

Rare earth oxide aero- and xerogels – tuning porosity and catalytic properties

Dissertation

zur Erlangung des Doktorgrades

der Naturwissenschaften

- Dr. rer. nat. -

Vorgelegt dem Promotionsausschuss

des Fachbereichs 2 (Chemie/Biologie)

der Universität Bremen

von

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Hamburg, November 2013

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Selbstständigkeitserklärung

Hiermit erkläre ich, Björn Neumann, dass ich die vorliegende Arbeit selbständig angefertigt und keine außer den angegebenen Hilfsmitteln verwendet habe. Diese Arbeit wurde nicht vorher an anderer Stelle eingereicht.

Hamburg, den

(Björn Neumann)

I am indebted to the following people and institutions for supporting me during my PhD project:

Prof. Dr. Marcus Bäumer: Danke!

Prof. Dr. Juan Claudio Nino: Thank you for giving me the opportunity to work with you and your group at the University of Florida and being my second referee.

Prof. Dr. Thorsten M. Gesing: Danke für die lehrreiche und professionelle Zusammenarbeit und das stetige persönliche Engagement.

PD Dr. Wolfgang Dreher: Danke für viele Einblicke in die Welt der NMR, die meine Arbeit unerwartet stark beeinflusst haben.

Prof. Dr. Helena Hagelin-Weaver: Thank you for having the opportunity to work in your lab, for many intensive discussions and the continuous personal and professional interest.

Dr. Alexander E. Gash: Thank you for guiding me through the „LLNL jungle“ and providing me enduring assistance for all sol gel related issues and beyond.

Prof. Dr. Sergey Vasenkov: Danke für viele inspirierende Diskussionen, sehr viel Kompetenz und größte Verbindlichkeit.

Prof. Dr. Vladimir Matólin: Thank you for the first explorative cooperation by sending Michal Vaclavu and a microreactor to Bremen and the following successful collaboration.

PD Dr. Volkmar Zielasek und Dr. Willian Menezes: Meine Einblicke in die Nanowelt habt ihr ermöglicht; die vielen Stunden die am TEM geopfert wurden, sind nicht vergessen.

Ute Melville, Karsten Koblitz und Martin Nowak: Dank für die technische Unterstützung ohne die vieles heute noch nicht fertig wäre.

Allen IAPClern: Dank an **Jun-Jie Shi, Jin-Hao Jhang, Ingo Bardenhagen, Eva Morsbach, Dr. Lyudmila Moskaleva, Dr. Andreas Schaefer, Miriam Klink, Lena Altmann, Pascal Penderak, Fedor Strygunov, Dr. Arne Wittstock, Andre Wichmann, Vera Suling, Brigitte Neimeier, Dr. Sebastian Kunz und Dr. Günter Schnurpfeil** für das angenehme Arbeitsumfeld.

Den Mitarbeitern in kooperierenden Arbeitsgruppen: **Robert Müller, Trenton W. Elkins, Dr. Robert Colmyer, Andrea Derenek, Andrii Rednyk, Michal Vaclavu, Sandra Maracke, David Pham und Florian Meierhofer.**

Dank der **Deutsch Telekom Stiftung** für die finanzielle Förderung, ohne die meine Promotion unmöglich gewesen wäre, aber gleichzeitig auch für eine hervorragende ideelle Förderung.

Dank der **Evonik Stiftung** für die Zeit während und nach der aktiven Förderung insbesondere für viele Einblicke in die Chemische Industrie gekoppelt mit großem persönlichen Einsatz.

This cumulative doctoral thesis is based on the following publications (chronological order) focusing on novel rare earth- and transition metal oxide materials. My work includes the synthesis, characterization and catalytic testing of these materials.

- I Clapsaddle, B. J., **Neumann, B.**, Wittstock, A., Sprehn, D. W., Gash, A. E., Satcher, J. H., ... Bäumer, M. (2012).
A sol-gel methodology for the preparation of lanthanide-oxide aerogels: preparation and characterization.
Journal of Sol-Gel Science and Technology, 64(2), 381–389. doi:10.1007/s10971-012-2868-6
- II **Neumann, B.**, Elkins, T. W., Dreher, W., Hagelin-Weaver, H., Nino, J. C., & Bäumer, M. (2013).
Enhanced catalytic methane coupling using novel ceramic foams with bimodal porosity.
Catalysis Science & Technology, 3(1), 89. doi:10.1039/c2cy20458d
- III Minnermann, M., **Neumann, B.**, Zielasek, V., & Bäumer, M. (2013).
Alumina-promoted cobalt and iron xerogels as catalyst for the Fischer-Tropsch synthesis.
Catalysis Science & Technology. doi:10.1039/c3cy00483j
- IV Mueller, R., Zhang, S., **Neumann, B.**, Bäumer, M., & Vasenkov, S. (2013).
Self-diffusion of carbon dioxide in samaria/alumina aerogel catalyst using high field NMR diffusometry.
The Journal of Chemical Physics, 139(15), 154703. doi:10.1063/1.4824635
- V Mueller, R., Zhang, S., **Neumann, B.**, Bäumer, M., & Vasenkov, S. (2013).
Study of Carbon Dioxide Transport in a Samaria Aerogel Catalyst by High Field Diffusion NMR.
Chemie Ingenieur Technik, 85(11), 1749–1754. doi:10.1002/cite.201300041
- VI **Neumann, B.**, Elkins, T.W., Gash, A. E., Hagelin-Weaver, H., Bäumer, M. (2013).
Sol-gel preparation of samaria catalysts for the oxidative coupling of methane.
Applied Catalysis A (submitted)
- VII **Neumann, B.**, Gesing, T. M., Rednyk, A., Matólin, V., Gash, A. E., Bäumer, M. (2013).
Sol-gel preparation of alumina stabilized rare earth areo- and xerogels and their use as oxidation catalysts.
Journal of Colloid and Interface Science C (accepted)

In addition to my own PhD project, I was involved in additional research activities (again in chronological order) at the University of Bremen focusing on the preparation, characterization, and application of novel metal (gold) catalysts:

- A) Wittstock, A., **Neumann, B.**, Schaefer, A., Dumbuya, K., Kübel, C., Biener, M. M., ... Bäumer, M. (2009).

Nanoporous Au: An Unsupported Pure Gold Catalyst?

The Journal of Physical Chemistry C, 113(14), 5593–5600. doi:10.1021/jp808185v

- B) Wichmann, A., Wittstock, A., Frank, K., Biener, M. M., **Neumann, B.**, Mädler, L., ... Bäumer, M. (2013).

Maximizng Activity and Stability by Turning Gold Catalysis Upside Down: Oxide Particles on Nanoporous Gold.

ChemCatChem, 5(7), 2037–2043. doi:10.1002/cctc.201200759

- C) Menezes, W. G., **Neumann, B.**, Zielasek, V., Thiel, K., & Bäumer, M. (2013).

Bimetallic AuAg nanoparticles: enhancing the catalytic activity of Au for reduction reactions in the liquid phase by addition of Ag.

ChemPhysChem: a European journal of chemical physics and physical chemistry, 14(8), 1577–81. doi:10.1002/cphc.201201100

Conference contributions

Deposition of Platinum Nanoparticles on Hybrid Aerogels by ALD,

Björn Neumann et. al

Vortrag Bunsentagung 2010

Katalyse mit Seltenerdoxid Aerogelen,

Björn Neumann, Alex E. Gash et al.

Vortrag Bunsentagung 2011

Catalytic Characterization of Rare Earth Oxide Foams

Poster International Congress on Catalysis (München) 2012

Statement regarding my contribution to the publications:

All stated publications are based on the collaboration of several researches. My specific contributions are described in the following:

- I: I was responsible for the preparation of the manuscript and partly responsible for the acquisition and evaluation of the data. (Another part of the data was collected at the Lawrence Livermore National Laboratory under the supervision of Dr. Alex E. Gash.)
- II: I synthesized the materials during a research stay in Gainesville, Florida, in the group of Prof. Dr. Juan C. Nino, participated in their catalytic testing in the group of Prof. Dr. Hagelin-Weaver, and was responsible for the preparation of the manuscript.
- III: I contributed the idea and the knowhow regarding the synthesis of the catalysts and was involved in the discussion of the data and their presentation in the manuscript.
- IV: I was in charge of the synthesis of the material and its characterization and contributed to the discussion of the data as well as to the manuscript for which I wrote the introduction. The NMR data were taken in the group of Prof. Dr. Vasenkov who also took the lead for the manuscript preparation.
- V: I was responsible for the synthesis of the material and its characterization and contributed to the discussion of the data. The NMR data were taken in the group of Prof. Dr. Vasenkov who also took the lead for the manuscript preparation in particular because this publication was dedicated to 70th birthday of Prof. Dr. Jörg Kärger the former scientific mentor of Prof. Dr. Vasenkov.
- VI: I prepared and characterized the materials and was responsible for the manuscript. The OCM data were collected and evaluated in the group of Prof. Dr. Hagelin-Weaver.
- VII: The synthesis and the characterization of the materials as well as their catalytic testing were my responsibilities. I took care of the evaluation of the data and the manuscript preparation.

Zusammenfassung

Trotz ihres stattlichen Alters – erste Konzepte und industrielle Anwendungen stammen bereits aus dem 19. Jahrhundert - ist die heterogene Katalyse kein alter Hut. Sie ist ganz im Gegenteil eine Schlüsseltechnologie des 21. Jahrhunderts, denn effiziente Katalysatoren sind der Dreh- und Angelpunkt für die gezielte und kostengünstige Herstellung von Chemikalien und Pharmaprodukten. Aber auch in Zukunftsbereichen wie Energiegewinnung und -speicherung (man denke an die Brennstoffzelle) oder Umweltschutz (Abgaskatalyse) spielen sie eine zentrale Rolle und sind eine der 12 Schlüsseltechnologien der Grünen Chemie.

Die Entwicklung effizienter Katalysatoren, mit denen chemische Reaktionen gezielter und unter geringerem Energieeinsatz durchgeführt werden können, ist jedoch immer noch eine große Herausforderung. Ihre Leistungsfähigkeit, die sich an Aktivität und Selektivität, d.h. an der Ausbeute für bestimmte Produkte aber auch an der Langzeitstabilität misst, hängt entscheidend von den strukturellen Gegebenheiten auf der atomaren Ebene ab. Dennoch spielt auch der Stofftransport - die Frage, wie effizient Pro- und Edukte in die meist poröse Struktur hinein- und hinausgelangen können - eine wichtige Rolle.

Bis heute werden heterogene Katalysatoren überwiegend per „trial and error“ entwickelt. Dies liegt daran, dass es mit Hilfe der traditionellen Herstellungsmethoden sehr schwierig ist, auf der Nanometerskala Strukturen gezielt herzustellen. Im Zuge der rasanten Entwicklungen in den Materialwissenschaften ist es jedoch möglich geworden, verschiedenste Materialien mit maßgeschneiderten Eigenschaften vom makroskopischen bis hinein in den Nanometerbereich herzustellen.

Ziel dieser Arbeit war es, dieses Potential für die Katalyse zu nutzen. Dabei bestand die Aufgabe darin, katalytisch vielversprechende Seltenerdoxide im Hinblick auf Porosität und Zusammensetzung so zu verändern, dass sie für Oxidationsreaktionen und die oxidative Kupplung von Methan gute Ergebnisse aufweisen. Dabei lag einerseits ein großer Schwerpunkt auf sol-gel-chemischen Methoden und hier besonders auf der sog. „Epoxide Addition Method“. Neben Aero- und Xerogelen der reinen Seltenerdoxide wurden auch Hybridsysteme aus den Seltenerdoxiden und Aluminiumoxid präpariert, umfangreich charakterisiert und katalytisch getestet. Des Weiteren wurden dünne Xerogel-Filme und makroporöse Monolithe, letztere mittels einer direkten Schäumungsmethode, hergestellt.

Die Ergebnisse der Arbeit belegen das große Potential v.a. der Sol-Gel-Chemie, poröse Materialien mit variabler und kontrollierbarer Porosität und Zusammensetzung für die heterogene Katalyse verfügbar zu machen und dabei leistungsfähigere Katalysatoren zu erhalten.

Outline

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1. Introduction: Impact, need, and prospect on catalysis

Today catalytic processes contribute to more than 35 % to the global gross domestic product ^[1]. As an interdisciplinary field catalysis, on the one hand, is highly important for our all health and nutrition and, on the other hand, constitutes a key technology for green chemistry, allowing the efficient use of energy and resources and thus ensuring a high quality of life ^[2]. One example, highlighting both aspects, is the Haber - Bosch process which makes ammonia as a basis of the fertilizer production available in large amounts and is thus indispensable to cover today's food demand ^[3].

In 1835, Berzelius was the first who described the phenomenon of catalysis. "Catalytic power actually means that substances are able to awaken affinities which are asleep at this temperature by their mere presence and not by their own affinity" ^[4]. Ostwald more precisely defined catalysts as substances which accelerate a chemical reaction without being consumed ^[5]. It is important to note that the catalyst does not change the thermodynamics of the reaction, but changes the path of a reaction by forming different intermediates which are kinetically easier accessible (Sabatier's principle) ^[6]. In order to provide a microscopic picture of catalysis, Langmuir proposed the existence of "active sites", these are energetically identical so that a specific molecule will adsorb always in the same way ^[7]. Although the early considerations already included reaction and adsorption, transport phenomena were not considered. Even today, the International Union of Pure and Applied Chemistry (IUPAC) does not even mention transport as an important part of the catalytic triangle, involving reaction, adsorption *and* transport:

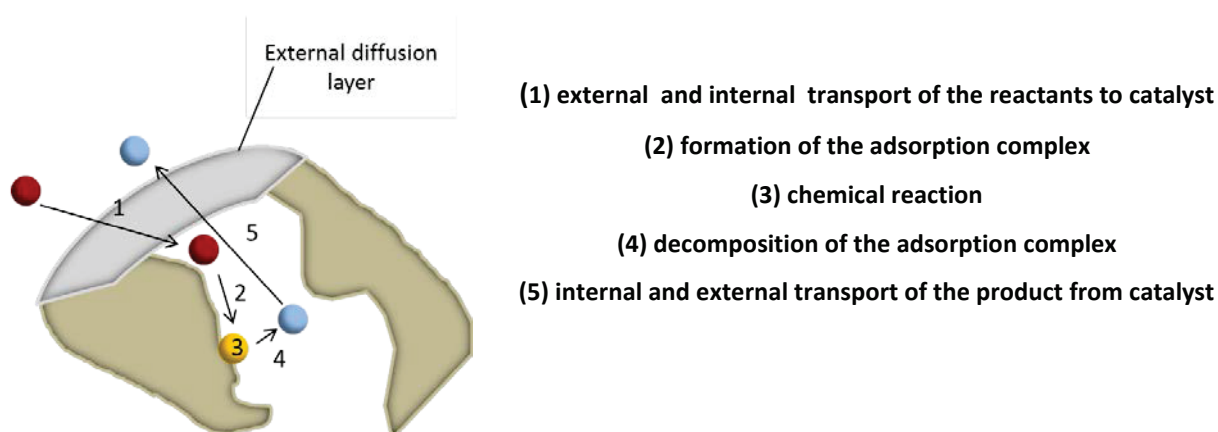


Figure 1: The different elementary steps in a heterogeneously catalyzed reaction

2. Case study of selectivity, porosity and mass transport:

The fluid catalytic cracking (FCC) catalyst

Cracking of hydrocarbons with high molecular weights into more valuable products, such as cracked naphtha and fuel oil, is an important process in the catalytic refinement of raw-oil. Due to the high commercial interest in this catalyst, it offers a solid basis for this case study illustrating the interplay of catalytic reaction and transport and the necessity to consider and improve the transport properties to achieve optimal yields. In addition to the major suppliers of the FCC catalyst BASF SE, Albermarle Corporation and W.R. Grace Company, there is also considerable interest from academic institutions all over the world.

Since the early 1960 Faujasite Y type is used as the active phase of FCC catalyst. Several modifications of the zeolite, such as an ultra-stabilized (USY) or rare earth exchanged (REY) forms, are available either to increase the (hydro)-thermal stability or to tailor acidic properties^[8,9]. As a result of the tetrahedrally coordinated Al atoms, the USY provides a large number of strong Brønstedt acidic centers with high activity and selectivity for the desired cracking products^[10]. In a model study of n-heptane cracking, USY showed a 4 times higher rate as compared to amorphous silica-alumina (ASA)^[11]. Unfortunately, the beneficial effect of the zeolite structure on the acidity (and its high specific surface area) is also its biggest disadvantage. A pore diameter of only 7.4 Å is far too small for many components of real FCC feedstock, such as Vacuum Gas Oil (VGO). Cracking of the heavy components therefore is limited to the outer surface of the zeolite so that the bulk part of the catalyst is basically not used for the reaction.

Commercial state of the art catalysts reduce, on the one hand, the mass transport limitations of the pure zeolite; on the other hand, they passivate impurities to substantially benefit from the high activity and selectivity of the zeolite. The active matrix of the catalyst consists of a hierarchical porous mineral, such as natural clay. This material hosts the particular zeolite and an additional synthetic silica alumina which cracks the bulky hydrocarbons in macropores. Afterwards, the pre-cracked molecules diffuse to the zeolite where they are effectively converted into the desired cracking products^[12]. This example demonstrates that the development of a technical catalyst involves more than producing sufficient amounts of the catalytically active phase at a low price but must be based on a proper composition and a structural design ensuring high activity and an optimal transport of the reactants at the same time.

With the discovery of M41S, a family of ordered mesoporous silica with MCM-41 (mobil crystalline material 41) as the most prominent representative the catalytic community saw new options for the FCC catalyst^[13]. In addition to the comparison of USY and ASA, Corma et al. also studied the cracking

activity of MCM-41, using n-heptane and VGO as feedstock. Due to the better mass transport, the rate of VGO cracking is higher in comparison to ASA but still lower than the activity of the zeolite. Unfortunately, the price for the better transport properties of the MCM-41 is a much smaller activity in comparison to the zeolite, resulting in a lower overall rate. Referred to the n-heptane, which is small enough to enter micropores, the zeolite shows a more than ten times higher activity.

The research and improvements on the FCC catalyst are a good example to illustrate that catalytic problems always involve at least two parameters to be optimized at a time. Materials with exceptional transport properties are not necessarily good catalysts and vice versa.

In the following chapters of this framework article, recent and fundamental contributions to the field of heterogeneous catalysis are summarized, focusing on

- a) transport properties as a leverage on catalyst performance,
 - b) novel preparation techniques allowing to tune composition and porosity, and
 - c) the assessment of porous materials with respect to their suitability as heterogeneous catalysts,
- including my own contributions to the respective field(s) as product of my PhD work.

3. Mass transport

The case study on the FCC catalyst has already elucidated that a heterogeneously catalyzed reaction is often strongly influenced by the transport of the educts to the active phase and the transport of the product away from the catalyst. Under steady state conditions, the exchange of reactants and products has to be as fast as the surface reaction takes place, or the observed reaction rate is a result of mass transport limitation. Thiele was one of the first who described this phenomenon ^[14]. He proposed the effectiveness η of a catalyst as the amount of a reactant that is converted, divided by the amount that *would* be converted if no mass transport limitation occurred.

The Thiele Modulus ϕ represents a dimensionless number that is a measure of the influence of mass transport on the reaction rate r_p within a pore with the aspect ratio a_p , assuming a reaction order of m and a concentration c_A of the component A:

$$\phi = a_p \sqrt{\frac{2}{m+1} \frac{r_p c_A^{m-1}}{D_{i,A}}}$$

The above definition of the Thiele modulus does not represent the native form anymore, but its generalization concerning shape and reaction order. Unfortunately, the calculation of η as a function of the Thiele modulus cannot be generalized but different models might be used ^[15]. In the case of first order reactions, the approximation of η according to the equation given below will generate results with a maximum error of 10 %, while especially in the case of smaller reaction orders the error will increase.

$$\eta = \frac{\tanh(\phi_A)}{\phi_A}$$

As already mentioned, $D_{i,A}$ is the variable which specifies the mass transfer; for the Thiele modulus formalism only diffusive mass transfer is considered, meaning that $D_{i,A}$ is a diffusivity within a single pore. Depending on the relation of the specific pore diameter to λ and the mean free path of the gas molecule, different diffusion regimes must be distinguished ^[16]. Within macropores ($d_p > 50$ nm), λ is much smaller than d_p so that collisions within the gas phase dominate the amount of total collisions and molecular diffusion mainly occurs. If the mean free path is similar to the pore diameter, the diffusivity can be obtained on the basis of the transition regime model. Here, the diffusion can be described by using a model which combines molecular diffusion and Knudsen diffusion. This, however, is only valid for a gas with at least two components as the collisions of different molecules are included in this model. For a pure gas the diffusivity already has to be expressed by the Knudsen model derived for mesopores ($2\text{nm} < d_p < 50$). Within such pores, the collisions between molecules

and the pore wall are dominant. The behavior is similar to molecules in vacuum, as also here gas-gas collisions are minimized. These similarities brought Martin Knudsen to derive a model based on the collision theory^[17]. Within the so-called Knudsen regime, the diffusion coefficient is not a function of the pressure p any more, but of the molecular mass M of the gas. The Knudsen diffusion coefficient D_K is defined as:

$$D_K = \frac{2}{3} r \sqrt{\frac{8RT}{\pi M}}$$

However, there is an important difference between molecules in narrow pores and molecules under vacuum becoming particularly evident if diffusion in the even smaller micropores ($d_p < 2\text{nm}$) is considered. Here, the pore dimensions approach the molecular dimensions which results in sterical hindrance of diffusion. In addition, the adsorption potentials of the surrounding surfaces overlap so that molecule-pore (e.g. sticking/adsorption) interactions become important. This regime is also known as intracrystalline diffusion, zeolitic diffusion, or configurational diffusion. Due to the strong interaction with the surfaces, diffusion becomes an activated process – meaning that additional energy is needed to weaken the molecule-surface interaction. In such small pores the transport is sometimes also described as a hopping transport^[18].

In addition to diffusive mass transport, a contribution of viscous flow can occur if the pressure at one end of the pore is different from the pressure at the other end. A transport coefficient formally similar to the fickian diffusion can be obtained on the basis of the Navier Stokes equation. Very often viscous flow is also called convection. Reference [19] may give further insight into diffusion phenomena important for heterogeneous catalysis^[19].

Table 1 shows a comparison of the contributions of the different transport regimes for different pore diameters at two different pressures at room temperature. Especially with increasing pressure the influence of the viscous flow increases so that even within mesopores the diffusive transport can be a combination of Knudsen diffusion and viscous flow (provided a pressure gradient exists).

Table 1: Contribution of different diffusion regimes in dependence of pressure and pore size. From reference ^[20]

p (atm)	D_m ($\text{cm}^2 \text{s}^{-1}$)	r (cm)	D_K ($\text{cm}^2 \text{s}^{-1}$)	D ($\text{cm}^2 \text{s}^{-1}$) ^{a)}	D_{vis} ($\text{cm}^2 \text{s}^{-1}$)	D_{total} ($\text{cm}^2 \text{s}^{-1}$)	$\frac{D_{vis}}{D_{total}}$
1.0	0.2	10^{-6}	0.03	0.027	0.0007	0.027	0.026
		10^{-5}	0.3	0.121	0.07	0.19	0.37
		10^{-4}	3.0	0.19	7.0	7.2	0.97
10	0.02	10^{-6}	0.03	0.012	0.007	0.019	0.37
		10^{-5}	0.3	0.019	0.7	0.719	0.97
		10^{-4}	3.0	0.020	70	70	1.0

Passing over from a single pore to a fixed bed reactor – which is commonly used for powder and pellet catalysts - the overall mass transfer becomes more complex. A typical catalyst bed consists – on the laboratory scale – of several hundred porous particles with a size of several 100 μm which are placed within a quartz or stainless steel reactor or – on the industrial scale – of a bed of catalyst pellets ^[21].

A constant viscous flow is used to exchange the gas phase around the catalyst. The gas hourly space velocity is commonly used to express how often the gas within the reactor is replaced per hour (on the basis of the hydrodynamic residence time within this volume divided by the overall flow.) Due to the catalyst bed, the flow pattern within the tube is of course different to an empty tube. The gas can only travel through the space between the catalysts particles. It is obvious that it is impossible to transport the same amount of gas through these small pores if the velocity of the flow stays constant. The pressure increases in front of the bed which finally leads to a higher velocity within the smaller channels of the bed.

However, the exchange of educts and products of each single catalyst particle and the bulk gas is dominated by a thin layer close to the interphase where only diffusion takes place. Within this diffusion layer so-called external diffusion takes place. Here, the concentration of the reaction gas changes by Δc , the difference of the gas phase concentration c_g and the concentration at the surface c_s of the catalyst particle.

For his model – to evaluate the catalyst efficiency -, Thiele only considered the mass transport starting at the surface of the catalyst particle, i.e., the so-called internal diffusion. Depending on the reaction rate of the reaction under consideration and the respective diffusivity, it is possible to calculate a concentration profile over a porous catalyst to estimate how much of the catalyst is used for a certain reaction.

Figure 2 shows as an example a concentration profile of CO for the CO oxidation over a single disc of a nanoporous catalyst ^[22]. The results can be considered as a model of a single catalyst particle or pellet. The application of the Thiele Modulus formalism allows evaluating what will be the best diameter to use the whole catalyst most efficiently. Many more models and measures are known for the evaluation of the catalyst efficiency with some of them also considering the inner and outer diffusion at the same time. Here, only the approach of Thiele is presented to give a fair warning how important transport phenomena are if the efficiency of a catalyst is evaluated. This also means that techniques which allow tailoring the size and morphology of porous catalyst are important for the preparation of catalyst.

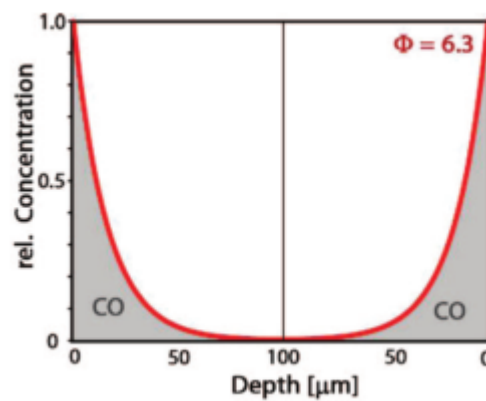


Figure 2: Concentration profile of carbon monoxide for the oxidation of CO over a nanoporous gold catalyst ^[22].

4. Surface chemistry and catalytic activity of rare earth oxides: Mars - van Krevelen mechanism, oxidation reactions, and acid-base properties

Apart from the transport properties, of course the catalytic properties of the material are important. In the present thesis, oxides and in particular rare earth oxides were in the foreground of the research. In heterogeneous catalysis metal oxides can either be used as supports – for example for a nano-structured metal catalyst – or as the active phase ^[23–25]. Due to the high amount of different metal oxides, the number of reactions catalyzed by this class of substances is innumerable. Rare earth oxides (REO) represent only a small but interesting part of the metal oxide universe. The catalytic applications, they can be employed for, include complete and partial oxidation reactions, oxidative elimination, hydrogenation and dehydrogenation reactions, coupling reactions and the selective reduction of NO ^[26–31].

Similar to many transition metal oxide catalysts a Mars - van Krevelen mechanism is the dominating oxidation mechanism over rare earth oxides. During their early work, Mars and van Krevelen showed that the oxidation of SO₂ and naphthalene over vanadia catalysts involves lattice oxygen of the catalyst as oxidizer ^[32]. The resulting vacancies are refilled in a second step. The activation of oxygen - necessary to refill the vacancies - includes the reduction of gas phase O₂ and the formation of different surface oxygen species as shown in figure 3. Please note that the term Mars – van Krevelen mechanism is used to indicate that lattice oxide is involved in the reaction, the elementary steps might be different from those originally proposed by Mars and van Krevelen ^[33].

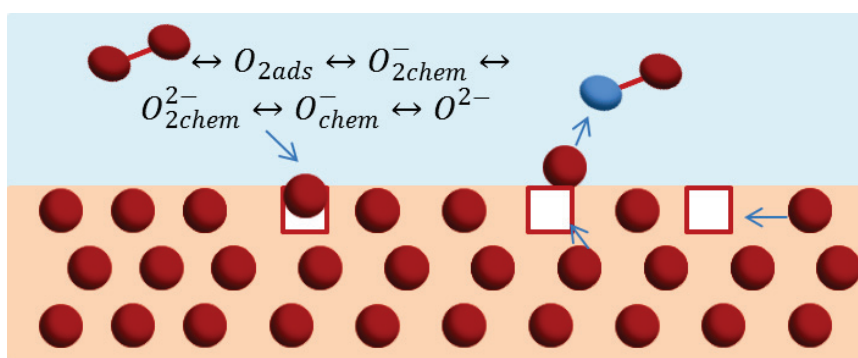


Figure 3: Schematic representation of the Mars-van Krevelen mechanism and the necessary steps of oxygen activation on the surface. In addition, the exchange of lattice oxygen and vacancy formation is shown. Oxygen mobility plays an important role for the transport of lattice oxygen.

Exposed lattice oxygen O^{2-} is known for its nucleophilic properties and is the responsible species for selective oxidation over rare earth oxides. O_2^- , O_2^{2-} and O^- , on the other hand, are electrophilic species and therefore strong oxidizers, being responsible for deep oxidation of organic compounds

over rare earth oxides^[34]. The kinetics of the oxygen activation, incorporation, and the properties of the oxide determine the surface coverage of the various species under reaction conditions. In addition, the oxygen partial pressure plays an important role as in particular electrophilic oxygen surface species become more abundant under high O₂ partial pressures.

Along with the change in the radii of the rare earth 3+ ions, there are some important differences within the series of oxides to consider when the catalytic properties are compared. For most REOs, the sesquioxides are the most stable phases under ambient conditions. However, there are 5 different modifications of Re₂O₃ known. Depending on the calcination temperature the cubic bixbyite structure (also known as C modification of rare earth sesquioxides), the monoclinic B modification, or the hexagonal A modification are found at ambient conditions. The modifications X and H are only observable at high temperatures^[35].

Praseodymia, terbia and ceria, however, are stable in different structures and also stoichiometries under ambient conditions. Pr₆O₁₁ as the stable phase of praseodymia can e.g. be considered as an oxygen deficient modification of cubic fluorite-like PrO₂ containing both tri- and tetravalent cations^[36]. For praseodymia, a homologous series with a large number of stoichiometries constitutes the praseodymium oxygen phase diagram with phases, such as Pr_nO_{2n-2}^[37]. For terbia, with Tb₄O₇ representing the most stable modification, the number of known phases is less pronounced^[38]. As an exception to all other rare earth metals, ceria exhibits 4+ as the dominant oxidation state, with CeO_{2-x} being the most stable modification (x indicates a variable concentration of oxygen vacancies within the structure). The ability to change the oxidation state from 3+ to 4+ and vice versa is highly important for certain redox reactions. Here, ceria shows the lowest ionization energy for the transition from the 3+ to the 4+ state. An excellent review on different phases and the phase diagrams of rare earth oxide phases including also the different modifications of the sesquioxides can be found in REF^[35].

Both, the structural differences but also the different redox properties of the rare earth oxides are important to understand the activity and selectivity of rare earth oxide catalysts for certain reactions. Due to these differences in the series, the rate limiting steps might be different. Antoshin et al. investigated the interaction of all rare earth oxides with oxygen by isotopic oxygen exchange and also the oxidation of hydrogen^[39].

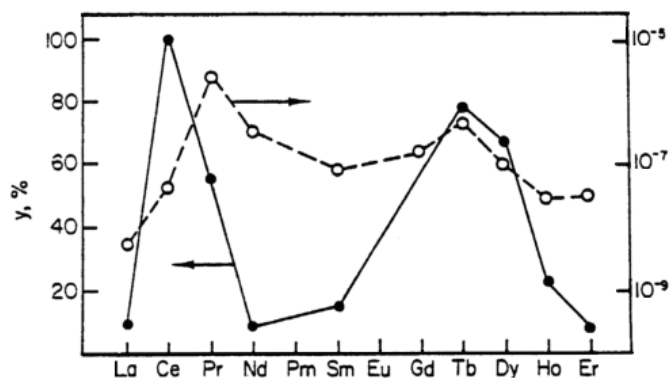


Figure 4: Relative catalytic activities of the rare earth oxides for oxidation of propene (left) and the initial reaction rate for isotopic exchange with molecular oxygen (right)

Praseodymia followed by terbium shows the highest activities for both reactions; also for the other REOs the rate of oxygen exchange correlates with the rate of hydrogen oxidation. However, the rate for total oxidation of propene over rare earth oxides does not correlate with the rate of isotopic O_2 exchange. Here, cerium oxide shows the highest rate for this reaction, followed by terbium; similar results were obtained for the total oxidation of other hydrocarbons ^[40].

Although these findings might be irritating at first sight, they can be easily understood comparing the requirements for the oxygen exchange reaction and the total oxidation of different hydrocarbons. For the isotopic oxygen exchange reaction of course a fast activation of oxygen is required. However, the exchange of chemisorbed oxygen and lattice oxygen close to the surface is not sufficient for a high rate. It is also de rigueur that the labeled oxygen is transported into the bulk. In comparison to all other rare earth oxides, praseodymia and terbium show the highest oxygen mobilities in the lattice. The mixed valence state within the lattice can be understood as an intrinsic doping which allows the stabilization of oxygen vacancies in the bulk as well as their transport. In addition, their crystal structure is tolerant to high concentrations of oxygen vacancies within the oxygen sublattice, meaning that the cation sublattice does not change (to a large extent). For hydrogen oxidation, a competitive adsorption of hydrogen and oxygen is assumed for most rare earth oxides. Again, the rate of oxygen transport through the lattice becomes important. If an adsorption site is blocked by adsorbed hydrogen, oxygen can still be provided by the lattice, with the rate limiting step being the oxygen transport so that the high rates for praseodymia and terbium can be understood.

For the oxidation of hydrocarbons the activity correlates with the ionization energy of the 3+ to the 4+ state of the respective rare earth oxide ^[41]. This indicates that the C-H activation is the rate limiting step during this reaction. In addition, the deep oxidation of hydrocarbons is known to occur via electrophilic oxygen species. The electrophilic oxidation over metal oxides is not considered as

Mars-van Krevelen mechanism, but represents a competing reaction which may contribute to the observed overall selectivity pattern in oxidation reactions.

Many representatives of the rare earth oxides are known for their selective oxidation properties (even in the presence of oxygen). The origin of different selectivity patterns for different oxides is often ascribed to nucleophilic oxygen (see above) and is then correlated with the acid-base properties of the respective oxide. Recently, Sato et al. systematically investigated the acid-base properties of rare earth oxides^[42]. With decreasing ionic radius an increase of the surface charge of the metal ion is observed which decreases the basicity of the lattice oxygen. This result was already stated several times in the literature. However, for the first time, Sato et al. included in their work a discussion on the different phases and structures of the rare earth oxides they investigated. The rare earth sesquioxides in C and B modification (except Sc_2O_3) show a linear correlation between the ion radius and the strength of basic sites. Oxides in different modifications (La_2O_3 , Nd_2O_3 , and Pr_6O_{11}) show a less pronounced correlation. Terbium, as Tb_4O_7 , follows the trend with regard to the strength of its basic sites but exhibits a much lower number of basic centers in comparison to most of the rare earth sesquioxides. CeO_2 shows hardly any basicity.

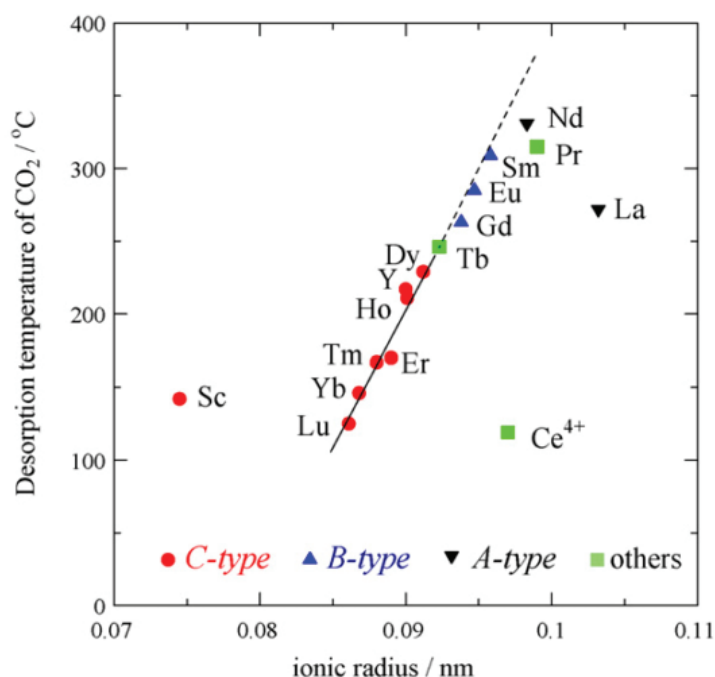


Figure 5: Desorption temperature of CO_2 as a function of the ionic radius of the respective rare earth 3+ (4+ in case of ceria) ion. The desorption temperature of CO_2 is a measure for the strength of basic sites. Taken from Ref.^[42]

Several authors have investigated the influence of the acid base properties of rare earth oxides on the selectivity pattern for different reactions, among them the dehydrogenation of alcohols and diols ^[28,43–45]. Especially recent results on methanol oxidation over ceria proved that the tendency towards oxidation on this oxide is strongly related to its oxidation state and the exposed crystallographic surface ^[46,47].

In summary, three important parameters influence the catalytic behavior of rare earth oxides. These are: a) oxygen mobility, b) the acid base properties, and c) the present phase of the oxide.

5. Oxidative coupling of methane: An example for a reaction catalyzed by rare earth oxides

5.1. The mechanism

Today, the majority of methane – independent of its source - is used for the generation of heat and electricity^[48]. Yet, its activation and conversion into higher hydrocarbons would open valuable pathways to use methane also for the production of chemicals which today are obtained from crude-oil. The oxidative coupling of methane (OCM) is one of the options in this respect and has thus attracted renewed interest recently^[48]. It allows the conversion of methane into ethane, ethylene along with CO and CO₂ as undesired by-products.

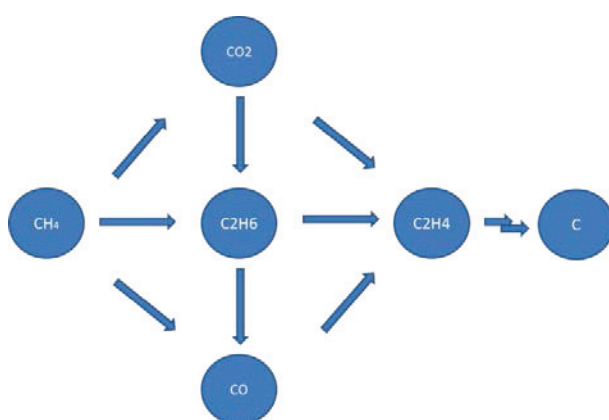


Figure 6: Reaction pathways during the oxidative coupling of methane. Heterogeneous and homogenous reactions are not distinguished.

OCM is one prominent example of chemical processes, for which REOs are recognized to be among the most active and selective catalysts^[49]. Along with the high economic significance, OCM is a reaction which is also very interesting from a scientific point of view. The OCM reaction follows a heterogeneous–homogeneous mechanism^[50,51]. After activation of the methane by H abstraction on the surface, methyl radicals are formed and ejected in the gas phase. Then, dimerization of these radicals occurs in the gas phase forming ethane.

Unfortunately, several heterogeneous and homogenous (gas phase) reactions take place either parallel or sequentially. Ethene is formed either via homogeneous or heterogeneous ethane dehydrogenation. According to selectivity–conversion relationships of the OCM reaction, carbon oxides are formed from methane and C₂ oxidation. Among the most promising OCM catalyst are Sm₂O₃, Li-doped magnesia and 5 %Na₂WO₄–2%Mn. However, the reactor type and in particular the configuration of the catalyst bed play an important role to balance the heterogeneous and homogeneous parts of the reaction network. Various reactor concepts have been studied so far, among them ceramic monoliths, membrane- and microreactors^[52–54]. Especially within monolithic

reactors the heat transport was proven to be better in comparison to conventional particle beds. However, the conversions and therefore the yields were found to be inferior due to the laminar flow pattern^[55-57].

Although today many promising catalyst types are already known for OCM, the combination of new reactor concepts and catalysts is still rare. In particular robust and adaptive preparation techniques are important to benefit from a chemically improved catalyst in an improved reactor exhibiting an optimal porosity.

5.2. Own contribution (PAPER II)

In order to contribute to such an effort, a monolithic REO catalyst was developed with a hierarchical porosity. Specifically, macroporous ceramic foams of samaria (and for comparison: ceria) were prepared using a direct foaming method based on polyurethane. The mechanically stable and open-cell foam was characterized using SEM, mercury porosimetry and 3D magnetic resonance imaging. As a characteristic feature of the employed foaming methodology, the process resulted in a bimodal pore size distribution, ensuring low-pressure drops on the one hand and sufficiently large surface areas on the other hand.

Figure 7 shows the resulting material which was tested as a catalyst for the oxidative coupling of methane. In comparison to honeycomb structures – showing inferior OCM yields due to the laminar flow pattern - the interconnected pores within our samaria foam exclude such a flow and show the expected advantage of a monolithic reactor concept. This was proven by comparative measurements with the samaria powder used for the fabrication of the monolith. Specifically, the samaria foam was benchmarked against a typical fixed bed of samaria particles and shows a ~3-4 times higher C₂ space time yield.

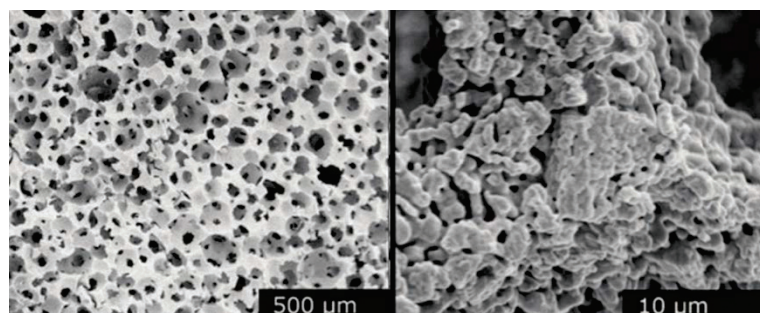


Figure 7: Scanning electron micrograph of a ceramic foam consisting of pure samaria. The foam shows large macropores and in addition smaller mesopores.

6. Sol-Gel Chemistry

6.1. Pure oxides

Whereas direct foaming, as presented in the last chapter, represents a way to create macroporosity, it does not allow the preparation of materials with high specific surface areas. Here, techniques from material science and chemical nanotechnology offer attractive novel routes. They also open the door to tune the composition as will be discussed in this chapter.

Traditional solid state reactions using oxide powders or their mixing in melts are common for the preparation of bulk oxide materials. These reactions are usually performed at high temperatures to obtain sufficient mobility of the respective atoms or ions or to melt the components^[58]. This approach gave and still gives access to new compounds and materials with desired properties. However, the high temperatures often limit these approaches to thermodynamically stable phases. During the last decades considerable effort was therefore made regarding the preparation of metastable phases resulting in the development of new preparation methods mainly based on kinetic control, such as flash combustion, microwave assisted combustion, and quenching.

All these techniques still require quite harsh conditions. Liquid phase approaches, however, allow to control different parameters of the synthesis even at low temperatures, such as composition, structure and even crystallite size and porosity. The sol-gel chemistry represents one of the available “soft” techniques, following the concept of hydrolysis and (poly)condensation in a way similar to polymerization reactions in organic chemistry^[58].

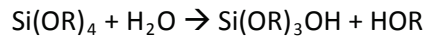
In this context, a sol is a solution containing colloidal particles (1-1000 nm). The interactions within this suspension are determined by short range forces, such as Van-der-Waals attractions and collisions due to Brownian movement, while gravitational forces can be neglected^[59]. A gel however, is according to Henisch’s description a “two componential system of semisolid nature rich of liquid”^[60]. The most popular precursors are metal alkoxides. Table 2 shows common side chains of alkoxides. So far, many basic principles of sol gel chemistry have been developed for silica based systems and extended to other metal oxides.

Table 2: Overview of typical precursors for the preparation of metal oxide aerogels.

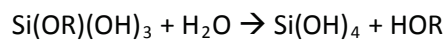
Alkyl		Alkoxy	
Methyl	-CH ₃	Methoxy	-OCH ₃
Ethyl	-CH ₂ CH ₃	Ethoxy	-OCH ₂ CH ₃
n-propyl	-CH ₂ CH ₂ CH ₃	n-propoxy	-OCH ₂ CH ₂ CH ₃
iso-propyl	-H ₃ C(-C)HCH ₃	iso-propoxy	-H ₃ C(-O)HCH ₃
sec-butyl	H ₃ C(-C)HCH ₂ CH ₃	n-butoxy	-O(CH ₂) ₃ CH ₃
iso-butyl	-CH ₂ CH(CH ₃) ₂	sec-butoxy	-OCH ₂ CH(CH ₃) ₂
ter-butyl	-C(CH ₃) ₃	iso-butoxy	-OC(CH ₃) ₃

Tetraethoxysilan (TEOS) is the most investigated molecule within the group of table 2 ^[61]. The first step of gel formation through the alcoxide route is hydrolysis. The proceeding formation of OH groups opens a new reaction path - the condensation - which will lead to the formation of a polymer and sol, respectively, if the monomers have at least two OH groups.

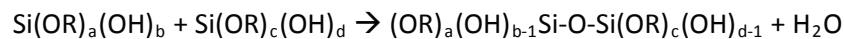
I: Hydrolysis



(2 further reactions)



II: Condensation



During this condensation, the monomers form large interconnected chains and the viscosity of the sol increases constantly. In an ideal gel the entire 3-dimensional network is formed by just one molecule. The moment where the condensation ceases and apparently no monomer is left is called the gel point ^[59]. Experimentally, the gel point can be determined by the stiffness of the gel. If, for example, the beaker containing the gel can be turned upside down, while it remains in its previous position, obviously not pouring out, the gel point is reached.

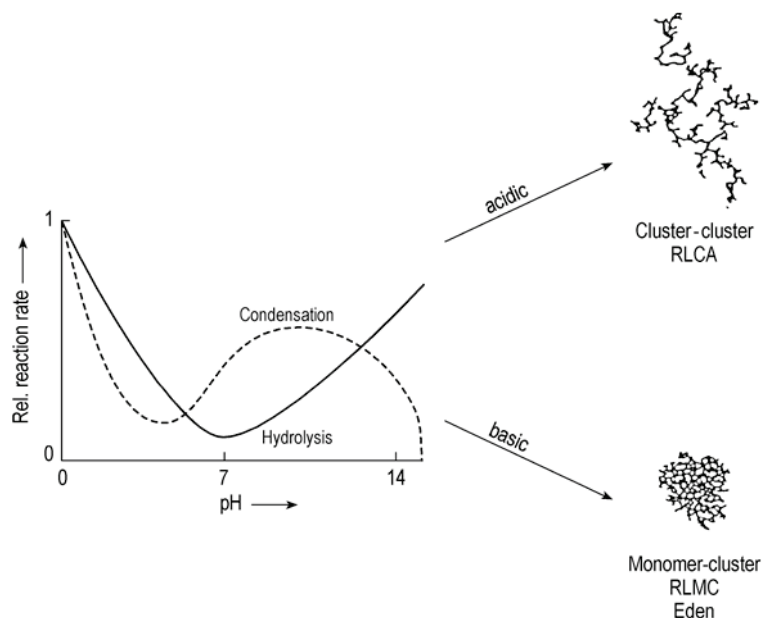


Figure 8: The pH dependence of hydrolysis and condensation in the sol gel process ^[62].

Taking advantage of reaction kinetics during sol gel chemistry, different gels can be obtained. Giving an example, figure 8 shows the reaction rates of hydrolysis and condensation as a function of the pH of the solution. The growth rate, i.e., the length of chains vs. the “branching” depends on the ratio of

the rates of condensation (length) and hydrolysis (branching). By adjusting the particular pH value of the solution, two different growth modes can be obtained. For example, under acidic conditions (pH < 6) the condensation proceeds faster than the hydrolysis which becomes the rate determining step of the reaction. This growth mode is called reaction limited cluster aggregation (RLCA), or cluster-cluster growth. On the contrary, for higher pH values the condensation (branching) becomes dominant. The resulting growth mode is called reaction limited monomer cluster growth (RLMC) ^[63].

Today sol-gel techniques provide a convenient approach for the preparation of oxide materials with different composition and structure (figure 9). It is possible to stop the condensation at the sol stadium so that nanoparticles are obtained. Allowing further condensation dense film, fibers, and even highly porous materials – so called aerogels – may be obtained ^[64].

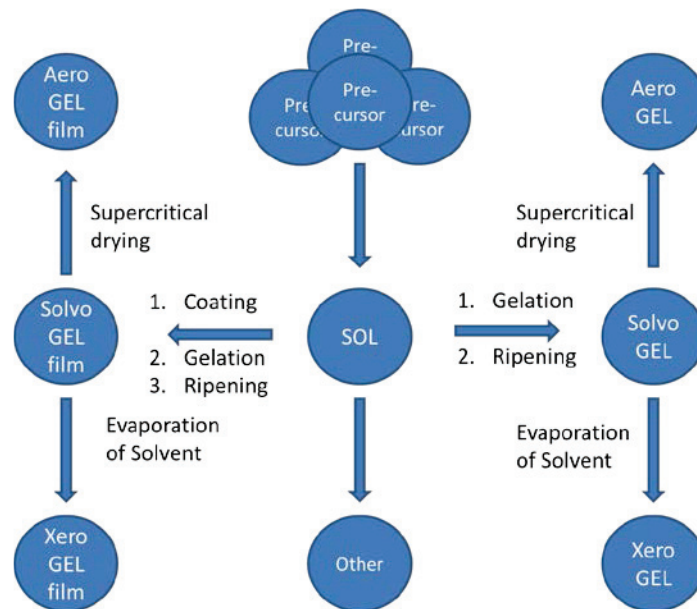


Figure 9: An overview on different reactions paths of sol gel chemistry.

In the case of aerogels, the pore liquid is exchanged by air. These materials are well known for their low density and high surface area. Kistler performed a first synthesis of silica aerogels already in 1931 ^[65]. However, the evaporation of solvent was accompanied by a significant shrinkage of the gel, which can be explained by capillarity forces occurring during the evaporation of the liquid and resulting in a weakening and destruction of the porous network of the gel. The supercritical drying of the alcogels solved Kistler's problem, as beyond the critical point no phase boundaries exist anymore so that it was possible to remove the solvent without destroying the pore structure of the gel.

Another way of drying aerogels is realized by taking advantage of a surface modification. Introduction of hydrophobic groups, e.g., can lead to a drastic decrease of solvent solid interactions and hence lower capillary forces. Still, the gel shrinks during the evaporation of the solvent. However, it will retain its porous structure ^[66]. At the moment the amount of solvent falls below a certain threshold, the structure will gain its full volume back, because of the lower capillary forces in comparison with the tensile strain within the material. Owing to this fact, this phenomenon is called “spring back”. Without a surface modification, ambient drying will result in the formation of xerogels which one can imagine as a compacted aerogel.

Similar to other sol-gel products, aerogels are not limited to silica; Kistler himself published routes to alumina, stannic oxide, tungsten oxide, gelatin, agar, nitrocellulose, cellulose and egg albumin aerogels and he saw “no reasons why this list may not be extended indefinitely”^[65]. Fulfilling this prediction, V₂O₅, Cr₂O₃, TiO₂, ZrO₂ and CeO₂ have been synthesized meanwhile to name a few examples ^[62,64]. The preparation of these non-silica aerogels can also be described by the above mentioned alcoxy-route. However, the high reactivity of many metal alcoxides can lead to a very fast, as the case may be, spontaneous polymerization and undesired precipitation of the respective metal oxides. In this case, the reactivity needs to be lowered by replacing the alcoxy ligands by for example acetic acid or acetylacetonate prior to hydrolysis. The reaction rate of these precursors is lower and the gel formation takes place again. Nevertheless, not all metal alcoxides are commercially available; others are expensive and their storage can be problematic due to their reactivity.

In 2001 Gash et. al. presented an alternative approach by adding propylene oxide to alcoholic solutions of iron(III)chloride and iron nitrate ^[67]. In the so-called epoxide addition method (EAM) propylene oxide (PO) is supposed to be a proton scavenger. The reaction of an anion with PO initiated the ring opening which requires a proton. In comparison to many Brønsted bases the reaction is much slower so that the PO is homogeneously distributed in the solution before the pH rises significantly. In this way, the sol has enough time to rearrange so that precipitation can be avoided.

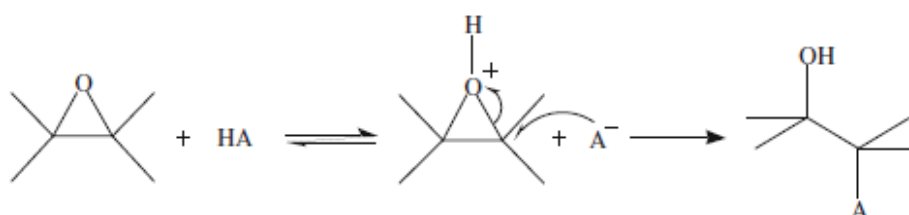


Figure 10: Reaction scheme of the ring opening reaction of propylene oxide. The consumption of protons leads to a homogenous increase of the pH-value within the solution.

Also for the EAM the structure and density of the three-dimensional porous networks is determined by reaction kinetics of hydrolysis and condensation during gel formation. As already mentioned previously, the pH value of the sol determines the growth mode of the corresponding polymers. Another parameter is the choice of precursor. Taking Al_2O_3 aerogels as an example, the choice between AlCl_3 and AlNO_3 determines the structure and density of the resulting alumina aerogel (figure 11) ^[68]. Aluminum-nitrate leads to a more cluster-cluster like formation (“branching” is favored), comparable to the structure of silica gels grown under basic conditions. On the contrary, aluminum chloride generates a more fibrous structure.

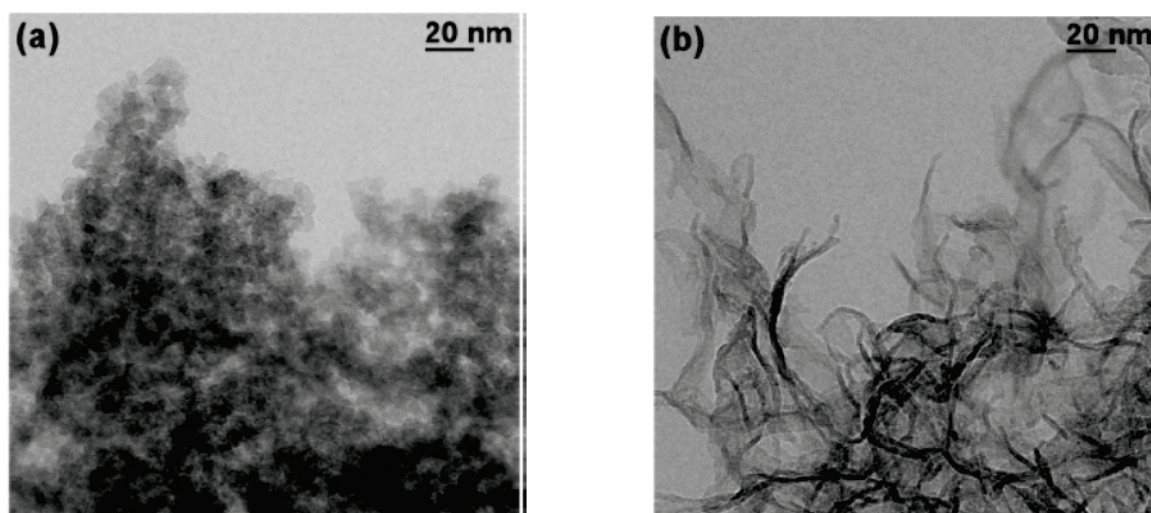


Figure 11: TEM images of alumina aerogels using aluminum nitrate (left) and aluminum chloride (right) as precursors. The different structure is the result of different reaction kinetics due to interactions with the anions. ^[68]

6.2. Own contribution (PAPER I)

The epoxide addition method was successfully adapted to the preparation of rare earth oxides aerogels. Both, rare earth nitrates and chlorides were tested as precursors. However, only the rare earth chlorides finally formed gels. Following the supercritical drying, all aerogels showed non-Bragg scattering, with the exception of ceria which was already present as cubic CeO_2 . Further characterization revealed (HR-TEM) that also within the other rare earth aerogels already small crystalline domains are present.

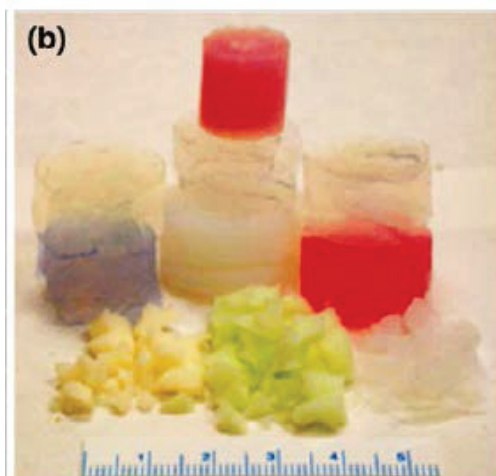


Figure 12: Aerogels of various rare earth oxides. Front row: SmOx, PrOx, EuOx; bottom row, back: NdOx, TmOx, HoOx; middle row, back: DyOx, GdOx, TbOx; top: ErOx. (Note: “Ox” is used as abbreviation for oxide; it does not contain information on the stoichiometry)

After annealing the samples at 650 °C, all aerogels showed x-ray diffraction patterns of the respective rare earth oxide. However, an additional phase was observed, which was identified as rare earth oxychloride. The stability of the respective rare earth-aqua-chloro complexes determined how large the amount of the oxychloride phase is. Annealing at $T > 800^{\circ}\text{C}$ results in a pure rare earth oxide. However, the structural changes during the heat treatment caused the monolithic aerogels to break into pieces. Aiming at avoiding chloride incorporation into the rare earth oxide lattice the EAM was modified and extended to hybrid (mixed) systems as discussed in the later course of this chapter.

6.3. Thin xerogel films

Similar to sol gel methods based on alcoxides, the EAM allows the preparation of thin films on surfaces. Koebel et al. applied the EAM to obtain ATO films for optoelectric applications^[69]. Aiming at preparing a dense and crack free film, only a small amount of propylene oxide was applied to the metal salt solution such that no gel formation occurred but small ATO particles were formed. After annealing the resulting material showed similar electrical resistivity as ATO films obtained by other wet chemistry techniques with – at the same time - even better optical transparency.

Just recently, Dawedeit et al. described a homogenous coating of the inner side of a glass cylinder^[70] with several functional oxides by EAM. It was demonstrated that by rotating the cylinder – which contained the sol – a more homogenous film can be obtained as compared to a classical dip coating approach. In addition, this method allows the coating of the inner surface so that the outer surface of the cylinder stays uncovered. Here, the amount of gelling agent was high enough to ensure gelation so that either xero- or aerogel films can be obtained.

In particular, the low initial viscosity of the sol allows the coating of the inner and outer surface of porous materials as demonstrated (preliminary results) in figure 9. In comparison to classical impregnation methods the structure of the surface film can be tailored by the sol-gel chemistry.

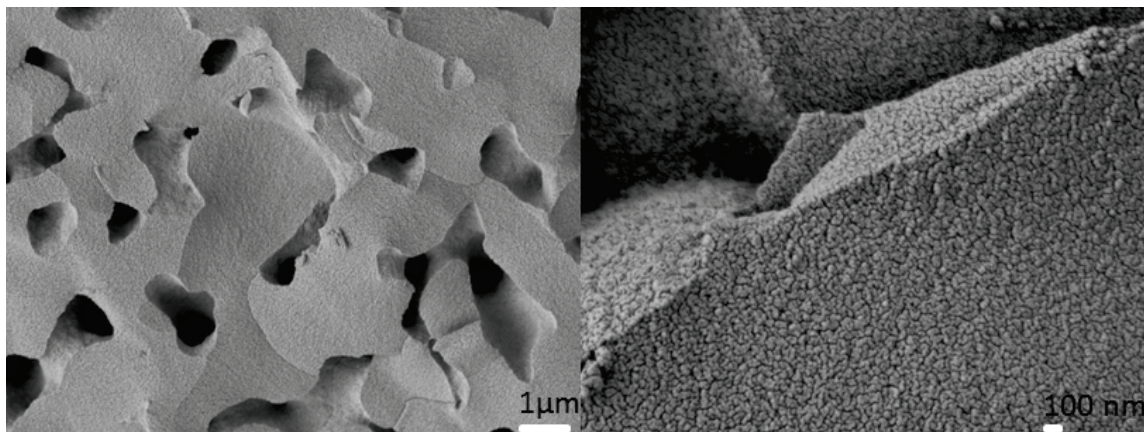


Figure 13: Scanning electron micrograph of (left) macroporous alumina prepared via EAM and (right) the same material coated with a thin layer of samarium oxide xerogel using the EAM.

Please note that also the macroporous alumina substrate in figure 13 was obtained using the epoxide addition method. Tokudome applied the famous concept of polymerization induced separation – introduced by Nakanishi – for the preparation of Al_2O_3 aero- and xerogels^{[71] [72]}. The diameter of the macropores and the final structure of the materials are controlled by the addition of the polyethylene glycol (PEG). During the gelation of the alumina sol, the organic and the inorganic (Al_2O_3) polymer underwent segregation. After thermal decomposition of the PEG a macroporous alumina is obtained.

6.4. Hybrid aero- and xerogels

In addition to gels containing one metal oxide, so called hybrid gels can be generated using combinations of different precursors. Referring to literature, three routes exist for the synthesis of hybrid systems^[73]:

a) Mixing metal salts before sol formation

b) Mixing metal oxide containing sols

c) Mixing metal oxide sol and a precursor solution

Depending on the particular procedure, different distributions of the metals can be achieved. When mixing the metal precursors before hydrolysis, both metals are contained in the resulting particles/polymers (“molecular mixing”). When mixing the particular sols, the resulting gel (ideally)

contains two different particles consisting of just one metal oxide. The third option results in a bimodal particle size distribution.

For different hybrid systems it has been shown that especially the molecular mixing does not work properly ^{[74][75]}. These results are not astonishing at all, considering the different reactivities of the precursors. In the case of a binary system, the gel formation is determined by at least ten (different) reaction rates (Figure 14). Only one of the three parallel reaction paths will end up in the formation of a molecular-scale mixed sol. Furthermore, even at the low temperatures of the sol gel process, thermodynamic reaction control might play a role; hence the formation of a specific phase – a mixed oxide for example - can be preferred.

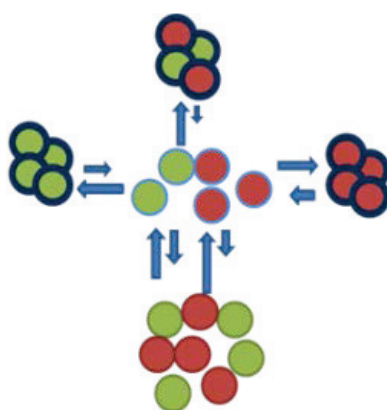


Figure 14: The sol gel process for the formation of hybrid systems is determined by different reaction rates. The ratio of the reaction rates determines the ratio of the obtained product.

6.5. Own contribution (PAPER VI): Sm/Al hybrid aerogels for OCM

Catalytic reactions represent one field of applications where it is not always necessary and sometimes not even desired to use the pure materials. Either the pure components are too expensive -then dispersing the catalytically active component onto or into an inert matrix is a more economical way - or the additional component even improves the properties of the active phase for example with respect to its thermal stability.

Focusing on the preparation of an OCM catalyst via sol gel chemistry, Sm/Al hybrid oxide aero- and xerogel were prepared and their catalytic activity was benchmarked against a) pure samaria and b) commercial nano-alumina impregnated with samarium nitrate. The xerogel obtained from aluminum chloride and samarium chloride shows a similar conversion and selectivity as compared to pure samaria. The fact that it only contains 20 at % of samarium renders it a very interesting catalyst in view of the samarium costs.

In addition, in the article was shown that the EAM allows the coating of the prepared catalyst on different supports, enabling the use of this catalyst also as a part of reactor concepts different from

fixed bed. As a proof of principle a flat SiO_2 substrate was coated with the most promising xerogel. A micrograph is shown in figure 15.

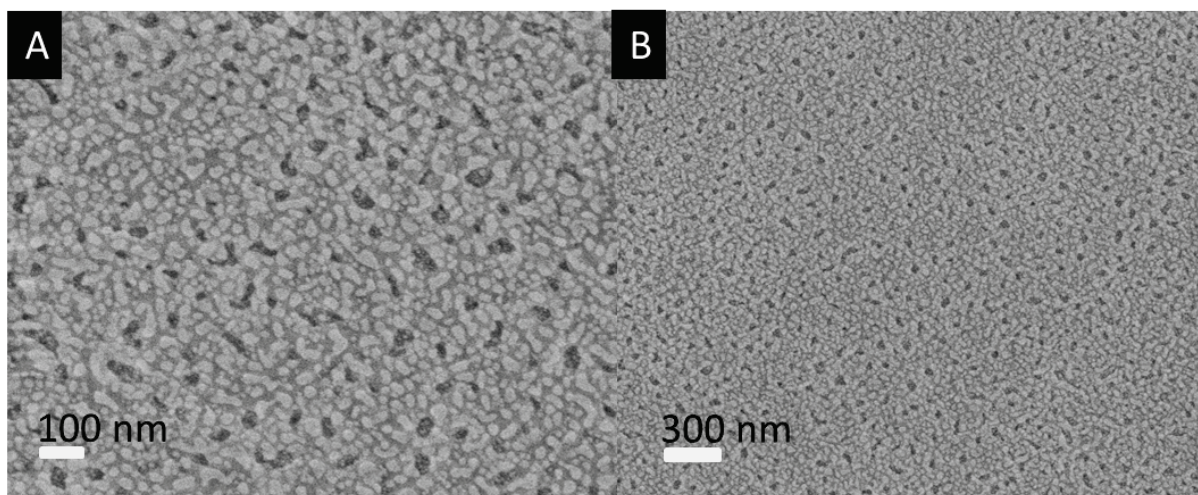


Figure 15: Scanning electron micrograph of a flat silica wafer coated with Sm/Al hybrid xerogel.

6.6. Own contribution (PAPER VII): Ce/Al and Pr/Al hybrid aero- and xerogels as oxidation catalysts

In addition to samaria/alumina hybrid aero- and xerogels, also the preparation of ceria and praseodymia hybrid gels with 20 at% REO and 80 at% alumina via the EAM was studied. In analogy to the samaria systems and in contrast to the pure REO gels, nitrates as well as chlorides could be used in the synthesis. Yet, only in the case of the nitrates pure oxide gels could be obtained, whereas in the latter case chloride residues remained in the sample. As far as the crystallinity is concerned, the hybrid ceria and praseodymia gels showed a rather different behavior. Whereas in the first case small ceria domains formed which grew with increasing calcination temperature, the praseodymia samples remained non-crystalline up to 875° C, where a mixed PrAlO_3 phase evolved. The difference is most probably the result of the different preference of oxidation states: Ce prefers oxidation state +4 favoring the formation of individual CeO_2 and Al_2O_3 domains, whereas Pr can also adopt +3 enabling it to form an aluminate phase.

Based on these structural differences, the catalytic activities for CO oxidation were found to be different. The ceria hybrid xero- and aerogels exhibited an activity which – when related to the ceria content – was competitive to pure ceria catalysts while showing a significantly improved resistance against sintering. The results for the praseodymia systems revealed an inferior thermal stability with respect to sintering and an inferior catalytic activity due to the aluminate formation.

7. How to measure transport

7.1. PFG-NMR

In the chapter about mass transport some common diffusion mechanisms were introduced and the importance of these processes for catalysis was demonstrated. This section is dedicated to experimental methods to measure diffusion within small pores. For catalytic applications, diffusion is important for the net transport of reactants. This transport diffusion needs to be distinguished from self- or tracer diffusion. While transport diffusion results in a macroscopic flux of molecules and occurs only under non equilibrium conditions (concentration gradient). Self- or tracer diffusion, however, is always present under equilibrium conditions. It can either be measured by labeling certain molecules or by following the trajectories of a large amount of single molecules as shown in figure 16.

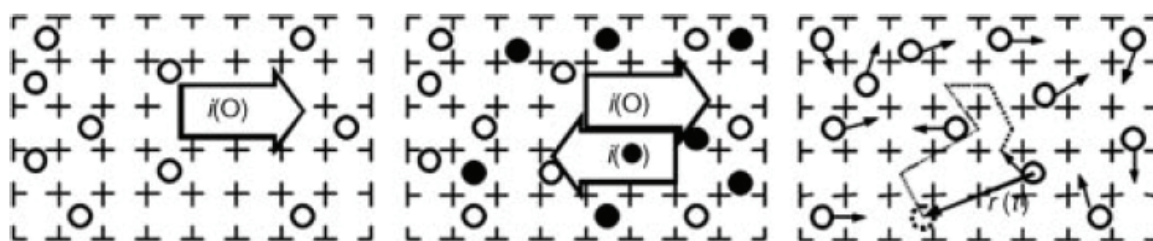


Figure 16: Transport diffusion results in a net flow with a concentration gradient as a driving force (right); tracer diffusion can be followed by measuring the flux after certain molecules have been marked (middle); self diffusion can also be measured by following the single trajectories of many individual molecules (left). Taken from ref. ^[20]

An overview on different techniques to measure transport, self and tracer diffusion is provided in figure 17. The classification macro-, meso, and microscopic refers to the length scale of transport which can be observed by using the respective technique. In the following, only pulsed gradient field (PFG)-NMR is discussed, a technique that allows to directly measure the mean square displacement within porous materials. (A detailed description and comparison of all available techniques is beyond the scope of this framework article. The interested reader, however, may find a comprehensive description in ^[20].)

To understand the principle of NMR self-diffusion measurements, we can base the discussion on the concept of NMR where the nuclear spins are precessing in the direction of a constant magnetic field B_0 with a certain Larmor frequency ω . The application of a radiofrequency (RF) pulse tilts the magnetization by a certain angle with the transvers magnetization being maximal after a 90° pulse ^[76]. This transvers portion of the total magnetization is used for the measurement. However, a single RF pulse is not sufficient for the measurement, as all (identical) molecules have the same

Larmor frequency –because their gyromagnet ratio γ is the same - and cannot be distinguished from each other.

$$\omega_0 = \gamma B_0$$

By making the magnetic field inhomogeneous, it becomes possible to distinguish identical molecules from another by their Larmor frequency. (This principle is the same as for magnet resonance tomography)^{[77][78]}. A gradient \vec{G} is applied in x,y, and z direction so that every molecule within the inhomogeneous magnet field has – at least at first sight -its individual Larmor frequency *as a function of its position* .

$$\omega = \gamma(B_0 + \vec{G}\vec{r})$$

In a real experiment the spatial resolution is limited by the magnetic field, the gradient, and the signal to noise ratio of the signal acquisition. A so-called spin echo or gradient echo experiment can be used to determine the mean square displacements. The classical spin echo experiment consists of a 90 ° RF pulse to obtain a maximum in transversal magnetization, a first gradient to code the spatial information, a 180 ° RF pulse to minimize the de-phasing contribution induced by B_0 inhomogeneity, and finally a second gradient. As a result of the first gradient the vector sum of the transverse magnetization decays. As the molecules diffuse in between the first and the second gradient– assuming no additional relaxation – the transfers magnetization is not fully restored. The difference in the vector sum is characteristic for root mean square displacement ^[79].

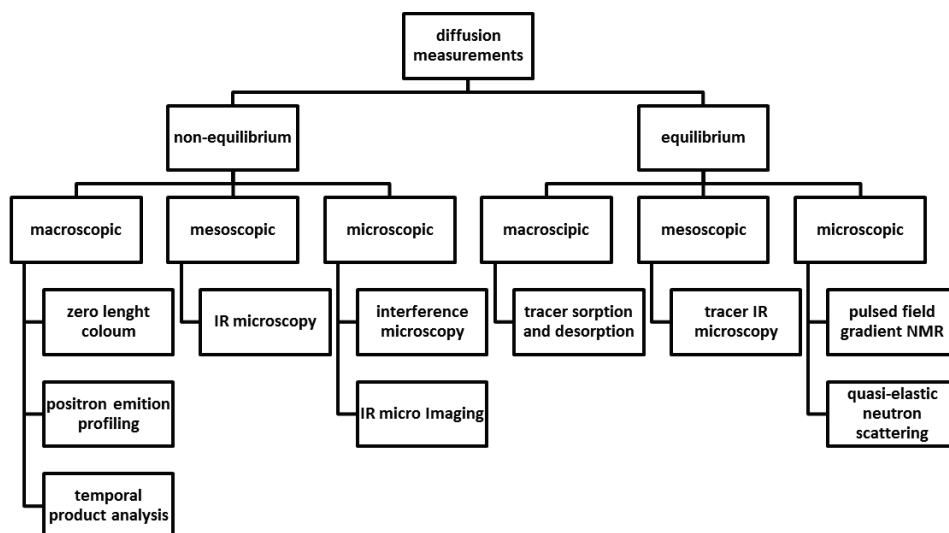


Figure 17: Overview on available techniques for the quantification of diffusivities.

For a long time the acquisition of gas phase diffusivities was impossible due to the low overall signal. At room temperature the small energy difference between the two possible nuclear spin states (for $I=1/2$) leads to a small difference in the occupancy of both states according to the Boltzmann distribution. By changing the ratio of occupancy of both spin states, the NMR signal can be enhanced by several orders of magnitudes. This hyperpolarization may be realized by several techniques, such as optical pumping or just cooling the gas together with a catalyst as the state of lower energy becomes more occupied with decreasing temperature ^[80]. Today, the ongoing improvements of the NMR hardware, especially in terms of stronger magnetic fields in combination with higher gradients, allow the use of gases without hyperpolarization yet achieving sufficient signal to noise ratios.

PGF-NMR was in particular used for the investigation of self-diffusion within microporous –mainly zeolitic – materials. Vasenkov et al. showed for example that the self-diffusivity of methane in ZSM-5 (figure 18) and n-butane in silicalite decreases with increasing root mean square displacement, i.e., with increasing the time interval between the first and the second gradient ^[81]. This finding indicated that molecules are facing additional resistance if they diffuse over longer distances. Finally, they found that these diffusion restrictions are not induced by the outer surface of the zeolite but given by an internal diffusion barrier within the zeolite structure. In a different study the apparent tortuosity factor within the identical structure was calculated for Knudsen and bulk diffusion ^[82]. The tortuosity within the Knudsen regime was found to be much higher as for the bulk regime.

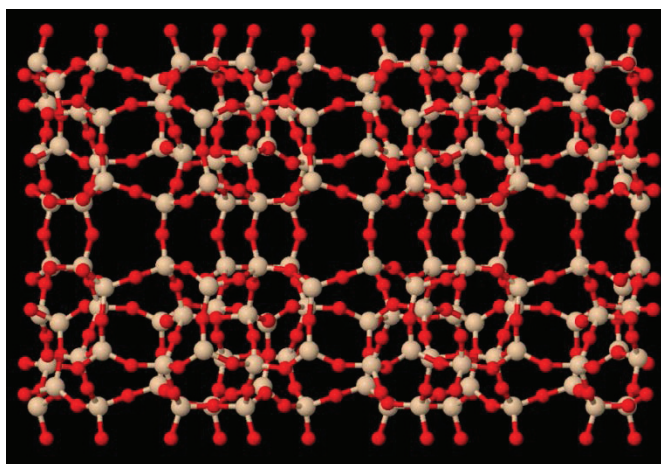


Figure 18: Structure of ZSM-5 zeolite

7.2. Own contribution (PAPER IV & V)

For the first time the self-diffusivities of carbon monoxide was measured within a mesoporous Sm/Al hybrid aerogel. Especially within mesoporous materials the density in the gas phase is lower in

comparison to microporous materials, which reduces the NMR signal and complicates the measurement. (Note that for microporous material an enrichment of gas molecules in comparison to the gas phase is expected ^[83]). However, the self-diffusivity within a monolithic aerogel – which was free of cracks – and a bed of particles consisting of the same mesoporous material could be measured and compared using PFG-NMR. The root mean square displacement (rMSD) of CO₂ molecules in the monoliths was much smaller than the monolith dimension. Therefore no influence of the external surface on the intra-monolith diffusivities is expected. For different CO₂ loading pressures (<1 atm – 10 atm) a single intra-monolith diffusivity was observed, no dependence on the rMSD value was found. This indicates that the transport within the monolith is homogeneous. The aerogel particle sizes were chosen such that the values of the root MSD of CO₂ molecules were in the same range. The PFG-NMR diffusion studies revealed the presence of two distinct diffusivities for two ensembles of molecules. The diffusivity of the first ensemble of molecules was found to be identical to the intra-monolith diffusivity. The second ensemble is in rapid exchange between the intraparticle and interparticle space.

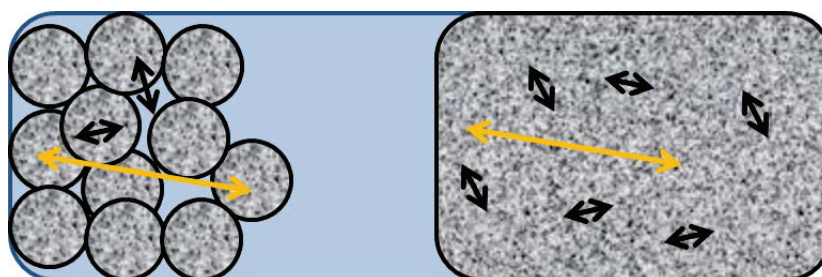


Figure 19: Different diffusivities found in the monolith and the particle bed. The orange arrows represent the long-range diffusivity. For the particle bed the displacement is so large that the CO₂ molecules are transported through several particles and the interparticle space so that the diffusion in the bed can be compared to the diffusion within the monolith.

Diffusivities obtained from displacements much larger than the sizes of individual particles – the so-called long range diffusivity – at low loading pressures of CO₂ were found to be much larger (e.g., by about a factor of 4 at a 0.3 atm loading pressure) than the corresponding intramonolith diffusivity. With increasing loading pressure, this difference was found to decrease and at a loading pressure of about 10 atm both diffusivities become indistinguishable within the experimental uncertainty. This result implies that at these high pressures a crushing of the catalyst into smaller pieces is useless to improve the transport properties. In other words, large chunks of the aerogel may be used without risking mass transport limitation. This of course would be of advantage in terms of catalyst handling and exchange.

Concluding remarks

Metal oxide catalysts represent an important part of available heterogeneous catalysts. They may be used as support materials e.g. for metal catalysts or – as in my own work – represent themselves the active phase of the catalyst. In addition to the nature of the specific surface chemistry, the structure of the catalyst - and in particular the porosity - plays a highly important role. This is due to the fact that diffusion of reactants – educts and products – can influence the overall rate and thus catalyst efficiency, if the transport rather than the reaction is rate limiting. We speak of mass transport limitation then. Many traditional catalyst preparation techniques do not allow the optimization of the active phase and the overall porous structure independently so that the concomitant optimization of both factors is often difficult to realize.

This changes whenever novel materials synthesis routes from materials science or even chemical nanotechnology are encountered. In particular the employment of soft chemistry – or chimie douce – for the synthesis of catalysts holds fascinating perspectives. New possibilities to tailor the composition and the structure of oxidic materials independently open up a new universe of possibilities to stimulate the important catalysts market and to provide new proving grounds for the scientific community to develop catalysts according to rational design principles. These new synthesis options go hand-in-hand with highly improved and sophisticated characterization techniques, in terms of microscopy, diffraction and spectroscopy helping to understand structure-reactivity relationships in more detail than before. In any event, an interdisciplinary approach involving chemistry, physics, materials science and chemical engineering is necessary to take advantage of these chances.

In the present thesis, such an approach was started based on rare earth oxides which hold interesting catalytic perspectives for a number of reactions which are yet not fully explored. One important example is the oxidative coupling of methane which could be one of the limited accesses to activate this molecule in order to produce chemicals, in this case valuable C₂ components. Other fields of application are partial and total oxidation reactions.

Sol-gel chemistry was used to prepare aero- and xerogels of various representatives of the series, including ceria, praseodymia, samaria and terbia, which exhibit different properties in terms of the abundance of different nucleophilic and electrophilic oxygen species present at the surface under oxygen containing atmospheres, their acid-base properties and oxygen mobilities. A special synthetic approach was used originally developed at the Lawrence Livermore National Laboratory (A. Gash): the so-called epoxide addition method. In collaborations with the LLNL this approach was extended to mixed REO / alumina hybrid gels. Different compositions, porosities, morphologies (in terms of the

ligament structures) and extents of crystallinity were obtained depending on the used precursors and preparation conditions. Aerogels derived from supercritical drying always exhibited a higher porosity and specific surface area as compared to xerogels which suffered from compacting during drying in air as a consequence of capillary forces.

In cooperation with various groups, a thorough characterization was possible. X-ray diffraction (collaboration with Th. Gesing) revealed that chlorine remains in the gels in form of oxychlorides if chlorides are used as precursors, whereas pure oxide gels could be obtained from nitrates. In contrast to pure REO gels, the hybrid gels with alumina remained amorphous up to high temperatures except for those containing ceria which early formed ceria crystallites. These differences can be well explained on the basis of the differently preferred oxidation states, with ceria preferring +4 at variance with the other rare earth elements so that the formation of oxychlorides and mixed alumina/ceria oxides is inhibited.

The catalytic properties of samaria gels were studied with respect to the oxidative coupling of methane (OCM, in collaboration with H. Hagelin-Weaver) and CO oxidation. For OCM, it is known that monolithic reactor concepts may have advantages as they allow short contact times which are advantageous to avoid deep oxidation to CO or CO₂. Therefore, not only powders of the crushed gels were tested but also macroporous foams prepared by a direct foaming technique (in collaboration with J. Nino). The foams exhibiting an open-cell morphology with channels in the sub-mm regime and mesoporous walls indeed provided higher C₂ yields as compared to fixed powder beds. The next step would be to coat a monolith of similar structure made out of an inert and cheap oxide, such as alumina, with a thin layer of a samaria gel. In this way, a more economical use of the expensive samaria could be achieved. Within this work, it could be shown that the EAM offers this option. First successful tests on planar substrates and ceramic foams were carried out.

CO oxidation was performed with those REOs which are known for their potential for total oxidation, i.e., ceria and praseodymia. For the xerogels standard lab reactors were employed whereas the aerogels were studied in a microreactor (in collaboration with V. Matolin). Particular attention was paid to the question whether the hybrid gels - where the catalytically active REO is embedded in an inert matrix in analogy to a supported catalyst (where the active component is dispersed on an inert matrix) - shows competitive activities to pure REO. Although a quantitative 1:1 comparison was not possible, high activities for ceria could be observed with the additional benefit of an increased sintering resistance. Again due to the different preference of oxidation states, praseodymia formed an aluminate phase with less favorable activities.

In addition to synthesis, characterization and catalytic properties also the question of transport in these novel materials was investigated in this thesis (in collaboration with S. Vasenkov). By means of PFG-NMR, the diffusion of CO_2 , as a catalytically relevant gas (CO oxidation and OCM), was characterized in a samaria aerogel monolith and in particle beds with different grain sizes. It was found that the long-range diffusivities for both situations merge at high pressures (10 atm) revealing that grinding of the material provides no advantage in this pressure regime. This observation implies that catalyst handling and exchange can be simplified by using larger pieces or small monoliths.

In summary, this thesis tackled successfully the task to explore a novel catalyst preparation technique allowing to tune porosity and composition in certain limits. Clearly, the very interdisciplinary approach was essential to gather the various pieces of information necessary to arrive at a conclusive picture. Therefore, I am particularly grateful to all collaborators providing this platform.

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