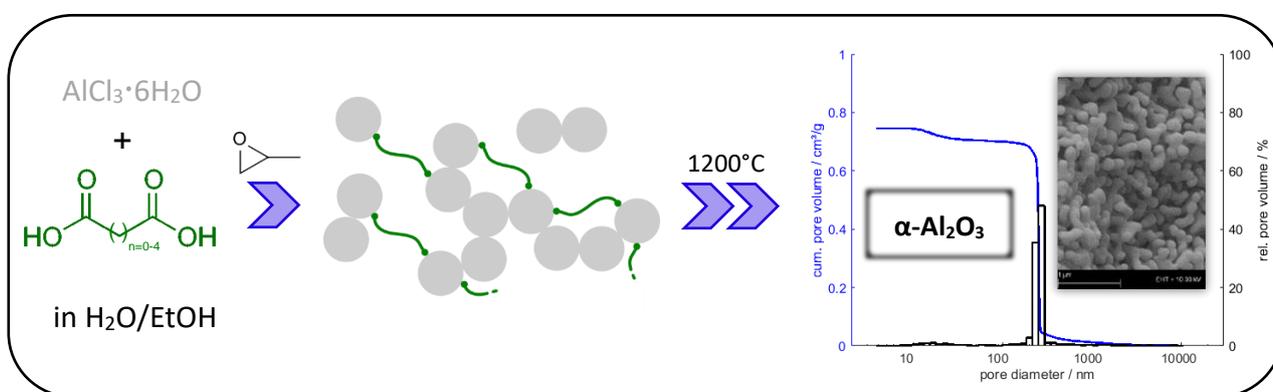


## Novel sol-gel approaches towards highly porous $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

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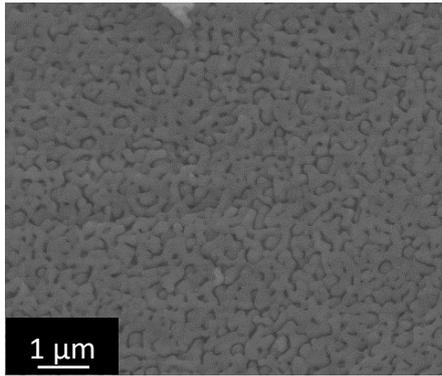
Aluminum oxide is being widely used as catalyst support, typically in its easily manageable  $\gamma$ -modification. However, in certain applications, e.g., catalytic cracking or emission reduction in combined heat and power units, catalysts can be subjected to temperatures as high as 1000°C. This brings about certain issues such as sintering, phase transition or spalling of the wash coat, all of which subsequently lead to deactivation of the catalyst.



In order to develop a refractory alumina apt for catalytic applications, inherently non-porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> needs to be rendered porous in a controllable way. The graphical abstract above shows an adaption of the well-established epoxide-mediated sol-gel process from dissolved aluminum salts, [1] which yields much more porous products when organic carboxylic acids are employed. Pore volumes can be increased from 0.12 to > 1.0 cm<sup>3</sup>/g, with pore diameters in the range of 115 nm to several  $\mu\text{m}$  in the pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, obtained after calcination at 1200°C. [2,3] During this modified sol-gel process, the pore building mechanism is altered by the formation of carboxylate-Al(III)-oligomers, as revealed by thermal analyses, NMR studies, and XRD results [3].

### Mutual cross-hydrolysis: a novel, epoxide-free approach

In a novel approach, the cancerogenic epoxide is rendered obsolete by mutual cross-hydrolysis of an aluminum alkoxide and an aluminum salt. This route has been utilized before to synthesize bimetallic oxides, e.g. yttria-alumina [4].



Upon dissolution, the aluminum salt dissociates into solvated anions and  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  complexes. In a concerted, simultaneous cross-hydrolysis, the Al-hexaaqua-complexes are then hydrolyzed by the much more reactive alkoxide, while at the same time the alkoxide is also hydrolyzed in the strongly acidic medium by nucleophilic substitutions of protonated

OR-groups by water. It hence disproportionates into  $[\text{Al}(\text{OH})_n(\text{H}_2\text{O})_{6-n}]^{(3-n)}$  complexes and solvent molecules. The Al-complexes undergo hydrolytic oxolation, yielding (upon drying and calcination at 1200°C) an alumina network quite similar to the one obtained during the classic sol-gel process, as shown by SEM imaging.

## References

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