition on the external surface or confinement in the nano-channels. In the first case, severe sintering during thermal treatment is often inevitable, due to the absence of sufficient metal–support interaction. This will lead to the formation of large particles. In the second case, however, the metallic particles are often highly dispersed even when subjected to temperature treatment, due to the confinement by the nano-channels. [79] For all CMK-5 impregnated samples, high dispersion of copper nanoparticles was achieved. The improved procedure of synthesis allows to produce metallic particles within the nano-channels of the carbon structure. After reduction, all Cu/CMK-5 samples were tested in methanol steam reforming. The results of the catalytic tests are presented in Table 4.3. As it was expected the highly distributed copper nanoparticles have a high activity. The yield of hydrogen increases in all three cases with increasing the temperature, which is in agreements with corresponding data. [5,6]
Table 4.3 Hydrogen yield in steam reforming of methanol over the 22 wt.-% copper impregnated CMK-5 samples.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pore diameter, nm</th>
<th>Hydrogen yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>250 °C</td>
</tr>
<tr>
<td>Cu/CMK-5-80</td>
<td>2.5</td>
<td>24</td>
</tr>
<tr>
<td>Cu/CMK-5-60</td>
<td>3.3</td>
<td>38</td>
</tr>
<tr>
<td>Cu/CMK-5-140</td>
<td>3.9</td>
<td>40</td>
</tr>
</tbody>
</table>

Reaction flow 260 ml/min, pressure 1.1 bar, CH$_3$OH÷H$_2$O ratio is 1:1, catalyst weight 100 mg, reaction temperature 250-300 °C

Fig. 4.16. TEM image of Cu/CMK-5-80 carbon, with a copper loading of 22 wt.-%.

We expected that the variation of the CMK-5 pore sizes would allow control of the copper particle sizes and thus has an influence on the catalytic performance of copper particles. In order to check this, TEM analysis were carried out. The TEM images of the
catalysts are presented in Fig. 4.14, Fig. 4.16, and Fig. 4.17. Unfortunately, the image resolution of the TEM instrument with the protective gas sample holder is lower than with the regular sample holder.

![TEM image of Cu/CMK-5-140 carbon, with a copper loading of 22 wt.-%.](image)

**Fig. 4.17.** TEM image of Cu/CMK-5-140 carbon, with a copper loading of 22 wt.-%.

Thus, the analysis of the particle sizes is difficult, and no clear correlation between textural parameters and Cu particle size could be established by TEM (Fig. 4.14, Fig. 4.16 and Fig. 4.17). Thus, at this point it is not clear whether the diameter of the copper particles is controlled by the pore sizes of the CMK-5 support, and whether there is a corresponding effect on catalytic activity.

### 4.1.2.1. Temperature programmed reduction (TPR)

It was expected that a correlation could be established between the catalytic activities of the samples and the pore sizes of the CMK-5 support materials. Direct analysis of particle size by TEM was found to be difficult. However, TPR should produce additional evidence. It is well known [142,143] that smaller particles are reduced at lower temperature. The
reducibility of Cu/CMK-n catalysts was thus studied by TPR analysis. The profiles obtained for the Cu/CMK-5-n catalysts are presented in Fig. 4.18. As already mentioned, CMK-5-100 has similar characteristics (pore volume and pore size) as CMK-5-60, and therefore, only CMK-5-60 was analyzed.

![TPR analysis of copper nanoparticles supported on CMK-5 ordered carbons with different pore sizes.](image)

**Fig. 4.18.** Temperature programmed reduction analysis of copper nanoparticles supported on CMK-5 ordered carbons with different pore sizes.

With increasing pore size of the hexagonally ordered carbon tubes, a slight shift of the peak maximum of hydrogen consumption to higher temperature was observed. The lowest reduction temperature at 232 °C was found for Cu/CMK-5-80 with the smallest pore size. It indicates that copper species are small, hence dispersion of the catalyst is higher. Generally a higher temperature is needed for the reduction of larger Cu crystallites. An increase in reduction temperature for the Cu/CMK-5-60 with the maximum reduction peak at 236 °C indicates that the size of copper crystallites increases with increasing pore size of CMK-5 support. The highest reduction temperature for the CMK-5 supported copper nanoparticles was observed for the Cu/CMK-5-140 sample, which has the highest pore diameter. Since the error of the measurement is around 5 °C, and the measurements all within or close to this
error, no firm conclusions can be drawn. However, a trend of increasing reduction temperature with increasing pore size, and thus possibly with increasing copper particle size can be seen. A similar trend was observed in a previous study on Cu reducibility by Robertson et al. [144] which showed that highly dispersed CuO/SiO$_2$ was reduced at much lower temperature than unsupported CuO particles. The broad or asymmetric TPR profiles may be related to the two-step reduction: Cu(II) $\rightarrow$ Cu(I) $\rightarrow$ Cu(0), as suggested by Lindstrom et al. [143] However, it can be noted that the two reduction steps of Cu(II) are not distinguishable by the TPR technique when Cu(II) species are highly concentrated. [52] This is due to a broadening of the peaks in the presence of a larger amounts of Cu(II), or the large heat release, which enhances the second reduction step. It should be noted that the amount of copper loaded corresponded to the amount of H$_2$ consumed, which can be determined from the peak area, indicating that full reduction of the samples was achieved under the reaction condition.

As shown in Table 4.3, at 250 °C the catalytic activity increases with increasing pore sizes of the CMK-5 support. Nevertheless, the highest hydrogen yield over the studied series of CMK-5 at 275°C was achieved for Cu/CMK-5-60. At 300 °C all catalyst showed a pronounced deactivation and a drop of 30% of the original activity after 80 min under reaction flow. One of the reasons was a fracture of the catalytic particles during the reaction. Before the reaction, all samples were pelletized (particle sizes 250-500 µm). The composite material (SBA-15_CMK-5) was previously palletized, because shaping is quite difficult for carbon material. However, the particles lose the original shape during reaction and they were found to fragment under reaction condition. Moreover, the pressure started to rise inside of the reactor during the reaction, which also damaged the particles. Finally, substantial amounts of fluffy carbon were present in the catalyst after reaction. In order to avoid this problem, the commercial pelletized activated carbon Kugelkohle with particles 150-200 µm in size and a mesopore diameter 3.6 nm was used.
4.1.2.2. Influence of the synthesis route of the Cu/CMK-5 samples

Before discussing results obtained with other carbons (CMK-3 and Kugelkohle) the influence of the CMK-5 synthesis method will be discussed. There are two methods (Ryoo’s [116] and Zhao’s [93]) available for the synthesis of SBA-15 and CMK-5 materials. In the case of SBA-15, the difference lies in the concentration of HCl in the micelle formation stage.

Table 4.4. Comparison of textural parameters SBA-15 silica template synthesized by Ryoo and Zhao methods.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (BET), m$^2$/g</th>
<th>D (BJH), nm</th>
<th>Volume, cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-90$^R$</td>
<td>644</td>
<td>6.9</td>
<td>1.16</td>
</tr>
<tr>
<td>SBA-15-90$^Z$</td>
<td>729</td>
<td>6.6</td>
<td>1.10</td>
</tr>
</tbody>
</table>

$^R$ Synthesized by Ryoo method.

$^Z$ Synthesized by Zhao method

For SBA-15 synthesized by the Zhao method, the micelle formation is carried out at 40 °C for 4 hours at high concentration of HCl, whereas in the of case Ryoo’s procedure the reaction takes place over 24 hours at 35°C and a lower concentration of HCl. The SBA-15 obtained by these two methods do not have essential differences in the structural parameters (Table 4.4). For the next step, the synthesis of CMK-5 ordered carbon, the difference lays in the polymerization stage.
Table 4.5. Comparison of textural parameters of CMK-5 type carbon synthesized by Ryoo and Zhao methods.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (BET), m²/g</th>
<th>D (BJH), nm</th>
<th>Volume, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMK-5-80⁺</td>
<td>1540</td>
<td>2.5</td>
<td>1.10</td>
</tr>
<tr>
<td>CMK-5-60⁺</td>
<td>1436</td>
<td>3.3</td>
<td>1.56</td>
</tr>
<tr>
<td>CMK-5-140⁺</td>
<td>1173</td>
<td>3.9</td>
<td>1.47</td>
</tr>
<tr>
<td>CMK-5-80⁻</td>
<td>1434</td>
<td>3.3</td>
<td>1.48</td>
</tr>
<tr>
<td>CMK-5-60⁻</td>
<td>1349</td>
<td>3.3</td>
<td>1.54</td>
</tr>
<tr>
<td>CMK-5-140⁻</td>
<td>1286</td>
<td>3.5</td>
<td>1.38</td>
</tr>
</tbody>
</table>

⁺ Synthesized by Ryoo method.
⁻ Synthesized by Zhao method

Ryoo proposed AlCl₃ as a catalyst for the polymerization of furfuryl alcohol. After introduction of alumina into the silica matrix, the samples were calcined at 560 °C, and thus, alumina combined with the silica walls. In this way, the polymerization process starts directly from the silica template walls. The textural parameters of samples prepared by this procedure are presented in Table 4.5. In the case of Zhao’s method for the synthesis of CMK-5, oxalic acid was used as a polymerization catalyst. [50] Oxalic acid was introduced into the silica template directly with the furfuryl alcohol. Thus, this method is shorter by one step, since the additional calcination step is not needed. However, the polymerization of furfuryl alcohol spontaneously started homogeneously all over the sample, and there is not a preferential direction of growth. The following calcination was carried out under argon. Despite the fact that Ryoo’s method of CMK-5 synthesis preferentially results in the carbon growing from walls, it was difficult to control the carbon tube size by tuning the silica tube size. As can be seen in Table 4.5 and Fig. 4.19, that the textural parameters, such as pore volume and pore diameter, of CMK-5 synthesized by the Ryoo method do not depend on the
silica used. In contrast to that, CMK-5 samples synthesized by the Zhao method show obvious differences in pore diameter as well as pore volume. (Fig. 4.15, Table 4.5)

![Graph showing adsorbed volume cm³/g vs. P/P₀ for different temperatures.]

**Fig. 4.19.** The isotherms of CMK-5 synthesized using the hard template SBA-15, which had been produced at different ageing temperatures in the range between 60 and 140 °C.

Another disadvantage of Ryoo’s method was found after the copper introduction stage. Fig. 4.20 shows a micrograph of the Cu/CMK-5 sample. The copper species are present in two phases. Copper particles are distributed in the carbon matrix as well as on the alamosilicate particles. This alamosilicate is a residue from the aluminum chloride, which was used as a catalyst for polymerization. It seems that after calcination the aluminum forms a compound with the silica wall which could not completely be removed during leaching. The amount of the remaining alamosilicate unsystematically varied between 5 and 10 wt.-%. Nevertheless, hydrogen productivities obtained with these samples as catalysts were comparable to those reported in Table 4.3, in some cases even exceeded those. However, it was not possible to control the fraction of copper located on the carbon and on the residual alamosilicate.
Fig. 4.20. Cu/CMK-5 sample prepared with CMK-5 synthesized by the Ryoo method.
4.1.3. Cu/CMK-3, Cu/Kugelkohle catalytic systems

It was presumed that the type of carbon supports should also affect the structure of the active component and, thus, the catalytic activities. Table 4.6 reports the hydrogen yields in the steam reforming of methanol for copper particles on several supports such as CMK-3, CMK-5 and Kugelkohle in a temperature range between 250 °C and 300 °C.

Table 4.6. Hydrogen yield over different carbon types as supports for copper nanoparticles. Copper loading is 22.0 wt.-% for all catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pore size, nm</th>
<th>Particle size, nm</th>
<th>Hydrogen yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/CMK-3(^a)</td>
<td>2.1</td>
<td>10±4</td>
<td>18 28 35</td>
</tr>
<tr>
<td>Cu/CMK-5(^a,b)</td>
<td>3.3</td>
<td>5±2(^c)</td>
<td>38 57 61</td>
</tr>
<tr>
<td>Cu/C</td>
<td>3.6</td>
<td>4±2</td>
<td>59 65 67</td>
</tr>
<tr>
<td>Cu/ZnO/Al(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>64 71 82</td>
</tr>
</tbody>
</table>

\(^a\) Surface of carbon was treated with 15 wt.-% hydrogen peroxide. 
\(^b\) The CMK-5 with a pore diameter 3.3 nm was used. 
\(^c\) The difference of the copper particle size supported on CMK-5, CMK-3 and Kugelkohle is larger than in case of nanoparticles supported on CMK-5, in which pore diameter was varied. Thus, according TEM measurements, for those materials it was possible to calculate the particle size distribution.

The highest activity was observed for the Cu/C system (copper nanoparticles supported on Kugelkohle). This catalyst produced more hydrogen than the best prepared from CMK-5 type carbon with 3.3 nm pore size. Nevertheless, the pore size in this case does not fully describe the structural properties of the Kugelkohle, other than for CMK-5 carbons. As was shown in Fig. 4.13, Fig. 4.16, and Fig. 4.17, we can clearly observe for Cu/CMK-5 that Cu particles with an average size of about 5 nm are highly dispersed (Fig. 4.21).
Large metallic copper particles are not present on the Cu/CMK-5 sample. In contrast, for Cu/CMK-3, where copper was deposited by the same method as for Cu/CMK-5, we can
observe many large particles with sizes between 6 and 14 nm deposited on the external surface of CMK-3 (Fig. 4.22).

![HRTEM image of one single copper particle supported on CMK-3 type carbon](image)

**Fig. 4.23.** HRTEM image of one single copper particle supported on CMK-3 type carbon

The average size of these copper particles is 10 nm. This material is different from CMK-5, and can not be described just as carbon with mesopores of 2.1 nm diameter. CMK-5 carbon has two different types of porosity: the first type of pores originates from the silica template, which also occur in the CMK-3 carbon, and the second type of pores is located inside the nanotubes. Usually CMK-3 type carbon is described as hexagonally packed rods. Thus, CMK-3 only has mesopores generated by the silica template, which are connected in such a way that metal particles have a possibility to aggregate. For this reason the copper impregnated on CMK-3 type carbon generates large particles on the surface after reduction. A close inspection of a single copper particle supported on CMK-3 type carbon shows that
this particle has a multiply twinned crystalline structure and is not a single crystal (Fig. 4.23). Such large particles may be formed by agglomeration of small nanoparticles of 3-5 nm in size.

Fig. 4.24 presents the TEM image of a Cu/C sample. Clearly visible are supported small (4 nm in diameter) copper particles distributed on the Kugelkohle (Fig. 4.21).

The catalytic activity of the samples in methanol steam reforming depends on the copper particle sizes. The most active Cu/C catalyst has the smallest copper diameter and, thus, the highest hydrogen yield (Table 4.6). For the Cu/CMK-5 sample with copper particles of 5 nm size slightly lower catalytic performance was observed. This is probably due to the copper particle size being 1 nm larger than for Cu/C. The catalytic activity obtained for the Cu/CMK-3 sample, is approximately two times lower in comparison with other tested materials (Table 4.6). The diameter of Cu/CMK-3 particles is also two times larger. Thus, the specific surface area of such large particles is smaller, and the catalytic performance is expected to be lower.

![Fig. 4.24. Cu/C sample after reduction at 250 °C in 5 % hydrogen.](image)
The Cu/C sample does not only show the highest catalytic activity but also the highest stability under reaction conditions in comparison with other studied carbon materials. The catalyst starts to lose the original activity after only 10 hours under reaction flow at 300 °C. One of the reasons for this is the mechanical stability of Kugelkohle under reaction conditions. There was no difference in the granular structure before and after reaction.

4.1.3.1. Specific surface area analysis of copper impregnated CMK-5, CMK-3 and Kugelkohle carbons

With regard to the essential nature of the active copper phase for the steam reforming of methanol, the metallic copper surface area generally has been assumed to be the main factor in the structure-activity correlation of Cu-based catalysts. [146-148] However, some recent studies have found no correlation between hydrogen yield with the surface area of metallic copper for Cu-based catalysts. [51,145-148] Bartley et al. [149] proposed, that only a small fraction of the copper (e.g. surface defects, particular surface facets etc.), rather than the total surface area may be important for the activity.

![Graph showing reaction rate vs. copper surface area at different temperatures](image)

**Fig. 4.25.** Dependence of reaction rate vs. copper surface area at three different temperatures.
These suggestions are supported by the observations of a nonlinear relationship between activity and copper surface. At this juncture, it is interesting to investigate the influence of copper surface area in steam reforming of methanol for copper/carbon catalysts. Furthermore, the information on specific copper surface area helps to estimate the influence of the copper particle size on the catalytic performance. The activity of the catalysts as a function of the copper surface area is shown in Fig. 4.25. A linear correlation albeit with substantial scatter between the reaction rate and the copper surface area was found for the studied catalysts in the temperature range between 250 °C and 300 °C. A similar correlation between the specific copper surface area of the catalyst and methanol synthesis activity has already been proposed by Chinchen et al. [150]. As it was expected, the highest copper surface area 24.3 m²/gCu was observed for the Cu/C sample. The specific surface area, which was obtained for Cu/CMK-3 material, is 3.3 m²/gCu and the catalytic performance of this catalyst is also low. As mentioned above, the increase in hydrogen yield with increasing temperature for all Cu/carbon catalyst was observed. Nevertheless, Fig. 4.25 shows that the reaction rate does not proportionally increase with the temperature. This can be due to instability of the Cu/CMK-5 catalyst under reaction flow at high temperatures.

**Table 4.7.** The weight specific rate of copper nanoparticles supported on CMK-3, CMK-5 and Kugelkohle mesoporous carbon.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Copper surface area, m²/gCu</th>
<th>Copper surface area⁹, m²/gCu</th>
<th>(-rCH₃OH)², molCuOH/min×gCu₂</th>
<th>250 °C</th>
<th>275 °C</th>
<th>300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/CMK-3</td>
<td>3.3</td>
<td>67</td>
<td>0.011</td>
<td>0.018</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td>Cu/CMK-5</td>
<td>13.0</td>
<td>135</td>
<td>0.024</td>
<td>0.036</td>
<td>0.038</td>
<td></td>
</tr>
<tr>
<td>Cu/C</td>
<td>24.3</td>
<td>169</td>
<td>0.037</td>
<td>0.041</td>
<td>0.042</td>
<td></td>
</tr>
</tbody>
</table>

⁹Copper surface area calculated according copper particle size.

²CMK-5 with a pore size of 3.3 nm was used for this studies.
However, the specific copper surface of Cu/CMK-5, Cu/CMK-3 and Cu/C calculated according its particle size is much larger than observed by frontal chromatography measurements (Table 4.7). If we assume that all particles are spherical with a diameter equal to half of the particle size (Fig. 4.21, Table 4.6), the copper surface area for the Cu/C should be $169 \text{ m}^2/\text{g}_{\text{Cu}}$ for Cu/CMK-5 and Cu/CMK-3 it should be $135 \text{ m}^2/\text{g}_{\text{Cu}}$ and $67 \text{ m}^2/\text{g}_{\text{Cu}}$, respectively. Thus, not all copper in copper/carbon materials is available for the N$_2$O adsorption and, therefore, for the methanol steam reforming process.

There could be several reasons for the partial inaccessibility of copper surface. It could be due to the blocking of carbon pores by the added copper. When a particle is in a pore, part of the surface area is inaccessible and the other particles in this pore are completely inaccessible, for the catalytic process. Another reason for the reduced copper surface could be the coverage of the particle by carbon.

4.1.3.2. Temperature programmed reduction (TPR)

In order to investigate the reducibility of the copper species supported on different mesoporous carbons, TPR measurements were carried out. The TPR profiles of the Cu/Carbon catalysts prepared by impregnation with 4.5 M copper nitrate solution into functionalized CMK-5, CMK-3 and Kugelkohle are presented in Fig. 4.26. For comparison, the TPR profile of the industrial catalyst Cu/ZnO/Al$_2$O$_3$ is also presented. The TPR profiles of all three copper catalysts supported on carbon are characterized by the presence of a single reduction peak.
Fig. 4.26. Temperature programmed reduction analysis of copper nanoparticles supported on CMK-5, CMK-3 and Kugelkohle in comparison with the industrial catalyst Cu/ZnO/Al$_2$O$_3$.

The maximum of the reduction peak for Cu/C is located at 239 °C, and those for Cu/CMK-5 and for Cu/CMK-3 at 236 °C and 239 °C, respectively. These values are identical within the error margin. All TPR traces exhibited characteristic shoulders left to the main reduction peak. The broad TPR profiles could be due to two causes: one is related to the two-step reduction of Cu$^{2+}$ to Cu$^0$ over Cu$^{1+}$ and the other is the presence of several particle dimensions. Copper particles supported on CMK-3 rod type carbon, as presented in Fig. 4.22 were significantly larger than those found for Cu/CMK-5 and Cu/C (Fig. 4.14, Fig. 4.21 and Fig. 4.24, respectively). Nevertheless, the expected shift of the reduction peak maximum for Cu/CMK-3 material to higher temperature was not observed. This is probably due to a high concentration of copper particle defects at which the reduction reaction can start (Fig. 4.23). [151] Surprisingly, the increase of temperature during the reduction process inside of the reactor was not linear, in contrast to the external heating. The pronounced step near the reduction maximum was observed for all TPR profiles of copper/carbon samples.
Fig. 4.27 shows the consumption of hydrogen during reduction versus the temperature of reactor (the temperature measured in the catalytic bed is different than the temperature of the reactor). The temperature peak is found near the maximum of the reduction peak for all studied samples. The reason for this phenomenon may be local combustion of the carbon support catalyzed by fresh metallic copper in the presence of oxidative NOX, which is generated from the nitrate. The reduction of the industrial catalyst proceeds with two peaks with a maximum at 201 °C. It may be concluded that the low-temperature reduction peaks arise from the reduction of very fine CuO particles that are well dispersed on the Al2O3-ZnO support, while the second peak was generated as a result of strong interaction between CuO and the ZnO in the catalyst. [152]

Furthermore, it was found that the Cu/CMK-5 sample reduced at 300 °C had lower hydrogen yield, which was similar to Cu/CMK-3. It was presumed that the Cu/CMK-5 reduced at this temperature have copper particle size comparable with the Cu/CMK-3.
Fig. 4.28. CMK-5 supported copper nanoparticles reduced at 300 °C.
Copper loading is 22 wt.-%.

Fig. 4.28 shows the copper particles supported on the CMK-5 with the pore size of 3.3 nm and reduced at 300 °C. The average size of the copper particles is much bigger than 5 nm. The copper particles of Cu/CMK-5 reduced at 300 °C have multiply twinned crystalline structure similar to that observed for Cu/CMK-3. As already seen for the Cu/CMK-3, the larger copper particles have lower catalytic activity. The agglomeration of copper particles could be explained by the high mobility of the small copper crystallites at elevated temperatures. However, this effect was not observed for copper particles supported on Kugelkohle. Copper impregnated on Kugelkohle samples, which were reduced at 300 °C and 400 °C (Fig. 4.29), exhibited the same copper particle size distribution, thus suggesting a favourable influence of the surface functional groups on the dispersion and sintering resistance of the Cu particles.
No sintering of the copper particles for Cu/C was observed after 10 hours under reaction conditions, and the copper distribution was still the same as it was in the as synthesized sample. It should also be noted, that the activated carbon is more stable to H$_2$O$_2$ treatment than the CMK-5 ordered mesoporous carbon. [130,136]
Nevertheless, even the Cu/C catalysts showed instability under reaction conditions and started to lose the activity after 12 hours. As shown in Fig. 4.30, copper particles start to move to the surface of the carbon and the catalyst pellets became brownish. Copper on carbon does not seem to be stable for long, and furthermore, at lower temperature in presence of some oxidative species (air, NO\textsubscript{x}, SO\textsubscript{x}), [73] copper uncontrollably catalyzes the combustion of carbon, resulting in partial degradation of the carbon support.

4.1.3.3. Adsorption measurements

The more stable Kugelkohle takes more time and harsher conditions to show evidence of structural degradation than the unstable CMK-3 and CMK-5. The data collected in Table 4.8 show the strong decrease of BET surface area for all carbons after reduction.

**Table 4.8.** Textural properties of carbon supports: CMK-5, CMK-3 and Kugelkohle and catalysts with 22 wt.-% copper loading: Cu/CMK-5, Cu/CMK-3 and Cu/C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area, m\textsuperscript{2}/g</th>
<th>D\textsubscript{adsorb}, nm</th>
<th>Volume, cm\textsuperscript{3}/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMK-3\textsuperscript{a}</td>
<td>1569</td>
<td>2.1</td>
<td>1.10</td>
</tr>
<tr>
<td>Cu/CMK-3\textsuperscript{a}</td>
<td>1006</td>
<td>2.2</td>
<td>0.62</td>
</tr>
<tr>
<td>CMK-5\textsuperscript{a,b}</td>
<td>1436</td>
<td>3.3</td>
<td>1.56</td>
</tr>
<tr>
<td>Cu/CMK-5\textsuperscript{a,b}</td>
<td>884</td>
<td>3.1</td>
<td>0.57</td>
</tr>
<tr>
<td>Kugelkohle</td>
<td>1928</td>
<td>3.6</td>
<td>0.98</td>
</tr>
<tr>
<td>Cu/C</td>
<td>1084</td>
<td>3.6</td>
<td>0.59</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Surface of carbon was treated with 15wt.-% hydrogen peroxide.

\textsuperscript{b}The CMK-5 was used with the pore diameter 3.3 nm.

The decrease of the specific surface area after copper impregnation is independent of the carbon type and it is not proportional to the amount of copper introduced. In the case of
CMK-5 the decrease of the pore volume after impregnation was more pronounced than for the other mesoporous carbons studied. For copper supported on Kugelkohle and CMK-3 samples the pore volume decrease is 0.4 cm$^3$/g. That is nearly two times more than it should decrease after impregnation of 22 wt.-% copper. Thus, the particular damage of carbons in the case of CMK-3, CMK-5 and Kugelkohle might have something in common. Due to the pronounced decrease of all textural parameters (surface area and pore volume) after reduction of the copper impregnated CMK-5 carbon, this carbon was used to study the effect in detail and for different amounts of copper (Table 4.9).

**Table 4.9.** Influence of copper loading and nitric acid treatment on textural properties such as pore diameter, pore volume and specific surface area of CMK-5 carbon.

<table>
<thead>
<tr>
<th>Cu amount, wt.-%</th>
<th>HNO$_3^a$, M</th>
<th>Surface area, m$^2$/g</th>
<th>Volume, cm$^3$/g</th>
<th>$D_{adsorb.}$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>1407</td>
<td>1.55</td>
<td>3.9</td>
</tr>
<tr>
<td>3.82</td>
<td>-</td>
<td>1004</td>
<td>1.11</td>
<td>3.8</td>
</tr>
<tr>
<td>7.64</td>
<td>-</td>
<td>884</td>
<td>0.99</td>
<td>3.9</td>
</tr>
<tr>
<td>15.27</td>
<td>-</td>
<td>770</td>
<td>0.81</td>
<td>3.8</td>
</tr>
<tr>
<td>22.90</td>
<td>-</td>
<td>590</td>
<td>0.57</td>
<td>3.8</td>
</tr>
<tr>
<td>26.72</td>
<td>-</td>
<td>483</td>
<td>0.45</td>
<td>3.8</td>
</tr>
<tr>
<td>30.54</td>
<td>-</td>
<td>461</td>
<td>0.40</td>
<td>3.8</td>
</tr>
<tr>
<td>-</td>
<td>3.33</td>
<td>1296</td>
<td>1.34</td>
<td>3.8</td>
</tr>
<tr>
<td>-</td>
<td>10</td>
<td>1198</td>
<td>1.20</td>
<td>3.8</td>
</tr>
</tbody>
</table>

$^a$For the influence of nitric acid treatment 65 mg of carbon was impregnated with 0.1 mL of 3.3 M and 10 M HNO$_3$, respectively.

For CMK-5 type carbon also pore blocking effects can take place by introducing copper in the pore structure. In order to investigate the influence of copper loading on the pore volume and specific surface area, CMK-5 samples with increasing copper
concentration from 4 to 30 % were examined by nitrogen sorption. Isotherms of copper impregnated CMK-5 carbon samples over the whole relative pressure range are shown in Fig. 4.31 a. The starting carbon support material is also included for comparison. The evolution of the pore size distribution of copper/CMK-5 samples with increasing copper loading from 4 up to 30 wt.-% is shown in Fig. 4.31 b. The first peak is attributed to the pores which were obtained from the silica template, and the second describes the pores within the nanopipes. The intensity of both peak decreased with an increasing amount of copper. Adsorption isotherms can be classified as type IV for CMK-5 type carbon and Cu/CMK-5 samples according to the Brunauer, Deming, Deming and Teller (BDDT) nomenclature. [134] With an increasing amount of copper in the samples, the specific surface area and pore volume were observed to decrease (Fig. 4.31 a, Table 4.9). The sample with 3.8 wt.-% copper exhibited a 29% decrease of the BET surface area compared to the CMK-5 as made sample. A 37% decrease of BET surface area was observed for the sample with 7.6 wt.-% copper loading. Similar numbers were obtained for pore volume changes: a pore volume decrease in 28% for the sample with 3.8 wt.-% copper loading and a pore volume decrease in 36% for the sample with 7.6 wt.-% copper loading (Table 4.9, Fig. 4.31 a). The changes observed for the surface area of the Cu/CMK-5 samples cannot only be explained by the mass increase of the samples due to the addition of copper. As mentioned before, a solution of copper nitrate was used as the copper source for the impregnation of the carbon support. During the reduction and thermal decomposition, NO\textsubscript{x} species, which have high oxidative potential, could be generated. In order to examine the damaging effect attributed to NO\textsubscript{x}, carbon samples were impregnated only with nitric acid. These samples were reduced in the same way as copper contained samples. The synthesis of the Cu/CMK-5 materials with copper loadings in the range 3.8 – 30.5 wt.-% was carried out by impregnation with 0.56 M – 4.5 M of Cu(NO\textsubscript{3})\textsubscript{2} solution.
Fig. 4.31. Nitrogen isotherms (a) and pore size distribution (BJH) of CMK-5 type carbon with copper loading between 3.8 and 30.5 wt.-% (b).

Thus, CMK-5 impregnated with 3.3 M and 10 M nitric acid solutions were used (3.3 M HNO₃ concentration is in the range of copper impregnated samples and 10 M HNO₃ concentration is two times in excess). However, as shown in Table 4.9, the decrease in specific surface area and pore volume was much lower upon nitric acid treatment of CMK-5 material. The 8% decrease of surface area was observed after treatment of CMK-5 with 3.3 M nitric acid and 15% after treatment with 10 M nitric acid (Table 4.9). This decrease of specific surface area is less than was observed for copper containing materials. Nevertheless, this experiment is not fully conclusive because the nitric acid influence during the reduction
and copper nitrate effect might be different. More precisely, the experiment in this case should be carried out with the nitrate of another metal, which has the same temperature of reduction maximum and does not have other effects on carbon. Thus, it was not possible to examine the damage which could be attributed only to \( \text{NO}_x \), because no proper reference experiment could be devised.

Nevertheless, there are several possible reasons for the decrease in BET surface area and pore volume for Cu/CMK-5 samples. First, there is the probability of pore blocking. This effect could play an important role for the samples where the concentration of copper is high, but should be insignificant for samples with low concentration of copper. However, as it was mentioned above, the decrease in specific surface area of 29% for the sample containing 3.8 wt.-% copper takes place. Obviously, a pore blocking effect at this concentration of copper can be excluded. Another reason could be local decomposition of the carbon by introducing the copper. The influence of adding copper can be easily calculated, if copper does not have any damaging effect on the carbon and just the additional weight is taken into account. In Fig. 4.32 one can see the decrease in specific surface area of CMK-5 obtained experimentally and by calculating the influence of added copper as described below. Mesoporous carbon \( \text{as made} \) has a specific surface area \( (S_{\text{CMK}}) \) of 1407 m\(^2\)/g. Metallic copper usually has a surface area \( (S_{\text{Cu}}) \) of 6-25 m\(^2\)/g. \cite{6} Thus, if we take into account only the decrease in specific surface area by the presence of copper, the 3.8 % copper loaded CMK-5 should have a surface area of \( (S_{3.8\%}) =(100-3.8)\times S_{\text{CMK}} + 3.8\times S_{\text{Cu}} \) (Fig. 4.32 a). However, as can be clearly seen, this statement does not correspond to the experimental data. In order to find a better fit for the experimental data, it was assumed that copper damages the ordered structure of the carbon already at a concentration level of 3.8 wt.-%.
Fig. 4.32. Calculated and measured surface area after introducing copper modelled under the assumption of no structural damage (a) and modelled under the assumption that damage already occurs at the 3.8% loading level (b).

Thus, the calculation starts from the second point $S_{CMK}$, taking into account that at 3.8 wt.-% the structure is damaged to result in $S_{CMK} = 1004 \text{ m}^2/\text{g}$, which is the surface area of CMK-5 with 3.8 wt.-% Cu. As can be seen in Fig. 4.32 b, the curves calculated are in good agreement with the experiment. The fit can be further improved by taking into account possible pore blocking at high copper concentrations or additional damage, depending on copper loading. Nevertheless, the pore blocking effect for the concentration of 22 wt.-% will be much smaller in comparison with the decrease in specific surface area already caused by 3.8 wt.-% copper. Therefore the observed diminution of specific surface area in the samples was predominantly attributed to the local destruction of the carbon structure by the copper.

The decrease of the surface area was also found for Cu/CMK-3 and Cu/C material with 22 wt.-% Cu loading (Table 4.8), probably caused by similar effect.

Another possibility to analyse the copper influence on the ordered carbon support is removing copper after reduction (by treatment with 1M solution of HNO$_3$ for 2 days at room
temperature). Fig. 4.33 shows the isotherms of the original CMK-5 material, treated with hydrogen peroxide, 10 wt.-% copper loaded CMK-5, and the same CMK-5 after removing the copper nanoparticles with nitric acid. The numerical values of the textural parameters of the samples are given in Table 4.10. The CMK-5, after removing copper, is different from the original. The surface area is decreased by 700 m²/g, and less than half of the pore volume is retained. Nevertheless, the pronounced hysteresis loop is still observed (Fig. 4.33).

Table 4.10. Textural changes of CMK-5 by impregnation and leaching of copper.

<table>
<thead>
<tr>
<th>Cu loading, wt.-%</th>
<th>Surface area (BET), m²/g</th>
<th>Volume, cm³/g</th>
<th>D_adsorb., nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>1656</td>
<td>1.87</td>
<td>3.5</td>
</tr>
<tr>
<td>10</td>
<td>1236</td>
<td>0.96</td>
<td>3.6</td>
</tr>
<tr>
<td>- a</td>
<td>902</td>
<td>0.71</td>
<td>3.8</td>
</tr>
</tbody>
</table>

*aCMK-5, which was impregnated by 4.5 M Cu(NO₃)₂ solution up to 10 wt.-% Cu concentration in carbon; then treated with 1M HNO₃ solution at room temperature for two days to extract the copper.

The pore diameter is also changed and seems to be expanded in comparison with the starting CMK-5. The pore volume as well as specific surface area of Cu/CMK-5 treated with nitric acid is lower than the parent sample with 10 wt.-% copper loading. The effect is much higher than observed after similar treatment of CMK-5 with 1M HNO₃ at room temperature. Thus, the copper locally destroyed CMK-5, and copper removal leads to further structural degradation. Nevertheless, due to above described difficulties to perform the independent experiment, we cannot completely exclude the damaging influence of NOₓ obtained during the decomposition copper nitrate on the carbon structure.
Fig. 4.33. Sorption isotherms of a) original CMK-5, b) Cu/CMK-5 with copper loading of 10 wt.-% and c) Cu/CMK-5 carbon after leaching copper by treatment with 1M HNO₃.

4.1.3.4. XRD measurements of copper particles supported on different mesoporous carbon

Another method to investigate the copper particle size is X-ray diffraction. However, XRD measurements in the 2θ range 20-70° did not show any resolved signals of copper species for samples with copper loading up to 26.8 wt.-% supported on CMK-5 type carbon (Fig. 4.34). Mesoporous carbon does not have pronounced reflections in the wide angle range.
Fig. 4.34. XRD patterns of CMK-5 with different copper loading at angles $2\theta$ between 20 and 70°.

Obviously, for the Cu/CMK-5 with a copper loading up to 26.8 wt.-%, we cannot observe any diffraction peaks which would correspond to the metallic copper phase, indicating either the amorphous nature of copper in Cu/CMK-5 or that the size of Cu is smaller than the XRD detection limit. Copper supported particles on CMK-3 are around 10 nm in diameter (Fig. 4.21 and Fig. 4.22).

Fig. 4.35. XRD patterns of (a) Cu/CMK-3 with a copper loading of 22 wt.-% and (b) CMK-3 at angles $2\theta$ between 20 and 70°.
Wide angle XRD measurements also for this sample did not show any reflections for metallic copper (Fig. 4.35). From closer TEM examination of one single Cu particle, a multiply twinned particle structure was detected (Fig. 4.23). In particular, it was observed that a single particle consists of several crystalline domains. This observation might therefore explain the difficulties detecting Cu reflections using XRD, since with XRD the sizes of coherently scattering domains determines the width of the reflection, not the particle size. The Cu/C sample has small particles of average 4.2 nm size (Fig. 4.21 and Fig. 4.24). Nevertheless, the XRD pattern illustrated in Fig. 4.36 shows a broad signal which can be attributed to Cu$^{1+}$ oxide. Possibly, copper is differently organized on the Kugelkohle support. Therefore the copper particles supported on Kugelkohle have the highest activity in steam reforming of methanol. Some authors [5,40-42] observed in in situ studies that the most active catalyst in methanol steam reforming has the copper in Cu$^{1+}$ oxidation stage. However, it cannot be only explanation for the highest activity Cu/C in methanol steam reforming in comparison with other copper/carbon systems (Cu/CMK-3 and Cu/CMK-5), due to the fact that copper particles have a risk of being partly oxidized during the sample preparation procedure for the XRD measurement.

**Fig. 4.36.** XRD patterns of Kugelkohle (a) and Cu/C with a copper loading of 22 wt.-% at angles 2$\theta$ between 20 and 70$^\circ$ (b).
4.1.4. Cu/CMK-3, Cu/CMK-5, Cu/Kugelkohle catalytic systems. Effect of copper loading on catalytic activity

In order to investigate the influence of the copper concentration on the catalytic activity, catalysts with different loadings of copper were synthesized and studied in the steam reforming of methanol. In the case of CMK-5 type carbon, the effect of the copper loading was studied in detail. CMK-5 has the highest pore volume, and the highest copper loading can be achieved by completely filling it with the concentrated solution of copper salt. It is possible to achieve even higher copper loading by repeating the impregnation steps. After completely filling the pore volume with concentrated solution, the samples were heated to 130 °C for nitrate decomposition under an inert atmosphere. Before repeating the impregnation procedure, the remaining pore volume was measured by nitrogen adsorption. Increasing the concentration copper in CMK-5 by a second impregnation step up to 26 wt.-% by this procedure, however, was unsuccessful. It can be seen in the TEM image presented in Fig. 4.37.

Fig. 4.37. CMK-5 type carbon impregnated in two steps to achieve 26 wt.-% loading.
The CMK-5 type carbon seemed to lose the ordered structure after the first impregnation and the reduction of copper, so that in the second step the copper was not confined to the pore system, but agglomerated in large particles. Thus, the copper loading is limited by the pore volume of the carbon support. As it can be seen in Table 4.11, yield of hydrogen increases with increasing copper loading for CMK-3 and Kugelkohle carbon supports.

**Table 4.11.** The influence of copper loading on catalytic properties of copper nanoparticles supported on CMK-3, CMK-5 and Kugelkohle mesoporous carbon.

<table>
<thead>
<tr>
<th>Support</th>
<th>Cu loading, wt.-%</th>
<th>Hydrogen yield, %</th>
<th>((-\text{rCH}_3\text{OH}),^b)</th>
<th>(\text{mol}_{\text{CH}_3\text{OH}})</th>
<th>(\text{min} \times g_{\text{Cu}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMK-3</td>
<td>5.5</td>
<td>2</td>
<td>5</td>
<td>6</td>
<td>0.012</td>
</tr>
<tr>
<td>CMK-3</td>
<td>11.0</td>
<td>9</td>
<td>15</td>
<td>19</td>
<td>0.019</td>
</tr>
<tr>
<td>CMK-3</td>
<td>22.0</td>
<td>18</td>
<td>28</td>
<td>35</td>
<td>0.018</td>
</tr>
<tr>
<td>CMK-5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.8</td>
<td>4</td>
<td>5</td>
<td>2</td>
<td>0.018</td>
</tr>
<tr>
<td>CMK-5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>7.6</td>
<td>10</td>
<td>11</td>
<td>11</td>
<td>0.019</td>
</tr>
<tr>
<td>CMK-5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.3</td>
<td>12</td>
<td>17</td>
<td>19</td>
<td>0.017</td>
</tr>
<tr>
<td>CMK-5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>22.9</td>
<td>25</td>
<td>46</td>
<td>57</td>
<td>0.028</td>
</tr>
<tr>
<td>CMK-5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>26.7</td>
<td>27</td>
<td>31</td>
<td>30</td>
<td>0.017</td>
</tr>
<tr>
<td>Kugelkohle</td>
<td>11.0</td>
<td>20</td>
<td>34</td>
<td>40</td>
<td>0.043</td>
</tr>
<tr>
<td>Kugelkohle</td>
<td>22.0</td>
<td>59</td>
<td>65</td>
<td>67</td>
<td>0.041</td>
</tr>
</tbody>
</table>

Reaction flow 260 ml/min, (0.00138 mol of \(\text{CH}_3\text{OH}/\text{min}\)), pressure 1.100 bar, \(\text{CH}_3\text{OH}:\text{H}_2\text{O}\) ratio is 1:1, catalyst weight 100 mg, reaction temperature 250-300 °C,

<sup>a</sup>weight specific rate was calculated as described in *appendix*

for the conversion of methanol at 275 °C

<sup>b</sup>CMK-5 with pore diameter 2.5 and pore volume 1.20 cm<sup>3</sup>/g was used for the studies.
As it was already mentioned, the XRD analysis in case of copper supported on CMK-5 type carbon as well as for copper supported on CMK-3 and Kugelkohle did not give any information about the particle size. (Fig. 4.34 – Fig. 4.36).

**Fig. 4.38.** TEM image of CMK-3 copper impregnated sample. Copper loading is 11.0 wt.-%.

**Fig. 4.39.** TEM image of CMK-3 copper impregnated sample. Copper loading is 22.0 wt.-%.
Thus, information about the sample morphology and copper particle size distributions has to be obtained by TEM analysis. Fig. 4.38 shows CMK-3 copper impregnated sample with 11.1 wt.-% loading. The copper is not homogeneously distributed on the sample, while for the Cu/CMK-3 with 22 wt.-% copper loading a homogeneous distribution was achieved (Fig. 4.39). The catalyst with 5 wt.-% loading has only low activities with a maximum hydrogen yield of 6.2 %. As it can be seen in Fig. 4.40, Cu supported on CMK-3 carbon with 5 wt.-% copper loading is present as isolated copper particles with diameters of approximately 16 nm.

![Figure 4.40. TEM image of copper supported on CMK-3 type carbon. Copper loading is 5 wt.-%.

We have also calculated a weight specific rate\(^1\). For CMK-3 with 22 wt.-% and 11 wt.-%

\[ \text{mol}_{\text{CH}_3\text{OH}} \frac{1}{\text{min} \times g_{\text{Cu}}} \]

\(^1\) The weight specific rate was calculated for the methanol reforming at 275 °C, because at 300 °C catalysts showed weak stability and the rate data are superimposed by the deactivation. The details of the calculation are described in the appendix.
CMK-3 impregnated with 5.5 wt.-% copper it is only 0.012 $\frac{mol_{CH,OH}}{min \times g_{Cu}}$. The low specific rate values could be explained by the larger particle sizes of the copper particles on CMK-3 impregnated with 5.5 wt.-% (Fig. 4.40), specifically, the specific copper surface area is low for this sample. Over the copper impregnated CMK-5 series similar tendencies of increased hydrogen yield with increasing copper loading were observed. Nevertheless, in contrast to CMK-3 impregnated carbon, weight specific rates calculated for Cu/CMK-5 samples are similar for the low and high copper loaded samples. The exception for the sample with 23 wt.-% copper loading was observed with the weight specific rate of 0.028 $\frac{mol_{CH,OH}}{min \times g_{Cu}}$. As can be seen in Fig. 4.41, the copper particles in Cu/CMK-5 sample with 23 wt.-% loading are highly distributed on the carbon surface. However, closer TEM examination of this sample shows that copper distributed on the carbon surface appears more like nanowires (Fig. 4.42). The nanowires should give low copper surface area in comparison with nanoparticles, but as it was already mentioned, not all copper impregnated in carbon is available for the reaction.

Fig. 4.41. TEM image of CMK-5 impregnated catalyst. Copper loading is 22.9 wt.-%
Fig. 4.43 shows the copper impregnated CMK-5 with 15.5 wt.-% loading. In contrast to Cu/CMK-5 with 22.9 wt.-% copper loading, this sample has small (3-4 nm) copper particles randomly distributed on the carbon surface. The 26.7 wt.-% copper loaded CMK-5 had lower activity at 275 °C and 300 °C than CMK-5 with 22.9 wt.-% copper.

Fig. 4.42. TEM image of CMK-5 impregnated catalyst. Copper loading is 22.9 wt.-%.

Fig. 4.43. TEM image of CMK-5 impregnated catalyst. Copper loading is 15.3 wt.-%.
The pore volume of CMK-5 in this case was 1.20 cm$^3$/g, so 300 mg of carbon was impregnated with 3 portions of solution of 120 µl each, resulting in 26.7 wt.-% copper. The concentration of copper achieved in this sample is higher but the yield of hydrogen is lower. The close examination of this sample shows that not all copper was well dispersed on the carbon surface, some copper particles were formed as another phase outside of the carbon surface (Fig. 4.44). Nevertheless, due to the fact that not all copper is available for the reaction in samples with low copper loading, this sample has the same specific rate the same like other catalysts except the 22.9% sample.

For the copper impregnated Kugelkohle, the weight specific rate has the maximal value of $0.04 \frac{\text{mol}_{\text{CH,OH}}}{\text{min} \times g_{\text{Cu}}}$ in comparison with other studied carbons. The hydrogen yield on the 11 wt.-% impregnated carbon was approximately two times lower than was achieved on the 22 wt-% Cu/C. Thus, the dependence of hydrogen yield vs. the copper loading was close to linear for this series of copper/carbon catalysts.

**Fig. 4.44.** TEM image of CMK-5 impregnated catalyst. Copper loading is 26.7 wt.-%. 
4.2. Influence of ZnO on the catalytic activity of Cu/CMK-3, Cu/CMK-5 and Cu/Kugelkohle

Many factors have been found to influence the catalytic activity Cu/carbon catalyst in methanol steam reforming, mainly through tuning the particle size and dispersion of Cu particles. [46] The types of carbon (CMK-5, CMK-3 and Kugelkohle) used as a support also have influence on methanol steam reforming, because copper supported on these structures has different size and distribution. A higher dispersion of Cu particles leads to higher catalytic activity. [59-61] Generally, the catalytic properties of a supported catalyst do not only depend on the nature of the metal and the support, but also on the shape and size of the metal particles, as well as on the interaction between metal and support. [50] Clearly, highly dispersed Cu particles are more active than large particles. [5,59] In the commercial catalyst, ZnO is a crucial component for high activity. It was therefore interesting to investigate the ZnO influence on catalytic activity of the copper/carbon samples which were prepared by a completely different pathway.

![TEM image of Cu-Zn impregnated CMK-5](image)

**Fig. 4.45.** TEM image of Cu-Zn impregnated CMK-5.
Zinc oxide should be introduced in the carbon matrix after the copper in order to avoid any influence of zinc already during generation of the copper particles.

**Fig. 4.46.** TEM image of Cu-Zn impregnated CMK-3.

**Fig. 4.47.** TEM image of Cu-Zn impregnated Kugelkohle.

There are two ways to deposit zinc into the carbon matrix: first, by impregnating the samples with concentrated copper nitrate solution, subsequently calcining it under argon at
130 °C for 2 hours to decompose the nitrates, followed by impregnating it with 1.0 M zinc nitrate solution. Afterwards, the samples were reduced in 5% H₂ in Ar directly in the reactor before the reaction. TEM images of the samples can be seen in Fig. 4.45, Fig. 4.46 and Fig. 4.47, with CMK-5, CMK-3 and Kugelkohle used as support, respectively. The second way of depositing zinc in the structure was easier. Carbons were impregnated with copper solutions, and dried at 90 °C overnight, and then the samples were impregnated with zinc nitrate by 3 portions of solution. Afterwards, the samples were reduced in situ before reaction.

Table 4.12. Influence ZnO on catalytic properties copper nanoparticles supported on CMK-3, CMK-5 and Kugelkohle mesoporous carbons.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ZnO, %</th>
<th>Particle size, nm</th>
<th>Hydrogen yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>250 °C</td>
</tr>
<tr>
<td>-</td>
<td>10±4</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>Cu/CMK-3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-5³</td>
<td>10±4</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>Cu/CMK-5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-5³</td>
<td>5±3</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Cu/C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-5³</td>
<td>4±3</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction flow 260 ml/min, pressure 1.100 bar,
CH₃OH÷H₂O ratio is 1÷1, catalyst weight 100 mg,
reaction temperature 250-300 °C

³ZnO was introduced in the Cu/carbon after calcination
³ZnO was introduced in the Cu/carbon after drying
³CMK-5 with a pore size of 3.3 nm was used for this studies.
The catalytic results for methanol steam reforming over these systems are presented in Table 4.12. To complete the information, data for the activity of the pure copper systems are included again. An increase of the particle sizes\(^1\) was not noticed for all the studied Cu/ZnO/carbon samples in comparison with the Cu/carbon samples (Table 4.12, Fig. 4.21 and Fig. 4.48). Nevertheless, the catalysts with ZnO show lower hydrogen yields than the catalyst without ZnO. The expected increase in catalytic activity by ZnO was not observed for any of the studied samples, but overall rather a slight decrease. For the samples with zinc oxide introduced in the carbon matrix after calcination the yield of hydrogen was higher than for samples when the zinc species was deposited after drying.

**Fig. 4.48.** The size distribution of copper particles in the samples Cu/ZnO/CMK-5 (a), Cu/ZnO/C (b) and Cu/ZnO/CMK-3 (c).

\(^1\) It is quite difficult to observe 0.5-1 nm difference in particle size by TEM analysis.
4.2.1. Specific surface analysis of copper and zinc impregnated CMK-5, CMK-3 carbons and Kugelkohle

As already mentioned, the analysis of copper surface area can help to estimate the influence of the copper particle size on the catalytic performance. The activity of the catalysts as a function of the copper surface area is shown in Fig. 4.49. For comparison with the results obtained for the Cu/ZnO carbon samples, the catalytic performance and the copper surface area of Cu/carbon samples are shown again.

![Graph showing dependence of reaction rate over the Cu (solid symbols) and Cu/ZnO (hollow symbols) supported carbon catalysts vs. copper surface area at three different temperatures.](image)

**Fig. 4.49.** Dependence of reaction rate over the Cu (solid symbols) and Cu/ZnO (hollow symbols) supported carbon catalysts vs. copper surface area at three different temperatures

No linear correlation between activity and copper surface area can be found. Similar to Cu/carbon catalysts, the specific surface area of Cu/ZnO/carbon materials is lower than calculated according its particle size. However, the copper surface area did not decrease after ZnO introduction, in some cases it even increased (Fig. 4.49). However, the data an specific surface area have to be treated with caution, since analysis of the fluffy samples is slightly difficult and total surface areas are rather low and thus have large error bars.
Cu/carbon catalysts show a higher methanol conversion than Cu/ZnO/carbon catalysts, in spite of the highest specific copper surface area of the latter catalyst. Recently, it was realized that after introducing zinc an additional factor influences the activity of copper catalysts. Kniep et al. [147,148] found on the series of hydroxycarbonate-derived Cu/ZnO catalysts that the increased micro strain in the nanostructured Cu particles (detected by XRD and XAS) showed an excellent linear correlation with the improved activity of Cu/ZnO in the steam reforming of methanol. The strain in the supported copper nanoparticles has been suggested to originate from an epitaxial orientation of Cu and ZnO, lattice imperfections caused by Zn incorporated into Cu, or an incomplete reduction of copper [17,147,148]. The study of the effect of the zinc on the activity requires further investigations which could not be completed in the framework of this thesis.

4.2.2. CO formation

As mentioned in the introduction, the main problem of using hydrogen produced by methanol steam reforming in a fuel cell is the formation of CO. Carbon monoxide is adsorbed on the Pt electrode and poisons the catalyst of the fuel cell. [152] For all studied catalysts an increase in CO concentration with increasing temperature (Fig. 4.50) was observed, in accordance with literature data. [6,25] The most active catalyst from the copper/carbon series Cu/C produced 0.18% CO at 250 °C with increasing formation up to 0.20% and 0.29% at 275 °C and 300 °C, respectively. This growth of carbon monoxide concentration was lower in comparison to an industrial catalyst Cu/ZnO/Al₂O₃ (~50% Cu), which produced 0.30% CO at 275 °C and 0.56% CO at 300 °C.
Fig. 4.50. CO formation over copper and copper zinc particles supported on Kugelkohle.

However, this concentration is still much higher than the 10 ppm CO being detrimental for the fuel cell electrode. [153] A slight decrease of CO formation was observed for the catalyst containing zinc oxide, but it is more probably due to the lower activity of the Cu/ZnO/C samples. For the other Cu/ZnO/CMK-5 and Cu/ZnO/CMK-3 samples the CO formation was slightly lower (0.09 – 0.20%) than for Cu/ZnO/C catalyst, which is also possibly related to lower activity of these samples.

4.2.3. Adsorption measurements

Table 4.13 shows how the textural parameters of the carbon support changes by introducing copper and zinc into the porous structure. As already mentioned, copper has an influence on the specific surface area of carbon, and the decrease of carbon surface area could not be explained only by the additional weight of the copper within the structure.
Table 4.13. Textural properties of carbon supports: CMK-5, CMK-3 and Kugelkohle and catalysts: Cu/CMK-5, Cu/CMK-3 Cu/C and Cu/ZnO/CMK-5, Cu/ZnO/CMK-3, Cu/ZnO/C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area, m²/g</th>
<th>D_{adsorb.}, nm</th>
<th>Volume, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMK-3</td>
<td>1569</td>
<td>2.1</td>
<td>1.10</td>
</tr>
<tr>
<td>Cu/CMK-3</td>
<td>1006</td>
<td>2.3</td>
<td>0.72</td>
</tr>
<tr>
<td>Cu/ZnO/CMK-3</td>
<td>987</td>
<td>2.2</td>
<td>0.58</td>
</tr>
<tr>
<td>CMK-5</td>
<td>1411</td>
<td>2.5</td>
<td>1.45</td>
</tr>
<tr>
<td>Cu/CMK-5</td>
<td>613</td>
<td>2.6</td>
<td>0.57</td>
</tr>
<tr>
<td>Cu/ZnO/CMK-5</td>
<td>587</td>
<td>2.6</td>
<td>0.54</td>
</tr>
<tr>
<td>Kugelkohle</td>
<td>1928</td>
<td>3.6</td>
<td>0.98</td>
</tr>
<tr>
<td>Cu/C</td>
<td>1284</td>
<td>3.6</td>
<td>0.59</td>
</tr>
<tr>
<td>Cu/ZnO/C</td>
<td>1255</td>
<td>3.6</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Reaction flow 260 ml/min, pressure 1.100 bar, CH₃OH: H₂O ratio is 1:1, catalyst weight 100 mg, reaction temperature 250-300 °C

*a* Surface of carbon was treated with 15wt.-% hydrogen peroxide,

*b* The CMK-5 with a pore diameter of 2.5 nm was used.

The specific surface area as well as pore volume slightly decreases in the samples containing ZnO for all carbon supports, but this is due to the fact that zinc was impregnated after copper and the materials gained weight. Fig. 4.51 shows the isotherms of Cu and Cu/ZnO impregnated samples. Obviously, the sorption isotherms for samples with copper and zinc look the same as for samples where only copper is present. The addition of zinc oxide does not change the surface properties of carbon and does not decrease the specific surface area of the studied carbon; this could not be, thus, the reason of lower hydrogen yiled in case of copper/zinc/carbon catalysts. In case of a random distribution of zinc and copper
Fig. 4.51. Isotherms of CMK-5, CMK-3 type carbons and Kugelkohle impregnated with Cu and Cu/ZnO.

particles with a low number of connections between ZnO and Cu the hydrogen yield should be the same for samples containing zinc and without it. Nevertheless, a decrease of hydrogen yield was observed for all copper/zinc/carbon catalyst. Thus, zinc has a negative
influence on the copper particles activity and must be associated with them. The possibility to find out more about zinc influence on copper particles is the investigation of the reduction temperature of copper nanoparticles with and without ZnO.

### 4.2.3. Temperature programmed reduction

In order to assess the reduction behavior of copper particles in presence and absence of zinc, TPR measurements were performed. The TPR profiles of the copper nanoparticles supported on different types of mesoporous carbons in presence and absence of zinc oxide and the industrial Cu/ZnO/Al₂O₃ catalyst from Süd-Chemie are shown in Fig. 4.52. For all catalysts the reduction was completed at 280 °C. The hydrogen consumption peak consists of one signal for all carbon supported materials. Very often ZnO influences the reduction of copper by hydrogen and acts as a promoter of the copper oxide reduction. [6] In our case we observed the opposite effect. The reduction peak maximum of the zinc containing samples shifts to higher temperature. For the copper nanoparticles supported on CMK-3 the reduction maximum is located at 239 °C, while after impregnation with zinc the peak maximum is shifted by 18 °C to higher temperature. A similar effect was observed for the reduction of all copper nanoparticles supported on carbons. In presence of zinc oxide, the maximum of the reduction peak for the copper particles supported on CMK-5 type mesoporous carbon and on Kugelkohle was shifted from 236°C and 239°C to 254 °C and 256 °C, respectively. A similar shift of the reduction maximum to higher temperature has been observed previously by Robinson et al. [155] in a TPR study of the interaction of CuO and ZnO. They have attributed this phenomenon to the presence of a specific type of strong interaction between the CuO and ZnO lattices.
Fig. 4.52. TPR analysis copper impregnated carbons with and without zinc.

However, the difference in particle size may also lead to shift in the reduction temperature. Such variation of the particle size was difficult to observe by TEM measurements (Fig. 4.44, Fig. 4.45 and Fig. 4.46). Thus, the observed temperature shift after ZnO impregnation can be attributed either to interaction of copper particles with the zinc oxide lattice or to increase in size of the copper particles caused by deposition of the zinc during the synthesis procedure. We do not have an additional evidence for one or the other interpretation.
Chapter 5

Conclusion

Highly distributed copper nanoparticles on carbon supports were synthesized for the first time. In order to deposit copper on the carbon surface, different solutions of copper nitrate (in acetone, ethanol, water and THF) and aqueous solutions of copper acetyl acetonate were used. Only wetness impregnation of carbon, which had previously been functionalized by oxidative treatment with 15% H$_2$O$_2$, with aqueous solution of copper nitrate resulted in the formation of the catalysts with a high distribution of copper particles. Small angle XRD and N$_2$-adsorption measurements showed that after treatment with 15% H$_2$O$_2$ CMK-5 material keeps the hexagonally ordered structure, whereas the treatment with 30% H$_2$O$_2$ lead to destruction of the carbon walls.

The samples synthesized with CMK-5 of different pore diameters, CMK-3 and Kugelkohle were also compared by means of transmission electron microscopy. It was found that carbon supports CMK-5, CMK-3 and Kugelkohle have an influence on the copper particle diameters. According to TEM measurements, copper particles with average sizes of 4 and 5 nm were obtained on Kugelkohle and CMK-5 type carbon, while on CMK-3 the average particle size was 10 nm.

The catalytic activity of the novel Cu/carbon catalysts was investigated in methanol steam reforming in the temperature range between 250 °C and 300 °C at atmospheric pressure. It was demonstrated that the catalytic activity depends on the copper particle size.

The Cu/C material showed the highest catalytic activity, which is comparable to the one shown by the industrial catalyst, and good stability under reaction conditions at 250 °C for
more than 16 hours. The weight specific rate for the copper particles supported on the carbon, calculated at 275 °C, was found to be not dependent on copper loading, with a maximal value of \(0.04 \frac{mol_{CH_2OH}}{min \times g_{Cu}}\) for Cu supported on Kugelkohle. In the case of catalysts prepared with ordered mesoporous carbons, the highest hydrogen yield was observed for copper supported on CMK-5 with a pore diameter of 3.3 nm. A linear correlation between the reaction rate and the copper surface area was observed for copper/carbon catalysts. The above reported results show that copper nanoparticles supported on different types of carbons showed remarkable activity in steam reforming of methanol even in absence of ZnO, which is considered essential in order to enhance copper activity and stability for the commercial Cu/ZnO/Al\(_2\)O\(_3\) system.

Introduction of zinc oxide in the copper/carbon structure did not bring any additional activity to the systems, but rather resulted in decreased activity. In particular, it was shown by comparison of copper/carbon and copper/zinc/carbon materials that zinc has a negative influence on hydrogen yield. Moreover, no linear correlation between activity and copper surface area was found for Cu/ZnO/carbon samples. No difference in CO formation over the Cu/ZnO loaded carbons and Cu/carbon systems were achieved.
6.1. Textural parameters of mesoporous materials

6.1.1. SBA-15

Fig. 6.1. The SBA-15 synthesized at different aging temperatures.

Samples synthesized at 60 °C and 140 °C were treated with 48% sulfuric acid. Thus, SBA-15-60 has higher pore diameter and volume than for SBA-15-80 °C. Material without sulfuric acid treatment experiences stress during burning of the polymer at 560 °C. SBA-15, which is treated with sulfuric acid, is more stable due to partial removal of polymer by sulfuric acid. Samples were heated to 300 °C for removing the residual polymer. Thus, pretreated SBA-15 has higher quality and higher pore volume than SBA-15 without pretreatment.
Table 6.1. The textural parameters of SBA-15 synthesized at different aging temperatures.

<table>
<thead>
<tr>
<th>Aging temperature, °C</th>
<th>H$_2$SO$_4$</th>
<th>Surface area (BET), m$^2$/g</th>
<th>D$_{adsorb.}$, nm</th>
<th>Volume, cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>-</td>
<td>967</td>
<td>5.5</td>
<td>1.01</td>
</tr>
<tr>
<td>60</td>
<td>+</td>
<td>644</td>
<td>6.9</td>
<td>1.16</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>605</td>
<td>6.3</td>
<td>1.40</td>
</tr>
<tr>
<td>140</td>
<td>+</td>
<td>448</td>
<td>10.2</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Table 6.2. The textural parameters of SBA-15 synthesized in parallel batches at an aging temperature of 140 °C and treated with H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Surface area (BET), m$^2$/g</th>
<th>D$_{adsorb.}$, nm</th>
<th>Volume, cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>448</td>
<td>10.2</td>
<td>1.32</td>
</tr>
<tr>
<td>486</td>
<td>10.1</td>
<td>1.48</td>
</tr>
<tr>
<td>468</td>
<td>10.1</td>
<td>1.25</td>
</tr>
</tbody>
</table>

In three batches a 4.0 g sample of Pluronic ((EO)$_{20}$(PO)$_{70}$(EO)$_{20}$) P$_{123}$ was dissolved in 30 g of water and 120 g of 2 M HCl solution. The solution was stirred until the polymer had completely dissolved. Then the solution was placed at 40 °C under thermostatic conditions and 8.50 g of TEOS was added. The resulting mixture was stirred for 4 h at this temperature and then kept at 140 °C for 24 h without stirring. The solid product was filtered, and dried without washing overnight at 90 °C. Afterwards, sample were treated with sulfuric acid before calcination. The sulfuric acid treatment was carried out as reported by Yang et al. [90]. To wash out the polymer template, 4.0 g of SBA-15 was mixed with 250 g of ethanol and 2 g 0.1 M HCl, and stirred for 1.5-2 h at room temperature. The solid sample was filtered and dried for 2 h at 90 °C. Afterwards the powder was added to 500 mL 48 wt.-% H$_2$SO$_4$ solution and refluxed at 95 °C for 24 h. The product was recovered by washing with
water, dried at 90 °C and subsequently calcined in air for 6 h at 200°C. Table 6.2 shows that SBA-15 synthesized in parallel batches have the same pore size distribution, but different pore volumes. Thus, for synthesis of CMK-5 the FA as well as TMB were added in amount according to the measured by N\textsubscript{2}-adsorption volume.

6.2. Calculations

Calculations of the activity and selectivity were carried out using Excel spread sheets. The analyses of the gas mixture were performed every 20 minutes. The IR and GC measurements were synchronized in such a way that on one GC injection four times IR analysis of CH\textsubscript{3}OH, H\textsubscript{2}O, CO and CO\textsubscript{2} proceeds. One sample was injected to analyze H\textsubscript{2} and N\textsubscript{2}. The concentration of CH\textsubscript{3}OH, H\textsubscript{2}O, CO and CO\textsubscript{2} were measured, as already mentioned, at three different wavelengths (Table 3.1). The calculations of all components were determined by calibration curves. Fig. 6.2 and Fig. 6.3 show the calibration curves for H\textsubscript{2}, N\textsubscript{2} and water. In the case of water, a linear (Fig. 6.3 a-c) or polynomial (Fig. 6.3 d-f) fit was used. For the CH\textsubscript{3}OH, CO and CO\textsubscript{2} the calibration curves are similar to the curves obtained for the water.

![Fig. 6.2. Calibration curves of H\textsubscript{2} (a) and N\textsubscript{2} (b).]
Fig. 6.3. Calibration curves of water; a linear (a-c) or polynomial (d-f) fit was used.

The calculations of the hydrogen yield and methanol conversion in Excel spread sheets were based on the following data:

- the initial flow ($F_1$), which consists of methanol, water and carrier gas N$_2$, coming into the reactor;
- in flow ($F_2$) after the reactor, consisting of residual water and methanol, the carrier gas N$_2$, and the reaction products hydrogen, CO, and CO$_2$;
- before the GC detector the gas line cooled down, and from the full flow ($F_2$) are removed residual methanol and water; the total flow is changed to $F_3$;
• the concentrations of CH$_3$OH, H$_2$O, CO, and CO$_2$ are detected by IR spectrometry in the flow F$_2$;

• H$_2$ and nitrogen are detected by GC in the flow F$_3$.

Fig. 6.4 shows the calculation scheme of the studied process.
Fig. 6.4. The calculation scheme of the methanol steam reforming process.

Where $\chi_N$ the normalized concentration of component gas mixture at flow $N$; with $\checkmark$ are denoted components with known concentrations and with $?$ the component which concentration is unknown in this step.
Thus for the $F_3$ the equation will be followed:

$$F_3 = F_2 \times (1 - X_2CH_3OH - X_2H_2O) \quad 6.1.$$  

The difference between $F_2$ and $F_3$ is the amount of methanol and water, which did not react.

The hydrogen, which is measured with GC, is not the hydrogen present in the gas mixture for the $F_2$. Taking into account eq. 6.1 and the hydrogen concentration measured by GC (eq. 6.2) we can get the unknown $X_2H_2$ in eq. 6.3:

$$F_2X_2H_2 = F_3X_3H_2 \quad 6.2.$$  
$$X_2H_2 = (1 - X_2CH_3OH - X_2H_2O) \times X_3H_2 \quad 6.3.$$  

The balance equation for “C” will be:

$$F_1X_1CH_3OH = F_1 \times (X_2CH_3OH + X_2CO + X_2CO_2) \quad 6.4.$$  

And as a result

$$F_2 = \frac{F_1X_1CH_3OH}{(X_2CH_3OH + X_2CO + X_2CO_2)} \quad 6.5.$$  

The balance equation for “O” should be:

$$F_1 \times (X_1CH_3OH + X_1H_2O) = F_1 \times (X_2CH_3OH + X_2H_2O + X_2CO + 2X_2CO_2) \quad 6.6.$$  

The balance equation for “H” should be:

$$F_1 \times (2X_1CH_3OH + X_1H_2O) = F_2 \times (2X_2CH_3OH + X_2H_2O + X_2H_2) \quad 5.7.$$  

From eq. 6.5 and eq. 6.6. it should be no problem to get the concentration of $X_2CO$ and $X_3H_2$:

$$X_2CO = \frac{X_1CH_3OH}{X_1H_2O} \times (X_2H_2O + X_2CO_2) - X_2CH_3OH - X_2CO_2 \quad 6.8.$$  
$$X_3H_2 = \frac{(2X_1CH_3OH + X_1H_2O) \times (X_2CH_3OH + X_2CO + X_2CO_2) - X_1CH_3OH \times (2X_2CH_3OH + X_2H_2O)}{X_1CH_3OH \times (1 - X_2CH_3OH - X_2H_2O)} \quad 6.9.$$.  

At initial molar ratio in reaction for $X_1\text{CH}_3\text{OH}-X_1\text{H}_2\text{O}$ is $1\div1$, and from eq. 6.8 conforms

$$X_2\text{CO} = X_2\text{H}_2\text{O} - X_2\text{CH}_3\text{OH} \quad 6.10.$$ 

And for hydrogen eq. 6.9 becomes:

$$X_3\text{H}_2 = \frac{X_2\text{CH}_2\text{OH} + 3X_2\text{CO} + 3X_2\text{CO}_2 - X_2\text{H}_2\text{O}}{1 - X_2\text{CH}_3\text{OH} - X_2\text{H}_2\text{O}} \quad 6.11.$$ 

In this way, it is possible to make a comparison of the measured value for each component in the mixture with the calculated value from the other components participating in the reaction. The variation between calculated and measured values was acceptable considered, if the difference was less than 5%.

Methanol conversion in % was calculated as:

$$C = 1 - \frac{X_2\text{CH}_3\text{OH}}{X_2\text{CH}_3\text{OH} + X_2\text{CO} + X_2\text{CO}_2} \times 100 \quad 6.12.$$ 

Hydrogen selectivity:

$$S = \frac{X_3\text{H}_2}{3(X_3\text{CH}_3\text{OH} - X_2\text{CH}_3\text{OH})} \times 100 = \frac{(1 - X_2\text{CH}_3\text{OH} - X_2\text{H}_2\text{O}) \times X_3\text{H}_2}{3(X_3\text{CH}_3\text{OH} - X_2\text{CH}_3\text{OH})} \times 100 \quad 6.13.$$ 

And hydrogen yield is methanol conversion×selectivity, so $Y = C \times S / 100$.

The calculations for the weight specific rate are as follows:

$$\text{Input} = \text{Output} + \text{Disappeared} + \text{Accumulated}$$

Where Input and Output is the $\text{CH}_3\text{OH}_{\text{in}}$ and $\text{CH}_3\text{OH}_{\text{out}}$ in $\text{mol/min}$, respectively; nothing is accumulated and reaction rate is the rate of methanol disappearing.

$$\left(\frac{\text{CH}_3\text{OH}_{\text{mol}}}{\text{min}}\right)_{\text{in}} = \left(\frac{\text{CH}_3\text{OH}_{\text{mol}}}{\text{min}}\right)_{\text{out}} + (-r\text{CH}_3\text{OH})dV \quad 6.14.$$
Where \((-rCH_3OH)\) is the weight specific rate measured in \(\frac{mol_{CH,OH}}{min \times cm^3}\).

Whereas \(CH_3OH_{out}\) can be calculated from \(CH_3OH_{in}\)

\[
\frac{(CH_3OH_{mol})_{out}}{min} = \left(\frac{(CH_3OH_{mol})_{in}}{min}\right) \times (1 - dCH_3OH) \quad 6.15,.
\]

Where \(dCH_3OH\) is deferential of methanol conversion.

Placing 6.15 in 6.14 we will obtain 6.16

\[
\left(\frac{(CH_3OH_{mol})_{in}}{min}\right) = \left(\frac{(CH_3OH_{mol})_{in}}{min}\right) \times (1 - dCH_3OH) + (-rCH_3OH)dV \quad 6.16.
\]

And 6.17

\[
\left(\frac{(CH_3OH_{mol})_{in}}{min}\right) \times dCH_3OH = (-rCH_3OH)dV \quad 6.17.
\]

After integration over the full bed volume we will get 6.18

\[
\int_0^c dCH_3OH = \int_0^v \frac{dV}{\left(\frac{(CH_3OH_{mol})_{in}}{min}\right)} = \frac{Vol._C}{\left(\frac{(CH_3OH_{mol})_{in}}{min}\right)} = \pi CH_3OH \quad 6.18
\]

Placing 6.18 in 6.14 we will obtain

\[
FlowCH_3OH_{in} = FlowCH_3OH_{out}(1 - C) + (-rCH_3OH)V \quad 6.19
\]

\[
(-rCH_3OH) = \frac{FlowCH_3OH_{in} \times C}{V} \rightarrow \left(\frac{molCH_3OH}{min \times cm^3}\right) \quad 6.20.
\]

where \(C\) is methanol conversion, \(V\) is volume of the catalyst (cm\(^3\)).
Chapter 7

Bibliography


List of Figures

2.1. Modeled energy consumption for various fuel feedstocks to achieve fuel processing system operating temperature .................................................................15

2.2. Reaction pathways for conversion of methanol with oxygen and/or steam at different stoichiometries .................................................................16

2.3. Adsorption of aldehydes on metals 1B group (Au, Cu) (a) and on metals 8A groups (Rh, Ru, Pt, Pd) (b) .................................................................26

2.4. Examples of micro-, meso-, and macroporous materials, showing pore size domains and typical pore size distributions .................................................28

3.1. Synthesis of carbon supported copper nanoparticles ........................................42

3.2. Langmuir isotherm (solid line) and BET isotherm (dotted line) ....................46

3.3. The experimental set-up for methanol steam reforming ................................52

4.1. Overview of the synthesized materials .........................................................57

4.2. Hydrogen yield from methanol steam reforming in the temperature range between 250 °C and 300 °C over Cu impregnated CMK-5 supports with hydrophobic surface in dependence of the solvent for the copper precursor ..............................58

4.3. TEM image of CMK-5 carbon impregnated with an ethanol solution of copper nitrate. Copper loading is 10 wt.-% .................................................................59

4.4. TEM image of CMK-5 carbon impregnated with water solution of copper nitrate. Copper loading is 22 wt.-% .................................................................60

4.5. TEM image of CMK-5 carbon impregnated with THF solution of copper nitrate. Copper loading is 10 wt.-% .................................................................61

4.6. TEM image of CMK-5 carbon impregnated with acetone solution of copper nitrate. Copper loading is 10 wt.-% .................................................................62
4.7. XRD patterns of CMK-5 type carbon treated with hydrogen peroxide (15-30%) in comparison with CMK-5 as made..............................................................................................64

4.8. The XRD patterns of CMK-5 type carbon treated with 15% hydrogen peroxide several times in comparison with CMK-5 as made........................................................................65

4.9. CMK-5 treated with 15% H$_2$O$_2$ one and three times in comparison with original CMK-5.........................................................................................................................67

4.10. Hydrogen yield in methanol steam reforming in the temperature range between 250 °C and 300 °C over Cu impregnated CMK-5* supports with hydrophilic surface in dependence of the solvent for the copper precursor.................................................................68

4.11. TEM image of CMK-5* carbon impregnated with ethanolic solution of copper nitrate. Copper loading is 10 wt.-%.........................................................................................................68

4.12. TEM image of CMK-5* carbon impregnated with aqueous solution of copper nitrate. Copper loading is 22 wt.-% .......................................................................................................69

4.13. TEM image of CMK-5* carbon impregnated with aqueous solution of copper acetyl acetate. Copper loading is ~2 wt.-%.....................................................................................................70

4.14. TEM image of CMK-5* carbon impregnated with aqueous solution of copper nitrate and reduced in 5% H$_2$ in Ar. Copper loading is 22 wt.-%.................................................................71

4.15. Isotherms of CMK-5 synthesized using the hard templates SBA-15, which had been produced at different aging temperatures in the range between 60 and 140 °C.....................73

4.16. TEM image of Cu/CMK-5-80 carbon, with a copper loading of 22 wt.-%.........................75

4.17. TEM image of Cu/CMK-5-140 carbon, with a copper loading of 22 wt.-%......................76

4.18. Temperature programmed reduction analysis of copper nanoparticles supported on CMK-5 ordered carbons with different pore sizes.................................................................77

4.19. The isotherms of CMK-5 synthesis using the hard template SBA-15, which had been produced at different aging temperatures in range between 60 and 140 °C..............81
4.20. Cu/CMK-5 sample prepared with CMK-5 synthesized by the Ryoo method.............82

4.21. The size distribution of copper particles in the samples Cu/CMK-5-60 (a), Cu/C (b) and Cu/CMK-3 (c).................................................................................................................................84

4.22. TEM image of copper particles supported on CMK-3 type carbon. Copper loading is 22 wt.-%.................................................................................................................................84

4.23. HRTEM image of one single copper particle supported on CMK-3 type carbon.......85

4.24. Cu/C sample after reduction at 250 °C in 5 % hydrogen ........................................86

4.25. Dependence of reaction rate vs. copper surface area at three different temperatures.................................................................................................................................87

4.26. Temperature programmed reduction analysis of copper nanoparticles supported on CMK-5, CMK-3 and Kugelkohle in comparison with the industrial Cu/ZnO/Al₂O₃.................................................................................................................................90

4.27. TPR profile of Cu/C.....................................................................................................91

4.28. CMK-5 supported copper nanoparticles reduced at 300 °C. Copper loading is 22 wt.-%.................................................................................................................................92

4.29. Cu/C after reduction at 400 °C in low of 5% hydrogen on argon .........................93

4.30. Cu/C sample after 12 hours under reaction flow....................................................93

4.31. Pore size distribution (BJH) (a) and nitrogen isotherms of CMK-5 type carbon with copper loading between 3.8 and 30.5 wt.-% (b)......................................................................................97

4.32. Calculated and measured surface area after introducing copper modelled under the assumption of no structural damage (a) and modelled under the assumption that damage already occurs at the 3.8% loading level (b)......................................................................................99

4.33. Sorption isotherms of a) original CMK-5, b) Cu/CMK-5 with copper loading of 10 wt.-% and c) Cu/CMK-5 carbon after leaching copper by treatment with 1M HNO₃.................................................................................................................................101
4.34. XRD patterns of CMK-5 with different copper loading at angles $2\theta$ between 20 and 70° ...........................................................................................................102

4.35. XRD patterns of (a) Cu/CMK-3 with a copper loading of 22wt.-% and (b) CMK-3 at angles $2\theta$ between 20 and 70° ...........................................................................................................102

4.36. XRD patterns of Kugelkohle (a) and Cu/C with a copper loading of 22wt.-% at angles $2\theta$ between 20 and 70°(b). ...........................................................................................................103

4.37. CMK-5 type carbon impregnated in two steps to achieve 26 wt.-% loading ........104

4.38. TEM image of CMK-3 copper impregnated sample. Copper loading is 11.0 wt.-% ...........................................................................................................106

4.39. TEM image of CMK-3 copper impregnated sample. Copper loading is 22.0 wt.-% ...........................................................................................................106

4.40. TEM image of copper supported on CMK-3 type carbon. Copper loading is 5 wt.-% ...........................................................................................................107

4.41. TEM image of CMK-5 impregnated catalyst. Copper loading is 22.9 wt.-% ....108

4.42. TEM image of CMK-5 impregnated catalyst. Copper loading is 22.9 wt.-% ...........................................................................................................109

4.43. TEM image of CMK-5 impregnated catalyst. Copper loading is 15.3 wt.-% ...........................................................................................................109

4.44. TEM image of CMK-5 impregnated catalyst. Copper loading is 26.7 wt.-% ...........................................................................................................110

4.45. TEM image of Cu-Zn impregnated CMK-5 .....................................................111

4.46. TEM image of Cu-Zn impregnated CMK-3 .....................................................112

4.47. TEM image of Cu-Zn impregnated Kugelkohle .............................................112

4.48. The size distribution of copper particles in the samples Cu/ZnO/CMK-5 (a), Cu/ZnO/C (b) and Cu/ZnO/CMK-3 (c). ...........................................................................................................114
4.49. Dependence of reaction rate over the Cu (solid symbols) and Cu/ZnO (hollow symbols) supported carbon catalysts vs. copper surface area at three different temperatures ................................................................. 115

4.50. CO formation over copper and copper zinc particles supported on Kugelkohle........ 117

4.51. Isotherms of CMK-5, CMK-3 type carbons and Kugelkohle impregnated with Cu and Cu/ZnO .......................................................................................................................... 119

4.52. TPR analysis copper impregnated carbons with and without zinc....................... 121

6.1. The SBA-15 synthesized at different aging temperatures................................. 124

6.2. Calibration curves of $H_2$ (a) and $N_2$ (b) ......................................................... 126

6.3. Calibration curves of water; a linear (a-c) or polynomial (d-f) fit was used........... 127

6.4 The calculation scheme of the methanol steam reforming process............... 129
List of tables

3.1. The wavelengths of analyses for different compounds ........................................54

4.1. Influence of H$_2$O$_2$ treatment on textural properties such as pore diameter, pore volume and specific surface area of CMK-5 carbon.................................................................66

4.2. The textural parameters of CMK-5 synthesized using different SBA-15 templates......72

4.3 Hydrogen yield in steam reforming of methanol over the 22 wt.-% copper impregnated CMK-5 samples.................................................................75

4.4. Comparison of textural parameters SBA-15 silica template synthesized by Ryoo and Zhao methods.................................................................79

4.5. Comparison of textural parameters CMK-5 type carbon synthesized by Ryoo and Zhao methods .................................................................80

4.6. Hydrogen yield over different carbon types as supports for copper nanoparticles. Copper loading is 22.0 wt.-% for all catalyst ..................................................83

4.7. The weight specific rate of copper nanoparticles supported on CMK-3, CMK-5 and Kugelkohle mesoporous carbon.................................................................88


4.9. Influence of copper loading and nitric acid treatment on textural properties such as pore diameter, pore volume and specific surface area of CMK-5 carbon...............................95

4.10. Textural changes of CMK-5 by impregnation and leaching of copper ................100

4.11. The influence of copper loading on catalytic properties of copper nanoparticles supported on CMK-3, CMK-5 and Kugelkohle mesoporous carbons.................................105

4.12. Influence ZnO on catalytic properties copper nanoparticles supported on CMK-3, CMK-5 and Kugelkohle mesoporous carbons.....................................................113

6.1. The textural parameters of SBA-15 synthesized at different aging temperatures………………………………………………………………………………………….125

6.2. The textural parameters of SBA-15 synthesized in parallel batches at aging temperature 140 °C and treated with H$_2$SO$_4$……………………………………………………………………………………125
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D</td>
<td>3-Dimensional</td>
</tr>
<tr>
<td>BET</td>
<td>Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CMK</td>
<td>Carbon Mesoporous Korea</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethylether</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct Methanol Fuel Cell</td>
</tr>
<tr>
<td>ED</td>
<td>Electron Diffraction</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-Dispersive X-ray</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FA</td>
<td>Furfuryl Alcohol</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>FSM-n</td>
<td>Folded Sheet Mesoporous Materials-n</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared Radiation</td>
</tr>
<tr>
<td>MCM-41</td>
<td>Mobil Composition of Matter No 41</td>
</tr>
<tr>
<td>MTS</td>
<td>Micelle-Templated Silicas</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton-Exchange Membrane</td>
</tr>
<tr>
<td>RFC</td>
<td>Reactive Frontal Chromatography</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small Angle X-ray Scattering</td>
</tr>
<tr>
<td>SBA-15</td>
<td>Santa Barbara Airport No 15</td>
</tr>
<tr>
<td>SEC</td>
<td>Size Exclusion Chromatography</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>TEM -</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethylorthosilicate</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programming Reduction</td>
</tr>
<tr>
<td>TMB</td>
<td>Trimethylbenzene</td>
</tr>
<tr>
<td>WAXS</td>
<td>Wide Angle X-ray Scattering</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
CURRICULUM VITAE

Nelli Muratova

Date and Place of Birth:
March 21, 1981,
Almaty, Kazakhstan.

Citizenship: Russia.

Education:
09/1988-06/1994 Secondary School, 125 Almaty, Kazakhstan
09/1994-06/1998 The specialized scientific study center for physics, mathematics
and chemistry education, Lyceum 165, Almaty, Kazakhstan
09/1998-06/2004 Student of Novosibirsk State University of Department of Natural
Sciences, Russia
management.
Thesis title: “Determination of quantity Mercury of Blood and human
hair, the method atomic absorption” Supervisor: Dr. O.V. Shuvaeva.
polioxometalaty of Keggin’s structure and using it as catalysts in
reactions of air oxidation of organic compounds” Supervisor: Dr. O.A.
Kholdeeva.
Since August 2004 Promotion at the Max-Planck-Institut für Kohlenforschung, Mülheim an
der Ruhr, Germany, under the direction of Prof. Ferdi Schüth (Abteilung
für Heterogene Katalyse). Dissertation title: “Highly distributed copper
nanoparticles on carbon supports for methanol steam reforming”

Professional Interests:
Kinetics and mechanism of the catalytic reactions, design of the catalytic centers.
List of the publications and conferences


