Materials Chemistry of Cu/ZnO-based Catalysts for Methanol Synthesis and Steam Reforming

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D 83

Kurzzusammenfassung

In dieser kumulativen Arbeit werden die Ergebnisse einer ausführlichen materialchemischen Studie über Cu/ZnO-basierten Methanolsynthese– und –dampfreformierungskatalysatoren beschrieben. Die Einleitung beginnt mit einem Literaturüberblick über diese beiden Reaktionen und die verwendeten katalytischen Materialien. Dabei werden der technisch ausgereifte Methanolsyntheseprozess und die Herausforderungen beim Übergang auf Energiespeicheranwendungen eingeführt. Es werden drei Schlüsselaufgaben für eine wissensbasierte Optimierung des Cu/ZnO-Systems identifiziert und im Folgenden tiefergehend behandelt: *i*. Die etablierte und komplexe Synthese von industriellen Katalysatoren benötigt besseres Verständnis und weitere Optimierung. *ii*. Die aktive Form von Cu soll umfassend charakterisiert werden, um die wesentlichen Merkmale der aktiven Zentren zu identifizieren. *iii*. Die Rolle von Promotorzusätzen soll entschlüsselt werden.

Das folgende Kapitel über Katalysatorsynthese beschreibt den Einfluss wichtiger Syntheseparameter auf den resultierenden Katalysator. Die Ergebnisse heben die Rolle der Vorstufenchemie hervor und zeigen Verbindungen zwischen Synthesebedingungen und wesentlichen Eigenschaften der Katalysatorvorstufen auf. Auf diese Weise konnte das industrielle Syntheserezept im Nachhinein verstanden und die Einzelschritte nachvollzogen werden. Insbesondere wurde ein wissenschaftliche Erklärung für das sogenannte "chemische Gedächtnis" dieser Katalysatoren erarbeitet. Aus diesen Ergebnissen wurde ein allgemeines Synthesekonzept aus stufenweiser Meso- und Nanostrukturierung der Katalysatorvorstufe abgeleitet und erfolgreich auf neue Vorstufensysteme übertragen. Diese Arbeiten ergaben eine Probenserie von Cu/ZnO-basierten Katalysatoren mit homogenen Mikrostrukturen.

Diese Materialien wurden im folgenden Teil der Arbeit genutzt, um die aktive Form der Cu-Partikel zu untersuchen. Durch Kombination verschiedener Analysemethoden wurden die strukturellen und mikrostrukturellen Eigenschaften der Proben umfassend charakterisiert und nach Trends dieser Eigenschaften mit der katalytischen Aktivität gesucht. Für die Konzentration von Flächendefekten wurde eine lineare Korrelation mit der intrinsischen Aktivität der exponierten Cu-Oberfläche beobachtet. Dieses Ergebnis mündete in der Entwicklung eines Modells für das aktive Zentrum der Methanolsynthese. Es konnte gezeigt werden, dass solche planaren Defekte an der Oberfläche der Partikel in Stufen terminieren, die als hochenergetische Plätze verstanden werden können. Neben der Existenz solcher Stufen, konnte die Anwesenheit von ZnO_x an der Oberfläche als zweite Vorrausetzung für hohe katalytische Aktivität identifiziert werden. Diese ZnO_x-Spezies bilden sich in reduzierenden Bedingungen durch starke Metall-Träger-Wechselwirkungen zwischen Cu und ZnO. Über dieses vielschichtige Modell kann sowohl die oft beobachteten Unterschiede in der intrinsischen Aktivität verschiedener Cu/ZnO-Katalysatoren als auch die sogenannte „Cu-ZnO-Synergie" erklärt werden.

Im dritten Teil der Arbeit wurde die Rolle der Promotorzusätze untersucht. Die Ergebnisse zeigen, dass etwa 3% des Al-Zusatzes schon in das Kationengitter der Katalysatorvorstufe eingebaut werden können. Die daraus resultierenden Katalysatoren waren deutlich aktiver als Vergleichsproben mit niedrigeren oder höheren Al-Gehalten. Für diesen Effekt wurden zwei Beiträge gefunden. Zum einen verläuft die Nanostrukturierung von Al-haltigen Vorstufen effektiver, was zu einer Erhöhung der Cu-Dispersion führt. Zum anderen gibt es einen positiven Effekt, der durch die Dotierung von ZnO mit Al-Kationen im Cu/ZnO:Al-Katalysator entsteht. Durch die Verbesserung der Promotierung konnte die Aktivität von herkömmlichen $Cu/ZnO/Al_2O_3$-Katalysatorn um 40% erhöht werden.

Als Kernergebnisse dieser Arbeit stellen sich die drei neuen Struktur-Funktions-Korrelationen dar, welche die Abhängigkeit der exponierten Cu-Oberfläche von der Kristallstruktur der Vorstufe, die Abhängigkeit der intrinsischen Aktivität von der Anwesenheit planarer Defekte in den Cu-Partikeln und die Abhängigkeit der Gesamtaktivität vom Promotorgehalt beschreiben.

Abstract

This Thesis describes the insights into the methanol synthesis and steam reforming reactions that have been obtained by a detailed investigation of the materials chemistry of Cu/ZnO-based catalysts. The introductory part provides a brief literature review of these reactions and of the applied catalytic materials. The mature industrial methanol synthesis process is described and the challenges related to application of methanol synthesis as an energy storage reaction are highlighted. Three important challenges are identified as pre-requisites for a knowledge-based catalyst optimization system for such energy-related applications: *i*. The highly successful and well-established industrial catalysts synthesis needs deeper understanding and further optimization. *ii*. The active form of Cu in the working catalysts needs to be studied to identify the crucial "ingredients" of the active sites. *iii*. The role of promoters for improvement of the low-temperature activity of the catalyst needs to be revealed.

The following part on catalyst synthesis describes detailed investigations of the influence of the synthesis parameters on the resulting catalysts. The results highlight the role of the precursor chemistry and relate the synthesis conditions with critical properties of the precursor material and, thus, help to rationalize in retrospective the optimization of the industrial recipe. In particular, explanations for the so-called "chemical memory" of the catalyst have been elaborated. A synthesis concept of hierarchical meso- and nano-structuring of the catalytic material was derived and successfully applied to other Cu,Zn-precursor systems. This effort yielded a materials library of different well-characterized Cu/ZnO-based catalysts with uniform microstructures.

These materials were used in the following part of this Thesis to address the active form of Cu in methanol synthesis. From combination of different analytical techniques, a consistent picture of the structural and micro-structural properties of the Cu/ZnO-based materials was elaborated and this information was used to find trends in the catalytic performances of the catalysts. The concentration of planar defects in Cu was found to correlate linearly with the intrinsic activity of the exposed Cu surface. This observation led to a model of the active site for methanol synthesis that involves the presence of planar bulk defects. It was shown that termination of such defects at the surface of the Cu particles causes a change in the surface faceting and thus a step or kink, which can be considered a high-energy surface site. As a second requirement for the active site, the model proposes the presence of ZnO_x species at the Cu surface. These species have been detected to form under reducing conditions on the catalysts by strong metal support interaction between Cu and partially reduced ZnO. The model can explain the often observed differences in intrinsic activities as well as the synergistic effect of ZnO on Cu-based methanol synthesis catalysts.

The third part of this Thesis addresses the role of the promoter oxide in high-performance methanol synthesis catalysts. It was found that approximately 3% of the Al promoter can be incorporated into the cationic lattice of the catalyst precursor. Resulting catalysts were found to be significantly more active than those with higher or lower promoter concentration. This effect was related to a geometrical and an electronic contribution. The former is due to a more efficient nano-structuring during synthesis and higher exposed Cu surface areas in the final catalysts. The latter was related to a significant fraction of Al being trapped as dopant in the ZnO lattice and a beneficial modification of the properties of ZnO. By efficient promoter incorporation through the catalyst precursor, the activity of state-of-the-art methanol synthesis catalysts could be improved by 40%.

The three new structure-function-relationships of Cu/ZnO-based methanol synthesis catalysts that have been elaborated in this Thesis – correlation of precursor crystal structure with exposed Cu surface area, correlation of planar defect concentration with intrinsic activity, and correlation of promoter content with total activity – are the core results of this work.

Table of Contents

Foreword

The selected and commented publications that compose this Thesis cover the results that I obtained with my team and our collaboration partners in the years from 2007 to 2012 as a project and group leader in the Department of Inorganic Chemistry of the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin. These introductory remarks shall be understood as a compendium of this Thesis providing a short general introduction to the topics under study. The aim is to highlight the motivation, the general and some specific challenges, the scientific approach, the methodology and the outline of this work. This part is not meant to comprehensively review the vast body of literature that exists on Cu/ZnO-based catalysts in methanol chemistry. Such overview of the results that can be found in the literature will be given later in Chapter One. At this point, the reader is for now referred the two basic overview articles by Hansen and Højlund Nielsen (*Methanol Synthesis* in *Handbook of Heterogeneous Catalysis*, Wiley 2008, 2920) and by Ott *et al.* (*Methanol* in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley 2000) and to the book *Beyond Oil and Gas: The Methanol Economy* by Olah *et al.* (Wiley 2006).

Methanol, CH_3OH, is the smallest alcohol and an important base chemical. All chemists are well-familiar with methanol as a common solvent that can be found in every laboratory. In fact, only a small fraction of the methanol produced worldwide is used as solvent. The by far larger amount is further converted into value-added products and intermediates, in particular formaldehyde, acetic acid and methyl tertiary butyl ether. Thus, methanol is a versatile platform molecule and the current annual worldwide production is more than 50 million tons. It is the starting point of several value chains and cornerstone of one of the important petrochemical routes from fossil resources to chemical products in today's industry. Methanol is industrially produced in a catalytic process from syngas, mixtures of CO_x and hydrogen. Syngas can be derived from natural gas or coal by steam reforming and gasification, respectively. Starting in 1923, a ZnO/Cr_2O_3 catalyst was applied at approximately 400 °C and 300 bar in a BASF process. In the 1960, when sulfur-free syngas was available, ICI presented the so-called low-pressure/low-temperature methanol synthesis process, which still is in operation today. They developed a highly active nano-structured Cu/ZnO-based catalyst, which is promoted, e.g. by Al_2O_3 or small amounts of other refractory oxides. This or closely related materials are still applied today in many large-scale methanol synthesis plants worldwide that operate at approximately 250 °C and 60 bar.

Of course, as an important applied material, the Cu/ZnO methanol synthesis catalyst has already been studied by many academic and industrial research groups since several decades. For instance, a very powerful synthesis method for high-performance catalysts has been developed by the ICI group and is well-established by now. However, it is fair to state that despite these numerous reported efforts, there still are many open questions in the field of methanol synthesis catalysis. Concerning the catalyst synthesis, the critical role of certain synthesis parameters has been empirically recognized and sometimes is mystically termed the catalyst's "chemical memory", but the progress in understanding and optimizing the complex synthesis recipe has been little in the last years. Also, no fundamental and generally consistent consensus has been reached concerning the active site for methanol synthesis so far. Related to this question, the synergetic role of ZnO has been controversially discussed in the literature and still is not conclusively understood. Along with these questions also the mechanism and the fundamental question whether CO or CO_2 is the carbon source for methanol synthesis from syngas has been debated since long time. Also the question if methanol synthesis over Cu-based catalysts is a structure-sensitive reaction or not is still controversial, i.e. if the activity differs for different exposed surface facets of crystalline Cu. The same is true for the mode of operation of the promoter species, which has been examined mostly in a phenomenological manner, while only little is known about the speciation and fate of the promoter during catalyst synthesis and activation. It can be concluded that despite the mature technology of industrial methanol synthesis, the science behind this catalytic reaction is not yet mature.

With regard to this vivid and often fruitful debate in the scientific literature, I would like to note that I feel indebted to the many researchers that have contributed to this field in the past, including my predecessors in our Department, whose work formed the basis for continuous progress. Their results have served as an inspiration for me and enabled the new insights and conclusions that are reported in this Thesis.

Beyond the industrial methanol synthesis process, additional relevance of the CO_x hydrogenation reaction results from the potential of methanol as a synthetic and sustainable fuel and sustainable chemical feedstock, provided it is not produced from a fossil carbon source, but from anthropogenic CO_2 and renewable hydrogen. Upon utilization of methanol as a fuel in a combustion engine or fuel cell, only exactly that amount of CO_2 is emitted that has been consumed during its production. Thus, the methanol synthesis process from non-fossil sources can be envisaged as one half of a prospective CO_2-neutral energy cycle. The so-called “methanol economy”, which is advocated by G.A. Olah in his correspondent book, has great potential to contribute to a regenerative and sustainable utilization of our global resources.

The difference between industrial methanol synthesis from syngas derived from fossil sources and CO_2 hydrogenation is mainly the lack of CO in the feed gas of the latter. This does not only shift the thermodynamic yield of methanol to a lower value, it also affects the redox properties of the Cu surface of the catalyst. Without CO in the feed, water, the by-product of methanol synthesis from CO_2, cannot be scavenged by the water gas shift reaction with CO to again yield CO_2 and H_2. Thus, the water concentration will be higher in particular under integral conditions. Water can cause product inhibition and poison the catalyst’s surface. Thus, the major challenges in catalyst development for CO_2 hydrogenation are to make the methanol synthesis catalysts more active at lower temperature to compensate the unfavorable thermodynamics and to make it more resistant against inhibition by water. One goal of the work described in this Thesis is to contribute to the development of the knowledge basis for such modification of the industrial methanol synthesis catalyst. Here again, the problems are related to the many open question mentioned above and to the limited understanding of phenomena such as synergy and promotion which prevents a more efficient exploitation of these effects at the moment.

Another energy-related aspect is the necessity to store the fluctuating energy from regenerative sources like wind and solar power. In times of high energy generation and low demand, the excess energy needs to be stored to be re-distributed temporally and locally. Chemical energy storage is especially attractive due to the process scalability, the flexible usage in chemical and energy applications and the durability of the produced energy-rich chemical compounds. One possible way of chemical energy storage is to use excess energy to split water by electrolysis and to produce hydrogen. Hydrogen, however, is despite its large gravimetric energy density not an ideal fuel for the consumers, because it is volatile. In this context, downstream CO_2 hydrogenation is a promising way to make the chemical energy of hydrogen lasting and manageable. Due to its physical properties, in particular because it is liquid at ambient conditions, methanol is easier to store and can be distributed with currently existing infrastructure like pipelines, road tankers and filling stations. It can be used as a combustion fuel or in a direct methanol fuel cell to re-generate electricity. It is noted, however, that the current efficiency of chemical energy storage in methanol upon re-conversion to electricity is still too low to be economically attractive. However, progress in catalysis research in electrocatalytic water splitting as well as in CO_2 hydrogenation will automatically improve the efficiency of the overall process and potentially make this approach feasible.

This scenario also explains the high interest in the second reaction studied in this work, the steam reforming of methanol, which is formally the back reaction of CO_2 hydrogenation to methanol. Accordingly, by steam reforming, hydrogen and CO_2 are re-released from methanol, which can be considered a chemical hydrogen storage molecule in this context. Production of hydrogen from methanol is particularly interesting for mobile applications of hydrogen fuel cells, e.g. in cars. A combination of CO_2 hydrogenation, methanol distribution and onboard steam reforming to power a fuel cell is an attractive option for individual mobility, as it is sustainable and combines the advantages of a carbon-based fuel with the clean and efficient hydrogen fuel cell technology. Cu/ZnO-based methanol synthesis catalysts are among the best systems known also for the steam reforming reaction and many of the open questions of methanol synthesis are also discussed in a similar manner for this reaction.

Thus, the motivation for this work is multifold. In addition to the quest for a better fundamental understanding of an applied catalyzed reaction and to the chance to improve the efficiency of an industrial process, especially these new energy-related aspects of CO_2 recycling account for a substantial share of my motivation to work on this topic.

The specific open questions that I have studied together with my team and our partner groups were:

> *Synthesis*: How can we understand the well-established and complex multi-step synthesis method for methanol synthesis catalysts? What is the reasoning behind the setting of the preparation parameters? Can this successful recipe be further optimized? And why is the catalytic performance of the resulting catalyst so extremely sensitive towards smallest changes even in the very early preparation steps, which leads to dramatic difference between catalysts prepared at different conditions or in different laboratories?
>
> *Active state of the catalyst*: How do such differences in preparation and performance translate into differences in the properties of the active Cu phase? What are the structure-performance relationships of this catalyst system? How does the interaction between Cu and ZnO – the “Cu-ZnO synergy” – operate in the industrial catalyst? Finally, what is the active site of industrial methanol synthesis?
>
> *Role of promoters*: Refractory oxide promoters such as Al_2O_3 improve the activity and stability of the catalyst. What is the best way to introduce these promoters to the Cu/ZnO catalyst? What is the fate of the promoter species in the active catalyst? What is the mode of operation of such promoters and how do they affect the performance? Can promotion be further improved?

In heterogeneous catalysis, which is by its nature an interdisciplinary field, the contribution of a solid state and materials chemist like me is naturally aimed at understanding the structural properties that are crucial for an active catalyst and at development of synthetic pathways to generate and stabilize these properties. Complementary to the prominent model catalysis approach that starts from well-defined materials at artificial conditions and requires an increase in complexity to extrapolate to “real world” catalysis, we have followed an inverse approach that used the functional high-performance catalyst as starting point. Our attempts to understand the functionality of applied nano-structured catalysts and to answer the above questions were submitted to the conservation of the complexity in materials and reaction conditions, i.e., whenever possible, we studied nano-structured powders under high-pressure conditions in realistic reactor environments.

This approach poses substantial limitations to the toolbox of analytical methods that are applicable and to the diagnostic insight that is available from these methods. To tackle this challenge, a large variety of conventional as well as highly specialized and also newly-developed complementary *ex-* and *in situ* methods has been applied in the laboratory and also at large scale research facilities. Among these are diffraction, imaging and surface-sensitive spectroscopic methods, with the aim to jointly result in a consistent picture of the complex catalytic material. *In situ* neutron diffraction to study a working industrial catalyst was a special technique that was developed and successfully applied in the framework of this Thesis. The combination of a conventional catalytic tube reactor and a neutron beamline was introduced as a new characterization tool that allows insights into the catalyst's structural properties under relevant high-pressure conditions. With this technique the first *in situ* diffraction patterns of an industrial $Cu/ZnO/Al_2O_3$ catalyst under realistic high pressure conditions have been obtained and analyzed.

With this experimental approach based on complex materials, an insight into the microscopic and atomistic details of the reaction mechanism is hardly possible, but the goal was rather to identify structural properties that are crucial for high catalytic performance by studying and comparing a variety of well-characterized materials. The role of synthesis as the basis for drawing the targeted conclusions is to be emphasized. A substantial effort has been made to produce proper materials – Cu/ZnO-based catalysts in different forms –, which are sufficiently uniform to enable a reliable correlation of (micro-)-structural properties with macroscopically observed catalytic performance data. In the best case, such results lead to the establishment of structure-performance-relationships that shed light onto the relevant features of a high-performance methanol synthesis catalyst and can be used, on the one hand, for knowledge-based further optimization of the catalyst and, on the other hand, to guide the design of model catalysts and theoretical calculations that are capable to deliver important mechanistic insights.

The results chapters are outlined along the three fields of research questions that have been phrased above. It will be shown there that this approach has been applied with success. New insights into the preparation and optimization of Cu/ZnO-based methanol synthesis catalysts have been obtained and a scientific model that explains the "chemical memory" will be reported. A model of the active site of industrial methanol synthesis that includes microstructural as well as synergetic aspects will be presented. The mode of operation of promoters in Cu/ZnO-based has been studied and the effects of the promoter species on the catalyst's micro- and defect structure have been discovered. It will be shown that by optimization of the Al_2O_3-addition, the activity of the state-of-the-art $Cu/ZnO/Al_2O_3$ methanol synthesis catalysts can be improved by as much as 40%. As core results of this work, three new structure-function-relationships of Cu/ZnO-based methanol synthesis catalysts have been elaborated and will be described in detail in this Thesis – the correlation of precursor crystal structure with exposed Cu surface area, the correlation of planar defect concentration with intrinsic activity, and the correlation of promoter content with total activity.

Certainly, in the field of methanol synthesis catalysis, enough challenging questions remain unanswered and need to be studied in the future with different complementary techniques and approaches to really achieve a comprehensive understanding of this reaction and this catalyst. There still is a long way to go, but I am optimistic that the selection of papers presented in this Thesis will prove to be a visible and recognized contribution at least to the material-related problems of this important reaction.

This Thesis is comprised of 17 selected publications, two of which are book chapters in review-style that form the introductory part. The others are peer-reviewed journal articles containing the results of our work obtained in the last years. Each publication is preceded by a short summary, with the purpose to put the specific results in the greater context of this Thesis and to guide the reader without making the paper's abstract and conclusions redundant. If the paper comes with supporting information, this is listed at the end of the Thesis in the Appendix. The main part finishes with a conclusion and outlook and the acknowledgements. Statements about my own contribution to those publications with co-authors can also be found in the Appendix as well as a CV and my full publication list.

Malte Behrens November 2012, Berlin

List of Publications Presented in this Thesis

(Sorted by date; * corresponding author)

M. Behrens,* F. Girgsdies, A. Trunschke, R. Schlögl, *European Journal of Inorganic Chemistry* **2009**, 7, 1347-1357.

M. Behrens,* *Journal of Catalysi*s **2009**, 267, 24-29.

M. Behrens,* I. Kasatkin, S. Kühl, G. Weinberg, *Chemistry of Materials* **2010**, *22*, 386–397.

M. Behrens,* F. Girgsdies, *Zeitschrift für Anorganische und Allgemeine Chemie* **2010**, 636, 919-927.

M. Behrens,* A. Furche, I. Kasatkin, A. Trunschke, W. Busser, M. Muhler, B. Kniep, R. Fischer, R. Schlögl, *ChemCatChem* **2010**, *2*, 816–818.

M. Behrens,* D. Brennecke, F. Girgsdies, S. Kißner, A. Trunschke, N. Nasrudin, S. Zakaria, N. Fadilah Idris, S. Bee Abd Hamid, B. Kniep, R. Fischer, W. Busser, M. Muhler, R. Schlögl, *Applied Catalysis A* **2011**, *392*, 93-102.

M. Behrens,* S. Kissner, F. Girgsdies, I. Kasatkin, F. Hermerschmidt, K. Mette, H. Ruland, M. Muhler, R. Schlögl, *Chemical Communications* **2011**, *47*, 1701-1703.

S. Kühl, M. Friedrich, M. Armbruester, **M. Behrens**,* *Journal of Materials Chemistry* **2012**, *22*, 9632-9638.

F. Conrad, C. Massué, S. Kühl, E. Kunkes, F. Girgsdies, I. Kasatkin, B. Zhang, M. Friedrich, Y. Luo, M. Armbrüster, G. Patzke,* **M. Behrens**,* *Nanoscale* **2012**, *4*, 2018-2028.

T. Kandemir, D. Wallacher, T. Hansen, K.-D. Liss, R. Naumann d'Alnoncourt, R. Schlögl, **M. Behrens**,* *Nuclear Instruments & Methods in Physics Research A* **2012**, *673*, 51-55.

M. Behrens,* F. Studt,* I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Kniep, M. Tovar, R. W. Fischer, J. K. Nørskov, R. Schlögl, *Science* **2012**, 18, 893-897.

M. Behrens,* M. Armbrüster, “Methanol Steam Reforming“ in *Catalysis for Alternative Energy Generation*, Editors: L. Guczi, A. Erdôhelyi (Springer) **2012**.

S. Zander, B. Seidlhofer, **M. Behrens**,* *Dalton Transactions* **2012**, *41*, 13413–13422.

M. Behrens,* G. Lolli, N. Muratova, I. Kasatkin, M. Hävecker, R. Naumann d’Alnoncourt, O. Storcheva, K. Köhler, M. Muhler, R. Schlögl, *Physical Chemistry – Chemical Physics*, in press, DOI: 10.1039/C2CP41680H.

M. Behrens,* E. Kunkes, “Methanol Chemistry“ in *Chemical Energy Storage*, Editor: R. Schlögl (de Gruyter) **2012**.

M. Behrens,* S. Zander, P. Kurr, N. Jacobsen, J. Senker, G. Koch, T. Ressler, R. W. Fischer, R. Schlögl, *Journal of the American Chemical Society* **2013**, *135*, 6061-6068.

T. Kandemir, F. Girgsdies, T. C. Hansen, K.-D. Liss, I. Kasatkin, E. L. Kunkes, G. Wowsnick, N. Jacobsen, R. Schlögl, **M. Behrens**,* *Angewandte Chemie International Edition* **2013**, *52*, 5166-5170.

Chapter 1: Introduction

The introductory section of this Thesis is comprised of two book chapters that provide reviews of relevant literature and introduce the reader to the current challenges and recent developments in the field of methanol synthesis and steam reforming over Cu/ZnO-based catalysts. Both chapters focus on the modern fields of energy-related application of catalytic methanol reactions. This is, on the one hand, the hydrogenation of CO_2 for its synthesis – a process that can help to store fluctuating regenerative energy into a feasible and CO_2-neutral synthetic fuel via, e.g., water electrolysis as a source of hydrogen. On the other hand, renewable hydrogen can be re-released from methanol acting as hydrogen storage molecule by the methanol steam reforming reaction. This process is in particular interesting if combined with mobile fuel cell applications. However, the mature industrial process of methanol synthesis from fossil natural gas- or coal-derived syngas and the large experience of scientists and engineers with this technology are recognized as the basis for such new and modified applications of Cu/ZnO-based catalysts. It is noted that some of the major results that are presented later in this thesis in more detail are already shortly reviewed and introduced in this first section.

Methanol Chemistry

By Edward L. Kunkes, Malte Behrens

In: *Chemical Energy Storage*, edited by Robert Schlögl, de Gruyter, Berlin, **2012** (ISBN: 978-3110264074).

In this book chapter, we describe the potential of methanol as a synthetic fuel and point out the challenges of a prospective change of the feedstock from fossil syngas ($CO/CO_2/H_2$) to CO_2 hydrogenation conditions (CO_2/H_2). The literature knowledge on the industrial process, the experimental and theoretical work on the reaction mechanism and the open questions are shortly reviewed. The thermodynamic boundary conditions and in particular the role of CO on thermodynamics and kinetics of the CO_2 hydrogenation and the water gas shift equilibrium is discussed. In a CO-free feed gas, the equilibrium yield of the exothermic CO_2 hydrogenation reaction is disfavored. Thus, an improvement of the low-temperature activity was identified as the major goal of catalyst development. However, it is concluded that, despite the maturity of the methanol synthesis technology and although significant progress has been made recently, the available experimental and theoretical data basis is not yet sufficient to allow for a knowledge-based optimization of the catalysts to efficiently operate under CO_2 hydrogenation conditions. Cu/ZnO-based catalysts, their synthesis and major properties are introduced as the currently industrially applied material and as the most promising catalyst system for CO_2-to-methanol. The unique microstructure of successful Cu/ZnO-based methanol synthesis catalysts is highlighted. These materials are metal-rich bulk catalysts and consist a porous aggregated of Cu and ZnO nanoparticles in an alternating arrangement. Large exposed Cu surface areas as guaranteed by access to the “inner” surface area of these aggregates. Additionally, this catalyst architecture provides many interfaces of Cu and ZnO for an efficient interaction. Room for improvement of the low-temperature activity is suggested by more efficient promotion of Cu/ZnO and by a more controlled exploitation of the Cu-ZnO synergy.

Methanol Steam Reforming

By Malte Behrens, Marc Armbrüster

In: *Catalysis for Alternative Energy Generation*, edited by László Guczi, András Erdöhelyi, Springer, New York, **2012** (ISBN: 978-1-4614-0343-2)

In this book chapter, the role of methanol steam reforming as a feasible hydrogen storage material is introduced with an emphasis on the catalyst materials that are active in this reaction. Methanol steam reforming allows releasing hydrogen and CO_2 from methanol and water. Thus, a combination of on-board reformer and hydrogen fuel cell is an attractive option to use clean fuel cell technology with an easy-to-handle liquid fuel. Surprisingly, there are many more literature reports on methanol steam reforming than on methanol synthesis and those recent reports dealing with Cu-based catalyst are reviewed. A reason for this imbalance might be that the steam reforming reaction can be studied more conveniently at ambient pressure. The paper highlights the benchmark position of the Cu/ZnO-based methanol synthesis catalysts also in the field of steam reforming catalysts. Formally, methanol synthesis and methanol steam reforming are forward and backward reactions, but practically they may well occur on different dynamic sites even if the same catalyst material is used, which is a result of the different conditions applied in both processes. The open questions towards the reaction mechanism, the synergetic effects of the catalyst components and the active sites are similar like in methanol synthesis. Due to the lower pressure more in-situ analysis is available for methanol steam reforming pointing at effects of Cu^+ species, Cu lattice strain or dissolved oxygen. However, care has to be taken when attempting to transfer the results to methanol synthesis conditions. It is noted that only the first two sections “Introduction” and “Cu-based catalysts” of this paper are part of this Thesis. The following part on intermetallic compounds, which was contributed by Marc Armbrüster, MPI for Chemical Physics of Solids, Dresden, Germany, is independent and not included here.

The section 5.3 “Intermetallic Compounds in Methnaol Steam Reforming” is not part of this Thesis and the pages 204–224 of this publication are omitted here.

Chapter 2: Synthesis

The role of synthesis for our research approach as outlined in the foreword cannot be over-estimated. The targeted identification of structural properties that are relevant for catalytic performance can only be reliable, if the characterization data obtained for a specimen of the material under study is representative for the whole catalyst bed. This is in particular important in the field of heterogeneous catalysis as minority species can easily dominate the overall catalytic properties of an inhomogeneous material. The results that we have obtained in our investigations of the synthesis of Cu/ZnO catalysts for methanol synthesis and steam reforming can be divided into two sub-sections. First, the well-established and proven synthesis technique to obtain high-performance catalysts has been investigated in detail with the aim of understanding not only how, but also why most successful catalysts are prepared exactly this way. This retrospective rationalization of the setting of synthesis parameters can be developed into a general synthesis concept applicable for different Cu/ZnO-based materials and examples are reported in the second section of this chapter.

The “Chemical Memory” of the industrially applied catalyst synthesis

The industrially applied synthesis of Cu/ZnO and promoted Cu/ZnO/Al_2O_3 catalysts was developed in industry in the 1960s. It is comprised of co-precipitation and ageing (and washing, drying) of a catalyst precursor material, its thermal decomposition and reduction. The precursor material is described in many literature reports as a phase mixture of different mixed Cu,Zn hydroxy carbonates, which are transformed into an intimate mixture of the binary oxides CuO/ZnO upon calcination. The nobler CuO component is reduced to Cu nanoparticles in the final activation step, while ZnO and the promoter(s) stay in their oxidic form. In a successful preparation, porous Cu/ZnO aggregates are obtained that expose a high Cu surface area and exhibit many Cu-ZnO interfaces. It is known, that in order to be successful, empirically optimized preparation parameters have to be strictly obeyed. This is in particular true for the early steps of co-precipitation and ageing – a phenomenon that coined the term “chemical memory” of Cu/ZnO catalysts. The aims of the work reported in this first section of the synthesis chapter aims at providing an understanding of this chemical memory through a detailed investigation of the synthesis process. The major synthesis parameters that have been studied and found to be responsible for the chemical memory are Cu:Zn ratio, mode of reactant addition during co-precipitation, precipitation pH and temperature as well as ageing time and conditions.

Minerals as model compounds for Cu/ZnO catalyst precursors: Structural and thermal properties and IR spectra of mineral and synthetic (zincian) malachite, rosasite and aurichalcite and a catalyst precursor mixture

By Malte Behrens, Frank Girgsdies, Annette Trunschke, Robert Schlögl

European Journal of Inorganic Chemistry **2009**, 7, 1347-1357.

The hydroxy carbonate compounds that are obtained after co-precipitation and ageing as catalyst precursors, their composition and phase fractions are known to vary as a function of preparation conditions, in particular with the Cu:Zn ratio. The compounds malachite, zincian malachite, rosasite, aurichalcite and hydrozincite have been identified. These materials occur in nature as minerals. The starting point of our investigation of the catalyst synthesis was to study these mineral phases and compare their properties to the synthetic materials that comprise the catalyst precursor. This paper reports the results of this study obtained by X-ray diffraction, infrared spectroscopy and thermal analyses. One major finding was that a detailed structural analysis of the precursor mixture can deliver valuable insights into relevant properties like the Cu:Zn ratio of the individual mixed phases. Importantly, careful analysis of the X-ray diffraction patterns revealed a structural change in the zincian malachite crystal structure as a function of Cu:Zn ratio in the cationic lattice of this phase. The different coordination requirements of the Jahn-Teller-ion Cu^{2+} (d^9) and Zn^{2+} (d^{10}) have been proposed as an explanation of this effect. On the other hand, it was clearly found the catalyst precursor can only be insufficiently described as a physical mixture of well-crystalline mineral reference phases.

Meso- and Nanostructuring of Industrial Cu/ZnO Catalysts

By Malte Behrens

Journal of Catalysis **2009**, 267, 24-29

In this paper, the Cu:Zn ratio in zincian malachite is correlated with the crystal structure of this precursor phase, with the exposed Cu surface area of the final catalyst and to some extent also with the activity in methanol synthesis. The characteristic d-spacing of the $20\overline{1}$ peak in the XRD pattern is introduced as a reliable and easy-to-measure indicator for the cationic composition of this phase. Based on this result, it was possible to explain important aspects of the chemical memory of Cu/ZnO catalyst synthesis: The Cu:Zn ratio should be chosen to enable a maximal Zn incorporation in the zincian malachite precursor phase without triggering the segregation of other Zn-richer by-phases like aurichalcite. With this information, the industrially applied Cu:Zn ratio of 70:30 can be rationalized. A model for the chemical memory that comprises the effect of Cu:Zn ratio and precursor phase formation is proposed. The success of this particular synthesis route is due to a hierarchical meso- and nano-structuring of the precursor phase during co-precipitation, ageing and calcination. This model explains why the early preparation steps are critical for the performance of the final catalyst and identifies zincian malachite as the relevant precursor phase for the industrial Cu/ZnO catalyst.

Structural Effects of Cu/Zn Substitution in the Malachite–Rosasite System

By Malte Behrens, Frank Girgsdies

Zeitschrift für Anorganische und Allgemeine Chemie **2010**, 636, 919-927

In this work, the crystal chemistry of synthetic zincian malachite is investigated in detail. Structure refinement revealed the anisotropic deformation of the malachite unit cell as Cu^{2+} is substituted by Zn^{2+}. The individual lattice parameters do vary linearly with composition according to Vegard's rule, but the anisotropy leads to a partially compensating effect for the peak positions in the X-ray diffraction pattern. This anisotropy explains why among the strong XRD peaks only the $20\bar{1}$ reflection is significantly affected. The average decrease in Jahn-Teller distortions with increasing Zn content was identified as structural origin of this effect. From the trends in the crystal structure the maximal Zn incorporation that can be achieved using this synthesis recipe was determined to be 28% of all cations. Furthermore, a fresh view on the structural difference between malachite and rosasite based on the relative orientation of the Jahn-Teller-elongated bonds was discussed. In this context, malachite and rosasite are suggested to be distortion variants of a hypothetical orthorhombic parent phase.

Understanding the complexity of a catalyst synthesis: Co-Precipitation of mixed Cu,Zn,Al hydroxycarbonate precursors for Cu/ZnO/Al_2O_3 catalysts investigated by titration experiments

By Malte Behrens, Daniel Brennecke, Frank Girgsdies, Stefan Kißner, Annette Trunschke, Nurain Nasrudin, Salamiah Zakaria, Nur Fadilah Idris, Sharifah Bee Abd Hamid, Benjamin Kniep, Richard Fischer, Wilma Busser, Martin Muhler, Robert Schlögl

Applied Catalysis A **2011**, 392, 93-102

This work summarizes the impact of other synthesis parameters than the Cu:Zn ratio on the precursor material, i.e. mode of reactant addition, pH and temperature. Simple titration experiments revealed that Cu, Zn and Al species precipitate sequentially at different pH values. From this observation, the influence of the mode of precipitation, e.g. increasing or constant pH, can be explained. From the shape of the titration curves, the ideal pH-window for an efficient co-precipitation can be easily determined and temperature-dependent titration experiments allow studying the effect of heated solutions. Furthermore, also the role of the counter ion during precipitation was studied by comparison of nitrate and formate solutions. The buffering effect of formate was found to have a positive effect on the Zn incorporation in the zincian malachite precursor. Interestingly, this effect was also reflected in higher catalytic performance of the formate-derived catalyst, while the Cu surface-normalized activity was similar. A result that is in excellent agreement with the proposed effect of the Cu:Zn ratio in zincian malachite on the effectiveness of nano-structuring in the final catalyst. Moreover, a new mixed Cu,Zn hydroxy formate phase was identified that is of potential interest for Cu/ZnO catalysts preparation. This work was conducted in collaboration with the groups of Sharifah Abd Hamid, Universtiy of Malay, Kuala Lumpur, Malaysia (titrations experiments) and Martin Muhler, Ruhr-University Bochum, Germany (catalytic tests).

In-situ EDXRD Study of the Chemistry of Aging of Co-precipitated Mixed Cu,Zn Hydroxycarbonates – Consequences for the Preparation of Cu/ZnO Catalysts

By Stefan Zander, Beatrix Seidlhofer, Malte Behrens

Dalton Transactions **2012**, 41, 13413–13422

This paper describes that application of in-situ analysis to the synthesis of the methanol catalyst precursor. The phase formation of the zincian malachite precursor from the initially amorphous co-precipitate was investigated at different conditions. For this purpose, a continuous co-precipitation of a master batch of unaged precursor material was followed by ageing experiments in artificial mother liquor. This unique approach allowed the decoupling of precipitation and ageing, which can be studied independent of each other. The amorphous starting material was crystallized at different pH values, different temperatures and in the presence of different additives. An intermediate crystalline by-phase, sodium zinc carbonate was observed before zincian malachite was formed in some experiments. In combination with the $d_{20\bar{1}}$-shift analysis and the knowledge obtained from the previously described titration experiments, a comprehensive model of the chemical memory was elaborated. In the industrial synthesis, the synthesis parameters have been empirically optimized to guarantee the highest possible degree of Zn incorporation in zincian malachite and the highest possible fraction of this phase. This work was conducted in collaboration with Beatrix Seidlhofer from the group of Wolfgang Bensch, University of Kiel, Germany, who is beamline scientist at HASYLAB, Hamburg, Germany.

Alternative Synthesis Approaches

In this sub-section of the synthesis part, the lessons learned on the industrial catalysts synthesis have been transferred to a preparation concept that was applied to synthesize new members of the Cu/ZnO catalyst family with modified properties. As described in detail above, the core of the industrial recipe is the controlled synthesis of a well-defined precursor compound with and a mixed cationic lattice accommodating Cu and Zn ions in a perfect distribution on the atomic level – zincian malachite in case of the industrial catalyst. By thermally and/or chemically induced segregation of the Cu- and Zn-species on the nano-level, a porous Cu/ZnO bulk-catalyst can be obtained. This approach was now adapted to other precursor systems than zincian malachite. Beyond the search for better catalysts, one important aim of this work was to generate a Cu/ZnO materials library with well-characterized functional samples that differ in various aspects of their (micro-)structural properties, but that are still similar enough to the zincian malachite-derived industrial benchmark to be sufficiently active and comparable. The application of such a series of materials for revealing structure-performance-relationships of methanol synthesis catalysts will be described in the following chapter.

Phase-pure Cu,Zn,Al Hydrotalcite-like Materials as Precursors for Copper rich Cu/ZnO/Al_2O_3 Catalysts

By Malte Behrens, Igor Kasatkin, Stefanie Kühl, Gisela Weinberg

Chemistry of Materials **2010**, 22, 386–397

The hydrotalcite or layered double hydroxide phase was often reported as a part of the precursor phase mixture if Al_2O_3-promoted Cu/ZnO catalysts were prepared. This paper addressed the role of this precursor compound for the final catalysts. To study the properties of the Cu/ZnO/Al_2O_3 domains, which evolve from layered double hydroxide precursors, phase-pure Cu,Zn,Al materials with different cationic compositions have been synthesized using a modified co-precipitation recipe. It was found that the Cu nanoparticles formed from the LDH precursor tend to be smaller than those in zincian malachite-derived benchmark catalysts. The oxidic component is mostly amorphous. The thermal segregation behavior of the catalyst components suggest that Cu/$ZnAl_2O_4$-type catalysts are obtained from layered double hydroxides precursors. The Cu nanoparticles posses an intimate interface contact to the amorphous oxide matrix, which makes them to a large part inaccessible for catalysis. The exposed Cu surface areas were low despite the successful nano-structuring of the Cu phase. It can be concluded that the layered double hydroxide compounds are very interesting catalyst precursors, but if obtained as a side-phase during the conventional Cu/ZnO catalysts synthesis, it does not contribute significantly to the exposed Cu surface area. Other synthesis methods and modified preparation recipes are required to exploit the potential of this precursor system.

Cu,Zn,Al layered double hydroxides as precursors for copper catalysts in methanol steam reforming - pH-controlled synthesis by microemulsion technique

By Stefanie Kühl, Matthias Friedrich, Marc Armbrüster, Malte Behrens

Journal of Materials Chemistry **2012**, 22, 9632-9638

In the previous publication, the strong embedment of the Cu particles in the oxide matrix in layered double hydroxide-derived $Cu/ZnAl_2O_4$ materials was found to limit the catalytic activity. In this paper, we report an attempt to solve this problem by an improved meso-structuring of the precursor particles. A pH-controlled co-precipitation in the micro-droplets of an inverse micro-emulsion was successfully applied. The total and specific Cu surface areas of the produced catalyst were found to be higher compared a conventionally prepared reference sample due to smaller $Cu/ZnAl_2O_4$ aggregates with less embedded Cu particles. Methanol steam reforming was applied as a test reaction to compare these two samples. Interestingly, the catalytic performance of the micro-emulsion-derived catalyst was only slightly higher, despite the substantially higher Cu surface area of this sample. This result highlights the role of the microstructural arrangement – interfacial embedding versus exposed surface – for the intrinsic catalytic performance of these catalysts. This work was conducted in collaboration with the group of Marc Armbrüster, MPI for Chemical Physics of Solids, Dresden, Germany (catalytic tests).

Microwave-hydrothermal synthesis and characterization of nanostructured copper substituted ZnM_2O_4 (M = Al, Ga) spinels as precursors for thermally stable Cu catalysts

By Franziska Conrad, Cyriac Massué, Stefanie Kühl, Edward Kunkes, Frank Girgsdies, Igor Kasatkin, Bingsen Zhang, Matthias Friedrich Yuan Luo, Marc Armbrüster, Greta Patzke, Malte Behrens

Nanoscale **2012**, *4*, 2018-2028

Besides other hydroxy carbonate phases like layered double hydroxides, also some oxides fulfill the requirement of a mixed cationic lattice and can be promising precursors for Cu/ZnO-based catalysts. In this work, $Cu_{1-x}Zn_xAl_2O_4$ spinel was prepared with high surface area by a microwave-assisted hydrothermal method, reduced in hydrogen and the resulting $Cu/ZnO/Al_2O_3$ catalyst was tested in methanol synthesis and methanol steam reforming. With this method, very small Cu particles with a high resistivity against sintering can be prepared. Despite a considerable exposed Cu surface area, the catalytic activity, however, was disappointing. This effect was related to the lack of synergistic interaction between Cu and the ZnO-species due to incorporation of Zn into the stable crystalline spinel lattice. This material is yet another example of substantially different intrinsic activities per unit surface area of Cu in differently prepared Cu/ZnO-based catalysts. This observation will be further addressed in the subsequent section on the active form of Cu in these catalysts. This work was conducted in collaboration with the group of Greta Patzke, Universtiy of Zürich, Switzerland (Ga-containing reference material, conceptual discussions).

Knowledge-based development of a nitrate-free synthesis route for Cu/ZnO methanol synthesis catalysts via formate precursors

By Malte Behrens, Stefan Kissner, Frank Girgsdies, Igor Kasatkin, Felix Hermerschmidt, Katharina Mette, Holger Ruland, Martin Muhler, Robert Schlögl

Chemical Communications **2011**, 47, 1701-1703

It was mentioned above that a new promising mixed precursor phase was discovered during the titration experiments in the formate buffer solution. In this paper, the mixed hydroxy formate compounds have been prepared in a phase pure form and have been structurally characterized by X-ray diffraction. An analogous synthesis concept as it was developed for the zincian malachite-derived catalysts has been applied for the novel formate precursors. Optimal precipitation conditions have been elaborated and the Cu:Zn ratio has been studied on basis of the crystal structure of the precursor phase. It was found that the concept of hierarchical meso- and nano-structuring of the mixed precursor also works efficiently for the formate-derived materials. Ex-formate Cu/ZnO catalysts with high exposed Cu surface areas can be prepared and similar intrinsic properties like unpromoted ex-zincian malachite catalysts have been observed. It is noted that this synthesis route does not require the use of nitrate solution for co-precipitation, but used directly mixed formate solutions. Thus, no nitrate-contaminated waste water is produced when methanol catalysts are prepared by this method. This work was conducted in collaboration with the group of Martin Muhler, Ruhr-University Bochum, Germany (catalytic tests).

Chapter 3: The Active Form of Cu/ZnO Catalysts

It has been mentioned throughout the papers presented in this thesis so far that differently prepared Cu surface can have significantly different intrinsic activities in methanol synthesis and steam reforming. In this section, the (micro-)structural origins of these differences are addressed. The aim was to carefully analyze what makes a Cu surface in functional catalysts more or less active and to find correlations that in the end deliver a model of the active site of the complex industrial Cu/ZnO/Al_2O_3 catalyst. Such correlations need to be obtained on suitable uniform materials and the results reported in the previous section about catalysts synthesis provide the toolbox for such approach. The working hypothesis that has previously been proposed in the literature was that the catalyst's microstructure, i.e. the microscopic arrangement of the catalyst's components and their defect structure, contribute to the catalytic performance. This part is divided into two sub-sections. The first one addressed the microstructural characterization and identification of the active site by structure-activity-relationships, while the second one focuses on in situ observations of a selected highly active catalyst to study the stability of the relevant structural features under real catalytic conditions.

Microstructure and active site of Cu/ZnO catalysts

It has been elaborated in previous work in our Department and reported in the literature that the microstructure of a Cu/ZnO catalyst, i.e. all structural features beyond the ideal crystal structure of the components Cu and ZnO like interfaces and surfaces, lattice strain and defects, particle size and shape etc., play an important role for the activity. The challenge is to identify those microstructural modifications of Cu that make it catalytically more active in the best catalysts. The next two papers describe examples of how this challenge can be tackled by comparative studies of differently prepared catalysts.

The Potential of Microstructural Optimization in Metal/Oxide Catalysts: Higher Intrinsic Activity of Copper by Partial Embedding of Copper Nanoparticles

By Malte Behrens, Andreas Furche, Igor Kasatkin, Annette Trunschke, Wilma Busser, Martin Muhler, Benjamin Kniep, Richard Fischer, Robert Schlögl

ChemCatChem **2010**, *2*, 816–818

This paper describes two $Cu/ZnO/Al_2O_3$ catalysts with the same composition and the same Cu particle size that differ substantially in their catalytic properties. As the major microstructural difference, the embedment of the Cu particles in the ZnO/Al_2O_3 component was identified. The results show how tailoring the Cu/oxide arrangement can affect the catalytic performance of Cu-based methanol synthesis catalysts and are in nice agreement with the results obtained on the layered double hydroxide-derived materials reported in the previous chapter. It was concluded that the interface area between Cu and the oxides has a beneficial effect on the intrinsic activity of the exposed fraction of the Cu particle probably by metal-support-interactions. At the same time, the effect of large interface area on the total exposed Cu surface area is detrimental at a given Cu particle size. Thus, a compromise between inter- and surface is envisaged as a design guide for this kind of catalysts. Interface area promotes the intrinsic activity, while surface contributes to the absolute activity. A novel preparation method that yields catalysts with an improved interface/surface ratio was proposed. This work was conducted in collaboration with the groups of Martin Muhler, Ruhr-University Bochum, Germany (catalytic tests) and our industrial partner at Süd-Chemie, Bruckmühl. Germany.

The Active Site of Methanol Synthesis over $Cu/ZnO/Al_2O_3$ Industrial Catalysts

By Malte Behrens, Felix Studt, Igor Kasatkin, Stefanie Kühl, Michael Hävecker, Frank Abild-Pedersen, Stefan Zander, Frank Girgsdies, Patrick Kurr, Benjamin-Louis Kniep, Michael Tovar, Richard W. Fischer, Jens K. Nørskov, Robert Schlögl

Science **2012**, 18, 893-897

Much of the knowledge that has been elaborated in the previous contributions accumulated in this paper, which certainly can be seen as a highlight of our work. It describes how the research approach outlined in the foreword was successfully applied to elaborate a model of the active site for methanol synthesis while taking the full complexity of the applied catalytic materials into account. A series of carefully prepared and fully characterized functional Cu/ZnO catalysts and a pure Cu reference powder have been catalytically tested in methanol synthesis under industrially relevant conditions. Dramatic differences in absolute and also in intrinsic, i.e. Cu surface area-normalized, activity have been observed. The trend in intrinsic activity was linearly reflected in the concentration of planar defects in the Cu nanoparticles, which was determined from neutron diffraction profile analysis. The role of planar defects in the bulk of the Cu particles for catalysis was rationalized on basis of high resolution transmission electron microscopy images that show generation of steps and kinks at the particle's surface at the location where the planar defect terminates. In addition, dynamic strong-metal-support interaction (SMSI), previously observed on model catalysts, has been confirmed on the applied materials by surface-sensitive in-situ X-ray photoemission spectroscopy. The role of the SMSI effect is to supply Zn species to the defective surface of the Cu particles. The beneficial effect of defects as well as the presence of Zn at the surface was confirmed by studying theoretical model surfaces with density functional theory. Thus, by the combination of controlled preparation, application of various complementary characterization methods and quantum chemical calculations it was possible to identify the two relevant structural properties of the active site for methanol synthesis out of the many structural features in real powder catalysts. The results suggest that only a fraction of the Cu surface is active under industrial conditions and that these sites combine a surface defect with the presence of Zn. This work was conducted in collaboration with the group of Jens K. Nørskov, Stanford University, USA (DFT calculations) and our industrial partner Süd-Chemie, Bruckmühl, Germany (catalyst testing). Michael Hävecker and Michael Tovar contributed as beamline scientists at HZB, Berlin, Germany.

In-situ observations of working Cu/ZnO catalysts using neutron diffraction

Nanostructured composite materials like heterogeneous catalysts can show a higher reactivity and different dynamic behavior compared to their bulk counterparts. In addition to irreversible processes like sintering and annealing, also reversible processes may occur that cannot be investigated by *ex situ* characterization of spent samples. For instance, reversible dynamic morphology changes of the Cu nanoparticles in Cu/ZnO have been reported in literature. It is therefore of general and fundamental interest to study heterogeneous catalysts not only in their fresh pre-reaction and their spent post-reaction states, but also *in situ* under working conditions. In case of the Cu/ZnO methanol synthesis catalysts such studies are relatively sparse due to the demanding conditions of the reaction, in particular the elevated pressure. In the context of this Thesis, it is important to confirm if the micro-structural features that have been claimed to be relevant also prevail under the harsher reactions conditions. Therefore, neutron diffraction has been applied as a suitable characterization method allowing insights into thick-walled and pressure-tight catalytic reactors.

In situ neutron diffraction under high pressure-Providing an insight into working catalysts

By Timur Kandemir, Dirk Wallacher, Thomas Hansen, Klaus-Dieter Liss, Raoul Naumann d'Alnoncourt, Robert Schlögl, Malte Behrens

Nuclear Instruments & Methods in Physics Research A **2012**, 673, 51-55

To use neutrons for an *in situ* study of a working methanol synthesis catalyst under realistic conditions, first a sample environment had to be developed that combines a continuous flow reactor with an *in situ* sample cell. This paper describes the design, manufacture and test measurements of our newly developed *in situ* reaction setup for neutron diffraction studies. A reaction tube was coupled to a gas dosing and analysis system. The catalyst bed in the tubular reactor can be heated to 330 °C and pressurized up to 60 bar allowing application of industrial methanol synthesis conditions at 250 °C and 60 bar. Test measurements of the catalyst activation and of the working catalyst have been conducted at different neutron facilities. The contribution of the reactor wall to the neutron diffraction patterns can be easily substracted from the signals of the catalyst and a true *in situ* study of industrial methanol synthesis was found to be feasible with this setup. The first *in situ* diffraction pattern of a working Cu/ZnO/Al_2O_3 catalyst at realistic conditions was reported. This work was conducted together with Dirk Wallacher (sample environment group at HZB, Berlin, Germany), Thomas Hansen (beamline scientist at ILL, Grenoble, France) and Klaus-Dieter Liss (beamline scientist at ANSTO, Lucas Heights, Australia).

In Situ Study of Catalytic Processes: Neutron Diffraction of a Methanol Synthesis Catalyst at Industrially Relevant Pressure

By Timur Kandemir, Frank Girgsdies, Thomas C. Hansen, Klaus-Dieter Liss, Igor Kasatkin, Edward L. Kunkes, Gregor Wowsnick, Nikolas Jacobsen, Robert Schlögl, Malte Behrens

Angewandte Chemie International Edition **2013**, 52, 5166 –5170

This paper reports on the detailed evaluation of the *in situ* neutron diffraction measurements of the methanol synthesis catalysts under industrial conditions that were obtained at two different beamlines. As the major result, besides a slight sintering, no clear indication for structural dynamics could be observed. The *in situ* formation of brass as well as of bulk-Cu hydrides or carbides was excluded. Brass was only formed at temperatures significantly higher than those used for methanol synthesis. Importantly, by comparison with a bulk-Cu reference, indications for the presence of stacking faults, which have been related to the active sites of methanol synthesis in our work, have been observed also in the *in situ* patterns confirming that these microstructural features are stable under working conditions. However, these defects can be annealed by heating up to 330 °C suggesting that they are kinetically trapped in the catalyst due to skillful preparation. The wider applicability of this method also for other catalytic processes at high-pressure such as ammonia synthesis or the Fischer-Tropsch-reaction is mentioned. This work was conducted together with Thomas Hansen (beamline scientist at ILL, Grenoble, France) and Klaus-Dieter Liss (beamline scientist at ANSTO, Lucas Heights, Australia) and Nikolas Jacobsen from our industrial partner group.

Chapter 4: The Role of Promoters

It is known that refractory oxides can act as structural promoters in Cu/ZnO catalysts improving the Cu dispersion and the thermal stability. Also beneficial effects on in the intrinsic have been described. The industrial catalysts are typically Al_2O_3-promoted, but other oxides have also been reported in literature. Generally, promotion, i.e. the addition of small amount of extra-elements to a proven catalytic system, is a phenomenon in heterogeneous catalysis that not well understood. The speciation and fate of the promoters in the active catalyst is not easy to characterize as promoters typically are present in low amounts and high dispersion. To get a better understanding of the effect of Al_2O_3-promotion of methanol synthesis catalysts, we have investigated the structural effect of Al incorporation into ZnO and structure-performance-relationships of $Cu/ZnO/Al_2O_3$ catalysts as a function of Al content.

The Effect of Al-doping on ZnO nanoparticles applied as catalyst support

By Malte Behrens, Giulio Lolli, Nelli Muratova, Igor Kasatkin, Michael Hävecker, Raoul Naumann d'Alnoncourt, Oksana Storcheva, Klaus Köhler, Martin Muhler, Robert Schlögl

Physical Chemistry – Chemical Physics **2013,** 15**,** 1374-1381

It has been shown earlier that low amounts of Al ions can be incorporated into ZnO by co-precipitation and calcination. We have prepared a ZnO/3% Al sample and compared it to a pure ZnO reference material. In this study, no Cu was added to avoid paramagnetic species that would interfere with the results obtained by nuclear magnetic resonance and electron paramagnetic resonance techniques. It was found that a significant fraction of the Al promoter was present on the Zn sites in ZnO giving rise the modification of the optical and electronic properties. Interestingly, the Al-doped ZnO was found to be dynamic if submitted to reducing conditions. In hydrogen a surface segregation of the Al species and pronounced changes in the electron paramagnetic resonance spectrum were observed that were not detected for the pure ZnO sample. The investigation of our model support clearly shows that Al can modify not only the electronic and optical properties, but in particular also interferes with the surface properties of ZnO:Al nanoparticles. Thus, an effect of the Al-promoter on the important Cu-ZnO interaction seems very likely and is proposed as a source of the promoting effect. This work was conducted in collaboration with the groups of Klaus Köhler, Technical University Munich, Germany, (electron paramagnetic resonance spectroscopy) and Martin Muhler, Ruhr-University Bochum, Germany (conceptual discussions). Michael Hävecker is beamline scientist at HZB, Berlin, Germany.

Performance Improvement of Nano-Catalysts by Promoter-Induced Defects in the Support Material: Methanol Synthesis over Cu/ZnO:Al

By Malte Behrens, Stefan Zander, Patrick Kurr, Nikolas Jacobsen, Jürgen Senker, Gregor Koch, Thorsten Ressler, Richard W. Fischer, Robert Schlögl

Journal of the American Chemical Society, **2013**, 135, 6061-6068

In this paper the effect of different amounts of Al on the Cu/ZnO/Al_2O_3catalyst synthesis, the structural properties of the resulting catalysts and their catalytic performance have been investigated. The investigation was based in the industrially applied synthesis route and accounted for the model of the chemical memory that was elaborated in a previous chapter of this Thesis. It was found that for Al contents between 3 and 4% a sharp maximum in the catalytic activity was obtained. This was due to two effects. The nano-structuring of the catalyst precursor was more efficient due to higher “dilution” of Cu in the zincian malachite precursor by Zn and Al. In addition, the intrinsic activity of these samples was higher compared to those with higher Al contents. It was concluded that Al-promotion works through two effects, a geometric one that generated more Cu surface area and an electronic one that generates a more active Cu surface by a synergistic effect. The latter was related to promoter atoms present in the ZnO lattice, which could be detected in the catalysts by application of element specific techniques on the promoter species. Interestingly, a linear correlation was obtained for the Cu content in the zincian malachite precursor phase (measured by the $d_{20\bar{1}}$-spacing) and the catalytic activity of the resulting catalysts indicating that a uniform distribution of all species including the promoter is the key to obtain high performance catalysts. The promotion mechanism by defect generation in the oxide through doping was proposed to be relevant also for other catalyst systems that show SMSI effects. This work was conducted in collaboration with the group of Jürgen Senker, University of Bayreuth, Germany, (nuclear magnetic resonance spectroscopy), the group of Thorsten Ressler, Technical University Berlin, Germany, (X-ray absorption near edge structure measurements) and our industrial partner Clariant (formerly Süd-Chemie, catalytic testing), Bruckmühl, Germany.

Conclusions and Outlook

Altogether, the results published in the above presented papers describe how the detailed study of an applied catalyst preparation process can provide a series of materials that after comprehensive characterization form the basis for elucidation of structure-performance-relationships. Application of this approach to the Cu/ZnO catalyst system has enabled new insights into the mature methanol synthesis process – the conversion of CO_x into methanol by hydrogenation. The most important contributions of this Thesis to the three fields of open research questions concerning the synthesis, the active site and the promotion of Cu/ZnO-based catalysts that have been outlined in the foreword of this Thesis are summarized here.

The well-established synthesis of high-performance methanol synthesis catalysts was understood as a multiple-step series of chemical reactions that allow transferring the ultimate homogeneous distribution of the mixed starting Cu^{2+}/Zn^{2+} solution to a large extent into the solid state to obtain highly inter-dispersed Cu and ZnO components in the final catalyst. The initial co-precipitation yields an amorphous hydrous material. This reaction, due to the difference in the precipitation-pH of Cu^{2+} and Zn^{2+} of approximately two pH units, needs to be conducted using the constant pH-technique to yield a well-intermixed co-precipitate. The pH-window for this step is given by the temperature-dependent precipitation pH of Zn^{2+} (ca. pH 5 at 65 °C) and the oxolation-pH of $Cu(OH)_2$ at ca. pH 9. The most critical step of the synthesis is the co-precipitate ageing in the mother liquor, which is equivalent to the crystallization of the hydroxy carbonate precursor phase.

On basis of a simple correlation between a detail of the crystal structure of zincian malachite, $(Cu,Zn)_2(OH)_2CO_3$, with the exposed Cu surface area in the final catalyst, this phase was identified as the relevant precursor phase for the industrial catalyst. Furthermore, this special structural feature, the d-spacing of the $(20\bar{1})$ lattice planes, was related to a crystal field effect that indicated the degree of substitution of Cu^{2+} by Zn^{2+} ions in the malachite lattice. Best catalysts were observed for highest Zn incorporation, which was found to be limited to approximately 28% under the conditions of the reported synthesis recipe. Thus, the industrially applied Cu:Zn ratio of the catalysts of ca. 70:30 can be rationalized by the solid state chemical constraint of maximal Cu-Zn substitution in the precursor phase. The joint mixed cationic sub-lattice of zincian malachite enables a perfectly atomic distribution of both species in the solid state, which gives rise to a highly inter-dispersed oxidic calcination product. The inter-dispersion is most efficient if the concentrations of Cu and Zn are similar, which explains the benefit of maximal Zn incorporation. It was found that the empirically determined conditions of ageing, Cu:Zn ratio $\approx$ 70:30, a pH of approximately 6.5 and a temperature of ca. 65°C, have been optimized in a unintended manner to yield a zincian malachite precursor with highest Zn content and a thin needle-like morphology. This particle shape of the precursor already pre-determines the porosity of the decomposition product to some extent and is responsible for the meso-structuring of the catalyst material, because the interwoven nature of the precursor needles leads to many inter-particle pores. The thermal steps of calcination and reduction at mild temperatures lead to segregation of the Cu and Zn components from the common precursor phase due to the limited miscibility of the oxides and the higher reducibility of CuO. Due to this final nano-structuring step, a unique porous microstructure of Cu/ZnO aggregates is obtained. Catalysts prepared according to this recipe consist of Cu and ZnO nanoparticles that are arranged in an alternating fashion to form inter-particle pores that allow to a certain extent access to the "inner" Cu surface area of the aggregates.

The results that have been briefly summarized in the two preceding paragraphs have helped to understand the industrial synthesis of methanol synthesis catalysts, to rationalize the optimization of the individual synthesis parameters in retrospective, and, in particular, to find scientific explanations for the "chemical memory" of the catalyst. Furthermore, the synthesis concept of preparation of a mixed precursor phase with decomposable anions, that already coins the properties of the resulting metal/oxide system, once recognized, was easily applied to other Cu,Zn precursor materials, such as mixed basic formates or layered double hydroxides. It was also successfully used in other projects of our group, e.g. for preparation of intermetallic catalysts, that are not part of this Thesis, but which show the generic relevance of this synthetic approach. In particular, this knowledge opens the door to a more rational further optimization that was indeed achieved for ternary promoted catalysts as will be described below.

In addition to the better understanding of the industrial recipe, the work on catalyst synthesis was also the foundation for a materials library of different Cu/ZnO-based catalysts, which exhibited different microstructures and properties, but could all be referenced to an industrial high-performance benchmark system. These samples were prepared according to the synthesis concept described above from different phase-pure precursor materials, amorphous gels or well-defined compounds, which guaranteed a uniform microstructure of the decomposition products and in final catalysts. The detailed structural characterization of the catalysts was performed using a variety of different techniques. While the classical solid state methods X-ray diffraction (XRD) and thermal analyses were very powerful to characterize the precursor compounds, they had to be complemented by imaging, surface-sensitive spectroscopy and probe molecule chemisorption to study the complex active state of the materials. Especially high resolution transmission electron microscopy (TEM), near-ambient X-ray photoemission spectroscopy (XPS) and N_2O reactive frontal chromatography have been applied to obtain a comprehensive picture of the active catalyst material. A special focus was on neutron diffraction techniques, which have been applied for the first time on high-performance Cu/ZnO catalysts and allow collection of diffraction data in particular at high scattering angles, where classical XRD delivers only limited diagnostic insight. A methodological highlight of this Thesis is the novel combination of *in situ* neutron diffraction with a high pressure catalytic reaction that enabled recording of the first diffraction data of a working methanol synthesis catalyst under industrial conditions.

From combination of all techniques a consistent picture of the structural and micro-structural properties of the Cu/ZnO-based materials under study was elaborated and this information was used to find trends in the catalytic performances of the catalysts. Inspired from previously published evidence that structural imperfections contribute to the catalytic activity in methanol synthesis, the defect structure of the Cu phase in the reduced catalysts was studied in detail. Using neutron diffraction pattern decomposition, the concentration of planar defects in Cu was estimated for a series of samples and found to correlate linearly with the intrinsic activity of the exposed Cu surface. This observation led to a model of the active site for methanol synthesis that involves the presence of planar bulk defects. It could be shown by high resolution TEM that termination of such defects at the surface of the Cu particles causes a change in the surface faceting and thus a step or kink, which can be considered a high-energy surface site. *In situ* neutron diffraction provided the important information that these planar defects are stable and not easily annealed under reaction conditions.

As a second requirement for the active site, the model proposes the presence of ZnO_x species at the Cu surface. These species have been detected to form under reducing conditions on the catalysts by strong metal support interaction between Cu and partially reduced ZnO as could be confirmed by XPS depth profiles. The trend in elemental distribution with information depth suggested the presence of a thin film of ZnO-species at the surface of the catalyst. A disordered surface layer of an approximate thickness of 1 nm has also been observed with aberration-corrected high resolution TEM. This model of the active site – a defective Cu surface with ZnO$_x$ being present in the surrounding – was supported by density functional theory calculations performed by our collaboration partners. These calculations proposed a lower energy pathway for methanol synthesis on stepped surfaces that were decorated with Zn atoms, which serve as anchoring sites for oxygenate adsorbates and can thus be considered as partially oxidized. The elaboration of this model of the active site from a combination of experimental and theoretical methods can be seen as a scientific highlight of this Thesis. The complex interplay of surface defects and strong metal support interaction can explain the often observed differences in intrinsic activity and the well-established synergistic effect of ZnO on Cu-based methanol synthesis catalysts. It also shows that a low number of highly active surface sites can open new reaction channels that operate only on the complex powder catalyst and become relevant under high pressure conditions. It has to be mentioned, however, that in addition to defectiveness and Cu-ZnO synergy, still a high total exposed Cu surface area plays a key role for a successful catalyst and can be seen the third requirement for high activity. It is intriguing to see, how the precursor-based catalysts synthesis yields a balance of all three pre-conditions: Defective Cu nano-particles are formed in close interfacial contact to ZnO with a large exposed surface area due to the nano-structuring of the mixed precursor material.

The third part of this Thesis addressed the role of the promoter oxide in high-performance methanol synthesis catalysts. It was found that also the promoter species Al^{3+} can be incorporated into the cationic lattice of the zincian malachite precursor. The amount is limited to approximately 3% of all cations, most likely due to the charge mismatch with the bi-valent Cu and Zn cations. However, this fraction of the promoter can be very finely dispersed in the catalyst and materials with 3% Al were found to be significantly more active than those with higher or lower promoter concentration. This effect was related to two contributions, a geometrical and an electronic one. The former is due to the higher dilution of Cu cations in the zincian malachite precursor than can be achieved with Zn and Al compared to Zn as the only substituent. This leads to a more efficient nano-structuring during decomposition to and higher exposed Cu surface areas in the final catalysts. Furthermore, a correlation of the promoter content in the zincian malachite lattice in the precursor stage and in ZnO in the final catalyst stage was found. This revealing of the fate of the promoter in the final catalysts was enabled by application of element-specific characterization methods like solid state nuclear magnetic resonance and X-ray absorption spectroscopy. The results show that a significant fraction of the homogeneously distributed Al cations is trapped as dopant in the ZnO lattice. It was shown on Cu-free model systems that Al-doped ZnO nanoparticles possess modified properties compared to pure ZnO due to the generation of defects. A dynamic effect of Al-migration towards the surface of ZnO was detected under reducing conditions. It is proposed that these effects – defect-induced modification of ZnO and the surface enrichment of the Al-dopant – affect the synergetic interaction of Cu and ZnO in a beneficial way. An analogous effect was also observed for Ga-doping. By efficient promoter incorporation through the zincian malachite precursor and application of the optimized promoter amount of 3%, the activity of state-of-the-art methanol synthesis catalysts could be improved by 40%.

The three new structure-function-relationships of Cu/ZnO-based methanol synthesis catalysts that have been elaborated in this Thesis – correlation of precursor crystal structure with exposed Cu surface area, correlation of planar defect concentration with intrinsic activity, and correlation of promoter content with total activity – are the core results of this work. These have contributed to a better knowledge about this important catalyst material and led to a significant improvement of its activity by a more efficient promotion. It has to be noted that the insight and understanding is not yet sufficient to overcome all the challenges related to synthetic fuel production by CO$_2$ hydrogenation, but further relevant progress can certainly be made in the future by continuous research efforts along these lines. Based on the results presented above, the challenging approach focused on a detailed investigation of the materials chemistry of high performance catalysts promises great potential if further developed for alternative catalysts synthesis routes, improved catalyst stability, highly effective catalyst promotion and, in collaboration with theory and model catalysis, towards a fundamental mechanistic understanding of the C1 reaction network over the different catalyst components. With the precursor-based hierarchical meso- and nano-structuring synthesis concept, the tunability of the catalyst's microstructure by different synthesis routes, the model of the active site and the concept of defect-induced promotion, this Thesis offers promising conceptual starting points for such investigations and we currently continue our work into these directions. Beyond the CO_2 hydrogenation over Cu/ZnO-based materials, the transfer of the results, in particular of the synthesis and activity concepts, to other potentially energy-relevant CO_2 conversion reactions that do not have an as mature technological foundation like methanol synthesis is of particular interest to foster progress, e.g. in methanization or reverse water gas shift. The *in situ* neutron diffraction technique is a methodological development originating from this Thesis with a generic potential for the investigation of dynamic changes of catalysts in other high-pressure such as ammonia or *Fischer-Tropsch* synthesis.

Acknowledgements

Foremost, I thank Robert Schlögl for his continuous support of my habilitation project and for his confidence to work with me as a project and group leader in his Department. Certainly, the results that we have obtained in the last years would not have been possible in this form without his trusting and generous sharing of resources and facilities. In the last years at the Department of Inorganic Chemistry, I have learned essential things about many different aspects of science. For me, this time has been and still is a really indispensable experience of an inspiring, exciting and efficient research environment. I scientifically and personally tremendously benefited from the trustful and fruitful teamwork with Robert.

Moreover, I am deeply indebted to my co-workers and group members. Only their commitment and motivation enabled a steady output of exciting results. I am not only grateful for the scientific progress that we achieved over the years, but in particular also for a friendly working atmosphere with the attitude to always help and care for each other. I really enjoyed working with you.

This latter statement also holds for the whole Department with my fellow group leaders and all scientific and non-scientific colleagues who supported me in the last years. Furthermore, many insights have been the result of collaborations outside the Department and I would also like to thank all colleagues from academic and industrial groups for the fruitful cooperation during the last years and also acknowledge the funding sources that granted financial support. Special thanks go to Thorsten Ressler for mentoring my habilitation at TU Berlin.

Finally, the patience, support and love of my wife Yasmin and my daughters Emma and Isabel made all this possible. Danke.

Appendix

Statements on the Own Contributions to the Papers in this Thesis

For all work presented in this Thesis, I have been responsible senior researcher and corresponding author of the publications. In two cases that are addressed below in more detail, the corresponding authorship was shared with collaborating colleagues. In general, I have conceived the research strategies, designed and partially performed the experiments, interpreted and partially evaluated the experimental data and administered the work. In all cases, where I am the first author of the paper, the manuscript has been (co-)written by myself. In the other cases, where I am the last author, the first draft of the manuscript was prepared by a Ph.D. student or Post-Doc from my group under my supervision, with the exception of one paper (see below). I have edited and corrected all manuscripts. A detailed overview on the individual contributions to those papers with multiple authors is listed below.

Malte Behrens November 2012

E. Kunkes, M. Behrens, "Methanol Chemistry" in *Chemical Energy Storage*, Editor: R. Schlögl (de Gruyter), in press:

> E.K. co-wrote the manuscript (mainly sections 5.3.2, 5.3.3, 5.3.4., 5.3.5). M.B. co-wrote the manuscript (mainly sections 5.3.1, 5.3.6, 5.3.7, 5.3.8) and designed its outline.

M. Behrens, M. Armbrüster, "Methanol Steam Reforming" in *Catalysis for Alternative Energy Generation*, Editors: L. Guczi, A. Erdôhelyi (Springer) **2012**:

> M.B. co-wrote the manuscript (sections 5.1, 5.2). M.A. co-wrote the manuscript (section 5.3, which is independent and not part of this Thesis).

M. Behrens, F. Girgsdies, A. Trunschke, R. Schlögl, *Eur. J. Inorg. Chem.* **2009**, *7*, 1347-1357:

> M.B. designed the experiments, conceived the research strategy, analyzed TGA and IR data, and wrote the manuscript. F.G. conducted and analyzed the XRD experiments. A.T. and R.S. discussed the data and gave conceptual advice.

M. Behrens, F. Girgsdies, *Z. Anorg. Allg. Chem.* **2010**, *636*, 919-927:

> M.B. designed the experiments, conceived the research strategy and wrote the paper, F.G. conducted and analyzed the XRD experiments.

M. Behrens, D. Brennecke, F. Girgsdies, S. Kißner, A. Trunschke, N. Nasrudin, S. Zakaria, N. Fadilah Idris, S. Bee Abd Hamid, B. Kniep, R. Fischer, W. Busser, M. Muhler, R. Schlögl, *Appl. Catal. A* **2011**, *392*, 93-102:

> M.B. designed and interpreted the experiments, conceived and supervised the research strategy and wrote the manuscript. S.K., D.B., N.N., S.Z. and N.F.I. performed the titration and characterization experiments and prepared the samples. F.G. performed the powder XRD structure refinement. W.B. and M.M. performed and evaluated the catalytic tests. A.T., S.B.A.H., B.K., R.F., M.M. and R.S. discussed the results and gave conceptual advice.

S. Zander, B. Seidlhofer, M. Behrens, *Dalton Trans.* **2012**, *41*, 13413–13422:

S.Z. performed and analyzed the experiments and wrote the manuscript, B.S. helped at the synchrotron beamline. M.B. conceived the research strategy, designed and supervised the experiments, discussed the interpretation of the results and edited the manuscript.

M. Behrens, I. Kasatkin, S. Kühl, G. Weinberg, *Chem. Mater.* **2010**, *22*, 386–397:

M.B. conceived and supervised the research strategy, prepared the samples, designed the experiments, analyzed TGA, IR and XRD data, and wrote the manuscript. I.K. conducted and evaluated the TEM experiments. S.K. helped with the revision of the paper. G.W. conducted the SEM experiments.

S. Kühl, M. Friedrich, M. Armbrüster, M. Behrens, *J. Mater. Chem.* **2012**, *22*, 9632-9638:

S.K. prepared the samples, conducted the characterization experiments and wrote the manuscript. M.F. and M.A. performed and evaluated the catalytic tests. M.B. conceived the research strategy, designed and supervised the experiments, discussed the interpretation of the results and edited the manuscript.

F. Conrad, C. Massué, S. Kühl, E. Kunkes, F. Girgsdies, I. Kasatkin, B. Zhang, M. Friedrich, Y. Luo, M. Armbrüster, G. Patzke, M. Behrens, *Nanoscale* **2012**, *4*, 2018-2028:

F.C. prepared the Ga-containing samples, conducted and evaluated the characterization experiments of these samples and co-wrote the manuscript. C.M. prepared the Al-containing samples and conducted the corresponding characterization experiments. S.K. evaluated the experimental results and co-wrote the manuscript. E.K. performed and analyzed the CO_2 hydrogenation tests. F.G. conducted and evaluated the *in situ*-XRD experiments. I.K. and B.Z. conducted and evaluated the TEM experiments. M.F., Y.L. and M.A. conducted and evaluated the methanol steam reforming tests. G.P. and M.B. designed and supervised the experiments, discussed the interpretation of the results and edited the manuscript. The corresponding authorship is shared between G.P. and M.B. covering the Ga-containing and Al-containing samples, respectively. In this Thesis, the focus is on the latter materials. F.C.'s Ph.D. was supervised by G.P.

M. Behrens, S. Kissner, F. Girgsdies, I. Kasatkin, F. Hermerschmidt, K. Mette, H. Ruland, M. Muhler, R. Schlögl, *Chem. Commun.* **2011**, *47*, 1701-1703:

M.B. conceived and supervised the research strategy, designed the experiments and wrote the manuscript. S.K., F.H. and K.M. prepared the samples and conducted the characterization experiments. F.G. conducted and evaluated the XRD experiments. I.K. conducted and evaluated the TEM experiments. H.R. and M.M. conducted and evaluated the catalytic tests. M.M. and R.S. discussed the data and gave conceptual advice.

M. Behrens, A. Furche, I. Kasatkin, A. Trunschke, W. Busser, M. Muhler, B. Kniep, R. Fischer, R. Schlögl, *ChemCatChem* **2010**, *2*, 816–818:

M.B. conceived the research strategy, prepared the sample Catalyst A, designed the experiments, evaluated the characterization experiments and wrote the paper. A.F. prepared the sample Catalyst B. I.K. conducted and evaluated the TEM experiments. W.B. and M.M. performed and evaluated the catalytic tests. A.T., M.M., B.K., R.F. and R.S. discussed the data and gave conceptual advice.

M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Kniep, M. Tovar, R. W. Fischer, J. K. Nørskov, R. Schlögl, *Science* **2012**, *18*, 893-897:

M.B. conceived the research strategy, prepared some of the samples, designed and supervised the characterization experiments and their interpretation and co-wrote the manuscript. F.S. co-wrote the manuscript. F.S. and F.A.P. performed the theoretical calculations. I.K. conducted and evaluated the TEM experiments. S.K. and S.Z. prepared some of the samples, conducted and evaluated the characterization experiments. M.H. evaluated the XPS experiments. F.G. performed the Rietveld analysis of the neutron data. P.K., B.L.K. and R.W.F. conducted and evaluated the catalytic tests. M.T. helped with the neutron experiments at the beamline. B.L.K., R.W.F., J.K.N. and R.S. discussed the results and gave conceptual advice. Corresponding authorship is shared between M.B. and F.S. covering the experimental and the theoretical parts of the work, respectively.

T. Kandemir, D. Wallacher, T. Hansen, K.-D. Liss, R. Naumann d'Alnoncourt, R. Schlögl, M. Behrens, *Nucl. Instr. Meth. Phys. Res. A* **2012**, *673*, 51-55:

T.K. built the apparatus, conducted and evaluated the neutron diffraction experiments and wrote the manuscript. D.W. and R.N.d'A. designed the apparatus and helped with the construction. T.H. and K.D.L. supported the experiments at the beamlines. R.S. and M.B. discussed the results and gave conceptual advice. M.B. conceived the research strategy, designed the experiments and edited the manuscript.

T. Kandemir, F. Girgsdies, T. C. Hansen, K.-D. Liss, I. Kasatkin, E. L. Kunkes, G. Wowsnick, N. Jacobsen, R. Schlögl, M. Behrens, *Angew. Chem. Int. Ed.* **2013**, *52*, 5166-5170:

T.K. conducted and evaluated the experiments and wrote the manuscript. F.G. conducted the Rietveld refinements, T.C.H., K.D.L., E.L.K. and G.W. supported the experiments at the beamlines. N.J. provided the catalysts and discussed the results. R.S. and M.B. discussed the results and gave conceptual advice. M.B. conceived the research strategy, designed the experiments and edited the manuscript.

M. Behrens, G. Lolli, N. Muratova, I. Kasatkin, M. Hävecker, R. Naumann d'Alnoncourt, O. Storcheva, K. Köhler, M. Muhler, R. Schlögl, *Phys. Chem. Chem. Phys.* **2013**,15, 1374-1381:

M.B. conceived and supervised the research strategy, designed the experiments and co-wrote the manuscript. G.L. designed and conducted the UV-vis spectroscopy experiments and co-wrote the manuscript. N.M. conducted and evaluated the XPS and NEXAFS experiments. I.K. conducted and evaluated the TEM experiments. M.H. supported the XPS and NEXAFS data evaluatation. R.N.d'A. and M.M. provided reference samples and discussed the results. O.S. and K.K. conducted and evaluated the EPR experiments. K.K., M.M. and R.S. discussed the results and gave conceptual advice.

M. Behrens, S. Zander, P. Kurr, N. Jacobsen, J. Senker, G. Koch, T. Ressler, R. W. Fischer, R. Schlögl, *J. Am. Chem. Soc.* **2013**, *135*, 6061-6068:

M.B. conceived the research strategy prepared some of the samples, designed and interpreted the experiments and wrote the manuscript. S.Z. prepared some of the samples and conducted and evaluated the characterization experiments. P.K., N.J. and R.W.F. conducted and evaluated the catalytic tests. J.S. performed the NMR experiments. G.K. and T.R. performed the XANES experiments. J.S., T.R., R.W.F. and R.S. discussed the results and gave conceptual advice.

Supporting Information of the Articles

In this section of the appendix the supporting information files are listed in the order of appearance of the articles in the main part. An overview can be found below:

M. Behrens, D. Brennecke, F. Girgsdies, S. Kißner, A. Trunschke, N. Nasrudin, S. Zakaria, N. Fadilah Idris, S. Bee Abd Hamid, B. Kniep, R. Fischer, W. Busser, M. Muhler, R. Schlögl, *Appl. Catal. A* **2011**, *392*, 93-102.

Sample overview, XRD patterns and discussion of XRD results

S. Zander, B. Seidlhofer, M. Behrens, *Dalton Trans.* **2012**, *41*, 13413–13422.

Sample overview, synthesis protocols, additional XRD and SEM results

M. Behrens, I. Kasatkin, S. Kühl, G. Weinberg, *Chem. Mater.* **2010**, *22*, 386–397.

Synthesis protocols, additional SEM and TEM results

S. Kühl, M. Friedrich, M. Armbruester, M. Behrens, *J. Mater. Chem.* **2012**, *22*, 9632-9638.

Microemulsion phase behavior, droplet size determination by DLS, synthesis protocol, N_2 physisorption data, TEM results and sample overview

F. Conrad, C. Massué, S. Kühl, E. Kunkes, F. Girgsdies, I. Kasatkin, B. Zhang, M. Friedrich, Y. Luo, M. Armbrüster, G. Patzke, M. Behrens, *Nanoscale* **2012**, *4*, 2018-2028.

Synthesis details, additional XRD, SEM, EDX, TGA, N_2 physisorption and TEM data

M. Behrens, S. Kissner, F. Girgsdies, I. Kasatkin, F. Hermerschmidt, K. Mette, H. Ruland, M. Muhler, R. Schlögl, *Chem. Commun.* **2011**, *47*, 1701-1703.

Experimental details, TEM micrographs, XRD patterns and refined crystal structure data

M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Kniep, M. Tovar, R. W. Fischer, J. K. Nørskov, R. Schlögl, *Science* **2012**, 18, 893-897.

Sample preparation and characterization and DFT details, XRD, TEM, EDX, ND and XPS results, sample overview

T. Kandemir, F. Girgsdies, T. C. Hansen, K.-D. Liss, I. Kasatkin, E. L. Kunkes, G. Wowsnick, N. Jacobsen, R. Schlögl, M. Behrens, *Angew. Chem. Int. Ed.* **2013**, *52*, 5166-5170.

Further details on sample preparation and catalytic experiments, neutron beamline configurations, data evaluation procedures, and additional discussion of fitting results

M. Behrens, G. Lolli, N. Muratova, I. Kasatkin, M. Hävecker, R. Naumann d'Alnoncourt, O. Storcheva, K. Köhler, M. Muhler, R. Schlögl, *Phys. Chem. Chem. Phys.* **2013**,15, 1374-1381.

Additional TGA, XRD and NMR results

M. Behrens, S. Zander, P. Kurr, N. Jacobsen, J. Senker, G. Koch, T. Ressler, R. W. Fischer, R. Schlögl, *J. Am. Chem. Soc.* **2013**, *135*, 6061-6068.

Details on sample synthesis, additional XRD, TGA, catalytic testing and XANES results

Curriculum Vitae

Malte Behrens (date of birth: January 28th 1977)

Research Interests

- Heterogeneous Catalysis
- Nanostructured Solids
- Energy Storage and Conversion

Education

1997 – 2002	Chemistry studies at the Christian-Albrechts-University (CAU) in Kiel, Germany
2002	Diploma degree in chemistry at the Institute of Inorganic Chemistry at CAU Advisor: Professor Wolfgang Bensch (solid state chemistry, solvothermal synthesis)
2002 – 2006	Doctoral degree (*summa cum laude*) at the Institute of Inorganic Chemistry at CAU, Advisor: Professor Wolfgang Bensch (solid state chemistry, intercalation reactions, thin multilayer films)
2006 – 2008	Post-doc with Professor Robert Schlögl at the Department of Inorganic Chemistry at the Fritz-Haber-Institute of the Max-Planck-Society (FHI-AC) in Berlin, Germany (heterogeneous catalysis)
2007 – 2008	Project leader “Cu in C1 Chemistry” at FHI-AC
Since 2008	Group leader of the Nanostructure group at FHI-AC

Awards / Functions

2003 – 2004	PhD-scholarship of the “Fonds der Chemischen Industrie”
2006	BASF-sponsored PhD-Award of CAU Kiel
2010 – 2012	Working group leader of WG2.2: “Nanoparticulate Synthesis” in the COST action CM0904 “Network for Intermetallic Compounds as Catalysts for Steam Reforming of Methanol (IMC-SRM)”
Since 2009	Member of the Ertl center for Electrochemistry and Catalysis, GIST, Gwangju, Korea
Since 2009	Member of the User Committee of the Helmholtz Zentrum Berlin (HZB)
Since 2012	Spokesperson of the young researchers (YoungGeCatS) within the German Catalysis Society (GeCatS)

Full Publication List (Dec. 2012)

(* These papers are part of this thesis)

Patents (2)

M. Behrens, K. Mette, A. Bergmann, J.-P. Tessonnier, P. Strasser, R. Schlögl, *EP 12 157 274.7*:
"Electrolytic Water Splitting using a Carbon-Supported MnO_x-Composite"

M. Behrens, A. Ota, M. Armbrüster, Y. Grin, R. Schlögl, *PCT/EP2011/052667*:
"Palladium-modified Hydrotalcites and their use as heterogeneous catalysts"

Edited books (1) and book chapters (4)

Heterogeneous Catalysis for the Conversion of Biomass and Its Derivatives, Editors: M. Behrens, A. Datye (Edition Open Access, epubli Verlagsgruppe Holtzbrinck) in press.

*E. Kunkes, M. Behrens in *Chemical Energy Storage*, Editor: R. Schlögl (de Gruyter), in press:
"Methanol Chemistry"

M. Behrens, R. Schlögl in *Characterization of Solid Materials and Heterogeneous Catalysts: From Structure to Surface Reactivity*, Editors: J. Védrine, M. Che (Wiley-VCH), **2012**:
"X-Ray Diffraction and Small Angle X-Ray Scattering"

*M. Behrens, M. Armbrüster in *Catalysis for Alternative Energy Generation*, Editors: L. Guczi, A. Erdôhelyi (Springer) **2012**:
"Methanol Steam Reforming"

M. Behrens, R. Schlögl in *Herausforderung Energie*, Editors: J. Renn, R. Schlögl, H.-P. Zenner (epubli Verlagsgruppe Holtzbrinck) **2011**:
"Energie ist Chemie – Katalyse als Schlüsseltechnik. Energie von Morgen: Eine Momentaufnahme"

List of peer reviewed publications (40)

Habilitation project (19)

*M. Behrens, G. Lolli, N. Muratova, I. Kasatkin, M. Hävecker, R. Naumann d'Alnoncourt, O. Storcheva, K. Köhler, M. Muhler, R. Schlögl, *Physical Chemistry – Chemical Physics* **2013**,15, 1374-1381:
"The Effect of Al-doping on ZnO nanoparticles applied as catalyst support "

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