Non-aqueous cross hydrolysis: an epoxide-free sol-gel route toward highly porous alumina monoliths

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Abstract

Highly porous alumina monoliths can be fabricated by simultaneous hydrolysis of aluminum alkoxides and salts as homonuclear precursors. The use of carcinogenic epoxides can thus be avoided. In this novel approach, no water is added to the system but hydrolysis is induced by the crystal water of the aluminum salt. Mechanical stabilization and significantly increased porosity values can be achieved when the sol-gel synthesis is performed in an autoclave.

Graphical Abstract

Highly porous, mechanically stable alumina monoliths via a novel epoxide-free sol-gel approach named *Cross Hydrolysis*

Keywords Alumina monoliths · Alumina xerogel · Evaporative drying · High surface area

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Highlights

- Synthesis of highly porous mechanically stable alumina monoliths.
- Simultaneous hydrolysis of aluminum alkoxide and salt as homonuclear precursors.
- Reaction takes place without an aqueous phase.

There are two different approaches in the sol-gel synthesis of porous alumina. Yoldas was the first to publish an approach using aluminum alkoxides as precursors in 1975 [1]. A patent from the University of Florida (1989) then used an aluminum salt as a peptizing agent for the alkoxide-based gel, yielding stable but non-porous alumina monoliths [2].

With less reactive aluminum salts, an epoxide-mediated route was later suggested by Gash and Baumann [3, 4]. Their approach has since been adapted and further developed by several groups [5–9].

Although this synthesis based on an aluminum salt was developed more than a decade later, the aforementioned patent [2] may be considered a combination of the Yoldas process [1] and the epoxide-mediated synthesis [3, 4]. This approach was further studied by the groups of Dressler and Nofz [10, 11]. When regarded as starting from the aluminum salt, this process may also be described as the replacement of the carcinogenic epoxide by an aluminum alkoxide. As the cited works all operate in an aqueous medium, this inspired our attempt to omit the aqueous phase, and further extend this combined alumina sol-gel route to the fabrication of highly porous monoliths.

In our approach, the synthesis takes place in a polar but non-aqueous medium, i.e., no water is added to the reaction solution. Hydrolysis of the alkoxide is hence only induced by the crystal water of the aluminum salt, while the alkoxide simultaneously takes on the role of a proton scavenger. Both precursors hence mutually hydrolyze each other in a concerted reaction. We name this novel process *cross hydrolysis*.

Upon dissolution, the aluminum salt dissociates into solvated anions and aluminum-hexaaqua-complexes $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, due to the presence of crystal water in the salt. These hexaaqua-complexes are in equilibrium with the deprotonated form, rendering the medium acidic, as Eq. 1 in Fig. 1 shows. However, the recombination of two pentaqua-hydroxo-complexes into a dimer does not occur voluntarily. Instead of the commonly used carcinogenic epoxide, an aluminum alkoxide is now employed. Complete hydrolysis of the alkoxide occurs immediately through a nucleophilic substitution of the OR-groups by excess crystal water from the salt precursor (Eq. 2 and 3). As the salt precursor solution is strongly acidic (pH 0.5), the colloidal $\text{Al}(\text{OH})_3$ is rapidly redissolved and peptized to form an alumina sol (Eq. 4), according to the Yoldas process [1]. Subsequently, hydrolytic olation between the sol particles,

which may contain only a few aluminum ions, and the aluminum-aquo-hydroxo-complexes now takes place. These primary particles interconnect to eventually yield an alumina network structure as depicted in the SEM images in Fig. 2.

With regard to the specific experimental procedure, equal masses of aluminum-tri-*sec*-butoxide $\text{Al}(\text{OC}_4\text{H}_9)_3$ and aluminum nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, corresponding to a molar ratio of 3:2, were dissolved in equal amounts of ethanol and 2-propanol. The sol-gel synthesis was then performed in an autoclave at 100 °C for 24 h, yielding an intact cylindrical lyogel. This is transformed into a mechanically stable monolithic xerogel after drying via a twofold solvent exchange with acetone and pentane. Both solvents exhibit high vapor pressures of 33.0 kPa and 73.5 kPa, respectively, at 300 K, which significantly reduces capillary stress within the pores during the drying process¹.

Fig. 1 Scheme of postulated reactions taking place in the solution to form dimeric aluminum-aquo-hydroxo-complexes from both precursors

Fig. 2 SEM images and inserted photographs of porous alumina monoliths synthesized via cross hydrolysis of aluminum nitrate and aluminum-tri-*sec*-butoxide. Calcination temperatures were 600 °C (left), and 1200 °C (right), respectively

¹ The solvents hitherto employed in the drying process, ethanol and 2-propanol, exhibit vapor pressures of only 9.1 or 6.5 kPa, respectively, at 300 K.

Fig. 3 N_2 sorption isotherms of a γ - Al_2O_3 monolith calcined at 600 °C for 6 h (adsorption in black, desorption branch in red). The inset shows the differential pore width distribution with a modal pore diameter of 35.0 nm, calculated from the adsorption branch with the DFT method

Upon calcination at 600 °C, the dimensions of the cylindrical monoliths were 10 mm in height and 25 mm in diameter, whereas calcination at 1200 °C reduces these values to 6 mm and 15 mm, respectively. Phase evaluation by XRD revealed moderately crystalline γ - Al_2O_3 for the samples calcined at 600 °C, and pure α - Al_2O_3 for those calcined at 1200 °C. Both results are in accordance with the expected phase compositions² [12].

Microstructural characterization of the γ - Al_2O_3 and α - Al_2O_3 monoliths was performed by mercury intrusion, nitrogen sorption, and SEM imaging³. The γ - Al_2O_3 monolith exhibits a pore volume of 4.17 cm³/g, calculated from the N_2 sorption measurement. The corresponding type IVa isotherm in Fig. 3 exhibits an almost perfect H1 hysteresis loop, indicating a mesoporous material with a narrow pore width distribution. A modal pore diameter of 35.0 nm was determined using the DFT method, as shown in the inlay in Fig. 3.

Due to the completed α -transition at 1200 °C, the porosity decreases, resulting in a pore volume of 0.44 cm³/g for the α - Al_2O_3 monolith. The pore diameter is shifted to 165 nm. Both values were calculated from the mercury intrusion data⁴. Consequently, the specific surface area determined by the BET method also decreases from 422 m²/g for the γ - Al_2O_3 monolith to 11 m²/g for the α - Al_2O_3 monolith. For porous alumina, these porosity values are already among the highest ones achieved to date [12]. Ongoing studies concentrate on the optimization of the procedure with special focus on the gel

formation as a key point of the synthesis. Moreover, variation of the synthesis parameters as well as the introduction of additives might not only alter but also further increase the porosity of the described alumina monoliths.

In conclusion, this communication presents an important step forward in the sol-gel synthesis of porous alumina monoliths. As described before by other groups, an aluminum salt and an aluminum alkoxide are employed as two homonuclear precursors [2, 10, 11]. In our approach, this was done without an aqueous phase for the first time, using ethanol and 2-propanol as a polar and acidic medium. The use of a carcinogenic epoxide to initiate hydrolysis is unnecessary, as both precursors readily hydrolyze each other. Moreover, mechanically stable gels can be reliably produced using an autoclave for the gel formation process. As the result of a meticulous solvent exchange and drying procedure, crack-free xerogels are obtained. These are convertible into different alumina modifications by an adequate calcination step. The omission of the carcinogenic epoxide as well as the improved procedure to fabricate porous alumina monoliths represent significant advancements in the sol-gel synthesis of alumina.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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² XRD patterns are plotted in Fig. S1

³ Experimental details on both the synthesis and characterization methods can be found in the ESI.

⁴ The corresponding mercury intrusion dataset is plotted in Fig. S2.

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