



Sol–gel preparation of alumina stabilized rare earth areo- and xerogels and their use as oxidation catalysts



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ABSTRACT

A new sol–gel synthesis route for rare earth (Ce and Pr) alumina hybrid areo- and xerogels is presented which is based on the so-called epoxide addition method. The resulting materials are characterized by TEM, XRD and nitrogen adsorption. The results reveal a different crystallization behavior for the praseodymia/alumina and the ceria/alumina gel. Whereas the first remains amorphous until 875 °C, small ceria domains form already after preparation in the second case which grow with increasing calcination temperature. The use of the calcined gels as CO oxidation catalysts was studied in a quartz tube (lab) reactor and in a (slit) microreactor and compared to reference catalysts consisting of the pure rare earth oxides. The Ce/Al hybrid gels exhibit a good catalytic activity and a thermal stability against sintering which was superior to the investigated reference catalyst. In contrast, the Pr/Al hybrid gels show lower CO oxidation activity which, due to the formation of PrAlO₃, decreased with increasing calcination temperature.

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1. Introduction

Rare earth oxides (REOs), also called Lanthanide oxides, play an important role in many today's technological applications, such as automobiles, wind turbines and computers [1]. Due to their special electrical, optical and magnetic properties, they are very promising ionic conductors (e.g. for solid oxide fuel cell applications), laser materials, colorants and contrast agents, just to name a few [2,3]. In addition, the chemical properties, including acid–base and redox properties, render REOs also interesting as catalysts or catalyst components [4,5]. Reactions for which REO catalysts are employed comprise complete and partial oxidation reactions and oxidative coupling of methane (OCM) [6,7].

In order to have high surface to volume ratios which are usually important for catalysis, a high porosity is needed. In particular, mesopores (2–50 nm) play a particularly important role as they ensure fast enough transport by diffusion (as compared to micropores <2 nm) while keeping the specific surface area (SSA) high (as compared to macropores). Interesting synthesis techniques for preparing materials with a suitable porosity for catalytic applica-

tions are sol–gel methods [8,9]. In a previous work, we reported the so-called epoxide addition method (EAM) to prepare areo- and xerogels of pure REOs. The approach turned out to be quite universal as basically all REOs can be processed in this way [10]. In contrast to other routes, using more expensive alkoxides, simple chloride salts can be used as precursors. (Notably, nitrates cannot be used as detailed in Ref. [10].) The gel formation is initiated by the addition of propylene epoxide which acts as a proton scavenger. During the ring opening reaction one equivalent of protons is consumed per equivalent of epoxide so that a slow and homogeneous increase of the pH is achieved in comparison to the addition of a conventional base [10]. A problem with the reported synthesis for the pure REOs was the formation of significant amounts of oxychlorides (depending on the lanthanide: up to 30 wt%), which could not be avoided because of their high stability.

Especially for catalytic applications it is not always necessary (and sometimes not even desired) to use pure materials. Pure compounds might be too expensive and dispersing the catalytically active component by supporting it onto or embedding it into an inert matrix of a cheap oxide is a much more economical way. Using sol–gel chemistry for preparing catalysts, such an option exists when synthesizing a hybrid material, where e.g. the inert oxide is the main component and the catalytically active oxide is dispersed in this matrix. Of course, it must be ensured that it is exposed at

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Table 1
Specific surface area of the hybrid aero- and xerogels and d_{10} and d_{95} according to the BJH evaluation of the samples calcined at 650 °C. After calcination at 1000 °C only the BET surface area was measured.

Notation	Temperature [°C]	BET specific surface area [m ² /g]	Pore volume [nm]	d_{10} [nm]	d_{95} ^a [nm]
Pr/Al-XG NO3	650	104	0.15	~3.5	~7
Pr/Al-AG NO3	650	204	1.3	~15	>70
Pr/Al-XG NO3	1000	<1	–	–	–
Pr/Al-AG NO3	1000	19	–	–	–
Ce/Al-XG NO3	650	160	0.17	~3.5	~7
Ce/Al-AG NO3	650	261	1.1	~15	>70
Ce/Al-XG NO3	1000	33	–	–	–
Ce/Al-AG NO3	1000	100	–	–	–

^a Additional macropores larger than 100 nm for the aerogels are likely so that d_{10} and d_{95} may be larger.

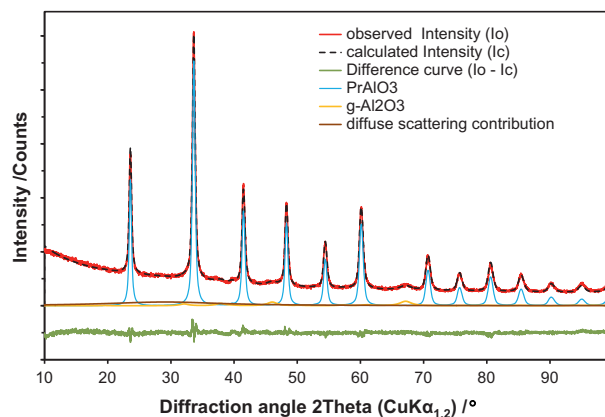


Fig. 1. X-ray diffraction pattern of the Pr/Al hybrid aerogel calcined at 1000 °C and the results of the Rietveld refinement. PrAlO₃ and γ -Al₂O₃ contribute to the observed Bragg-scattering for this sample.

the surface and not incorporated in a mixed oxide which may have no or inferior catalytic activity for the respective reaction.

For several transition metals mixed oxides have already been prepared in this way. Recently, we reported on the successful preparation of alumina promoted Co and Fe catalysts for Fischer–Tropsch synthesis with the EAM approach [11]. Here, however, the catalysts were finally reduced (before the catalytic application) resulting in a phase separation and the formation of metallic Co or Fe domains. The question arises whether in the case of an oxide catalyst the approach is also successful. Therefore, we have extended the EAM method to the preparation of rare earth/Al hybrid aero- and xerogels taking ceria and praseodymia as examples. In the present paper, we report the synthesis, the characterization by TEM and XRD and their use as oxidation catalysts, taking CO oxidation as an example (testing the ability for total oxidation).

The results show that the Pr/Al hybrid systems remain non-crystalline up to temperatures where pure alumina and REO systems already crystallize. On the contrary, the Ce/Al system behaves differently and the formation of small ceria domains with diameters in the range of 3–12 nm is observed. In line with these findings, the ceria catalyst shows catalytic properties similar to pure ceria yet exhibiting a distinctly superior sintering stability. The Pr/Al system, on the other hand, is less suited as a catalyst since the catalytic activity and sinter stability are inferior as compared to a pure praseodymia reference system.

2. Experimental

2.1. Sol–gel preparation

Rare earth–aluminum oxide aero and xerogels were prepared in analogy to the epoxide addition sol–gel method established by

Gash et al. for pure REO aero- and xerogels [12]. All reactants were reagent grade or better and used as received. The rare earth/aluminum oxide precursor mixture consisted of aluminum nitrate nonahydrate (Alfa) and rare earth (III) nitrate hexahydrate (Chempur, Karlsruhe, Germany). The ratio was chosen such that gels with 80 at-% Al and 20 at-% Ce or Pr, respectively, were obtained. 3 mmol metal salt were dissolved in 5 g of ethanol; the molar ratio of metal salt to gelling agent was 0.1. In addition to the nitrates, also chlorides were used as precursors. Here, aluminum chloride hexahydrate (Alfa) and rare earth (III) chloride hexahydrate (Chempur, Karlsruhe, Germany) were employed. As in the case of the nitrates, the metal salts were dissolved in absolute ethanol (VWR international, Germany). Propylene oxide (Sigma Aldrich) was added as gelation agent. All samples were prepared in PE vials. Following the addition of the gelling agent, the gels were aged for at least 24 h under ambient conditions. The resulting materials were then immersed in a bath of absolute ethanol. These alcogels were either processed to aerogels in a BALTEC supercritical point drier or dried under ambient conditions resulting in so-called xerogels. In the former case the alcohol in the gel was exchanged for liquid CO₂ for 3 days at about 10 °C, after which the temperature of the vessel was ramped up to about 45 °C, not exceeding a pressure of ~100 bar. The vessel was then depressurized slowly. The resulting aero- and xerogels were calcined at 650 °C or 1000 °C, respectively (4 h in air).

For comparison of the catalytic properties, pure oxides of Ce and Pr were prepared by thermal decomposition of the rare earth nitrates at 650 °C and 1000 °C (4 h in air).

2.2. Characterization

Powder X-ray diffraction (PXRD) data were acquired for the xero- and aerogel samples, using a PANalytical X'Pert MPD Pro I diffractometer in Bragg–Brentano geometry. The setup was equipped with a secondary Ni filter, Cu K $\alpha_{1,2}$ radiation and a X'Celerator multi strip detector. The temperature-dependent X-ray powder diffraction data were collected on the same diffractometer using an Anton Paar HTK1200 N heating chamber. The sample was placed using acetone on a flat corundum holder having small evaporation channels that served for optimum space during thermal expansion of the samples. Diffraction was carried out between 25 °C and 999 °C with a ramping slice of 25 °C. Each diffraction pattern was recorded from 5° to 100° 2 θ with a step size of 0.0167° and a 180 s/step total data collection time. For the data evaluation, Rietveld refinements were carried out. The fundamental parameter approach, where the fundamental parameters were fitted against a LaB₆ standard material, was applied for the Rietveld refinement using “Diffrac^{Plus} Topas 4.2” software (Bruker AXS GmbH, Karlsruhe). For this purpose the atomic coordinates of the structures were extracted from the ICSD data base (Fachinformationszentrum Karlsruhe, Germany) and fixed during the refinements.

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