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Synthesis and characterization of carbon-coated calcium aluminate aerogels

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Introduction

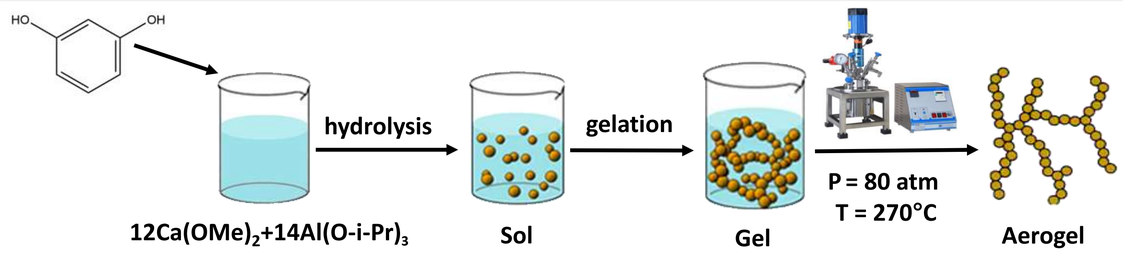
Calcium aluminate $12CaO•7Al_2O_3$ (commonly denoted as C12A7), also known as mayenite, is an object of particular scientific interest. This material possesses a number of rather peculiar physical and chemical properties originally described in detail by Hosono et al. [1]. Its structure includes a cationic framework $[Ca_{24}Al_{28}O_{64}]^{4+}$ compensated by the presence of an anionic lattice $4X^-$.

High specific surface area and developed pore structure are among the key requirements for efficient use of materials as catalyst supports or adsorbents. The aerogel technique involving supercritical drying of a gel is one of effective ways for synthesis of finely dispersed materials including calcium aluminates of various stoichiometry [2,3].

One of significant limitations for application of metal oxide nanomaterials as catalysts or adsorbents is their tendency to adsorb water, which gradually leads to deactivation. In addition, various phase transformations accompanied by considerable sintering of the material can occur at elevated temperatures. One of the prominent ways to solve these problems is coating of metal oxide particles with porous carbon. Carbon coating eliminates direct contact between different metal oxide nanoparticles considerably enhancing the thermal stability of the material [4].

In this study, resorcinol added to the reaction mixture before the hydrolysis step was used as an organic precursor for deposition of a carbon coating on the surface of finely dispersed calcium aluminate. The samples after different temperature treatment were characterized using low temperature nitrogen adsorption and X-ray diffraction analysis. The morphology of carbon-coated calcium aluminate was studied via transmission electron microscopy.

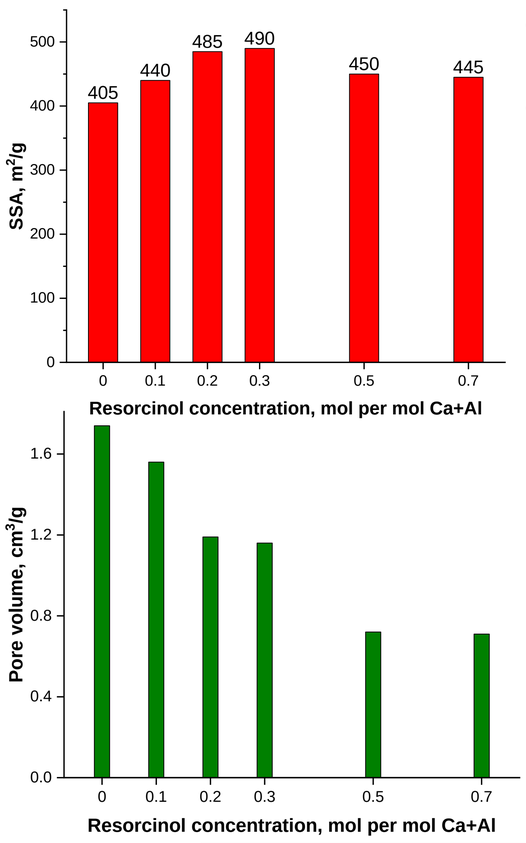
Synthesis method



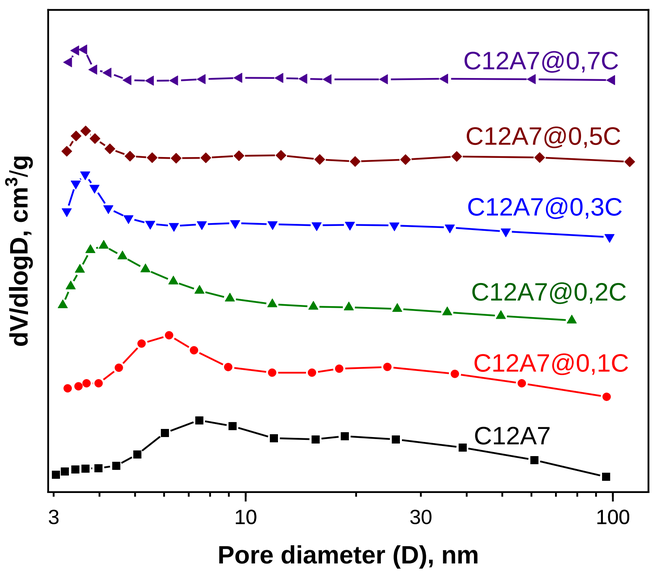
Aluminum isopropoxide and calcium methoxide were used as precursors for the synthesis of calcium aluminate aerogel with mayenite stoichiometry. These alkoxides were dissolved in a mixture of methanol and isopropanol with addition of toluene which acts as gelation accelerator. The resulting solution was subjected to hydrolysis with stoichiometric amount of deionized water, followed by aging for 16 hours and drying in an autoclave at 270°C. For synthesis of the organic-modified samples desired amount of resorcinol was added to the reaction mixture prior to the hydrolysis step. The resulting samples were denoted as C12A7@nC, where n stands for molar resorcinol concentration normalized to the sum of calcium and aluminum concentrations in moles. To obtain the carbon coating, resorcinol-modified aerogels were treated in an argon flow at high temperatures.

Textural properties

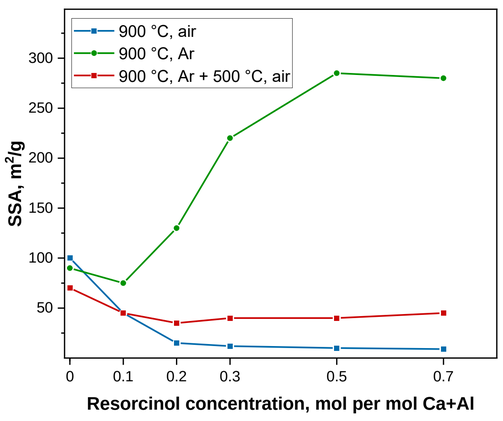
After supercritical drying at 270°C



- Addition of resorcinol increases the SSA up to 490 m^2/g after drying in autoclave at 270°C.
- The higher resorcinol concentrations favor formation of smaller (4-9 nm) pores and lead to the decrease of the total pore volume.

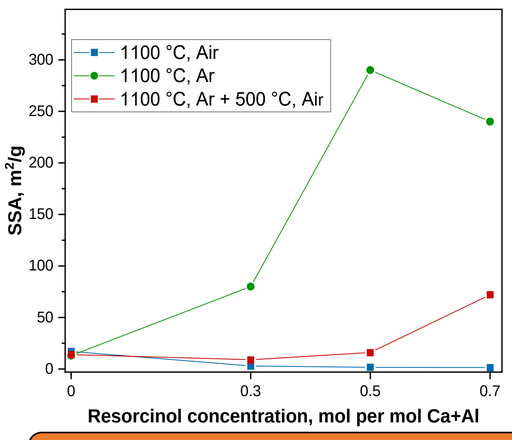


After treatment at 900°C under different atmospheres



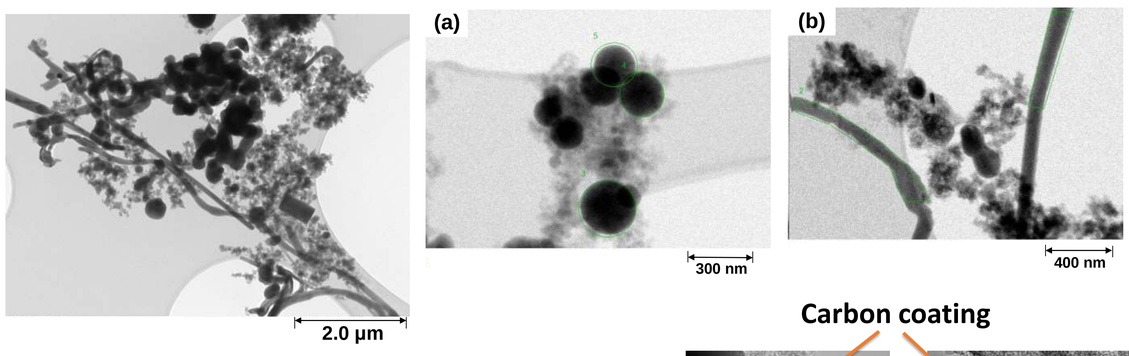
- Annealing of the resorcinol-modified samples in an air flow leads to considerable decrease of the observed SSA values.
- After treatment at 900°C in an argon flow a significant enhancement of the surface area was observed with increasing amount of resorcinol. It indicates that the formation of a carbon coating during the resorcinol pyrolysis in the inert atmosphere prevents sintering.

After treatment at 1100°C under different atmospheres



- Direct burnout of organic additives leads to the collapse of the porous structure and yields the very low SSA (~2-3 m^2/g)
- After treatment at 1100°C in an argon flow with subsequent burnout of carbon at 500°C, sample with the highest resorcinol concentration (C12A7@0.7C) demonstrates considerably higher thermal stability compared to the pristine C12A7 sample.

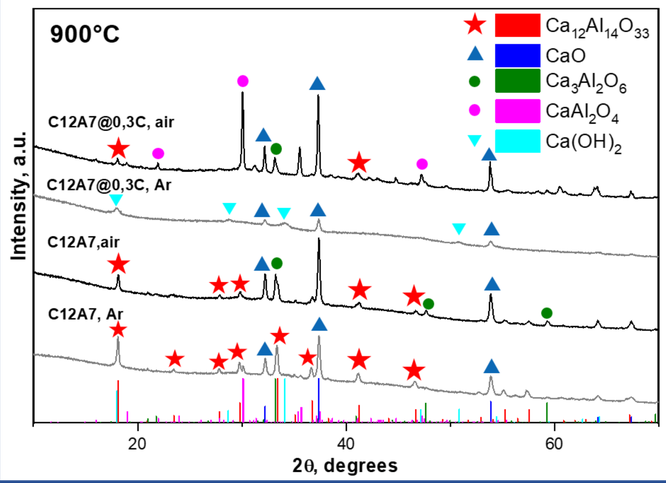
TEM images of C12A7@0.7C



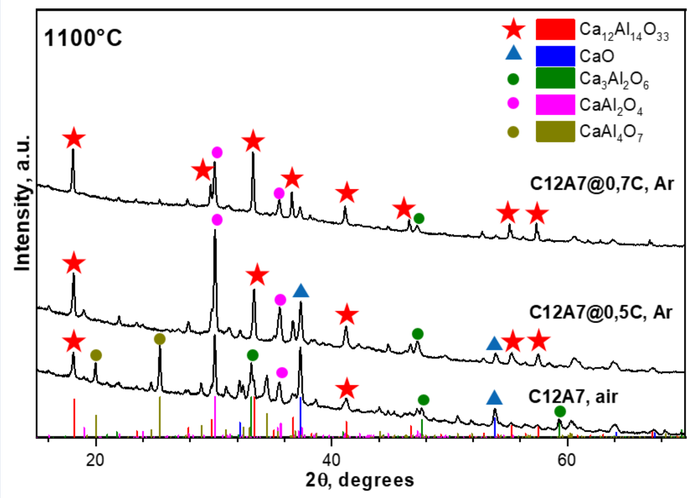
Molar Al/Ca ratio according to EDX results	
spherical particles (a)	whiskers (b)
2,2	1,9

- **TEM images of the C12A7@0.7C sample indicate that it consists of carbon-coated particles of different sizes and shapes, including spherical particles (a) and whiskers (b).**
- **EDX analysis reveals that the elemental composition of these two kinds of particles closely resembles the composition of the $CaAl_2O_4$ phase implying that the mayenite phase ($Ca_{12}Al_{14}O_{33}$) may be present in this sample in the form of smaller particles.**

XRD patterns



- None of the crystalline mixed calcium-aluminum phases were observed for the C12A7@0.3C sample after its treatment under Ar atmosphere probably due to the small size of particles.
- Other samples contain various calcium aluminate phases along with CaO in different proportions.



- Resorcinol-modified samples exhibit higher relative content of the mayenite phase and lower content of CaO after treatment at 1100°C in an argon flow compared to the pristine C12A7 sample.
- The XRD patterns of carbon-coated samples remain almost unchanged after subsequent burnout of carbon at 500°C

Conclusions

✓ A series of the resorcinol-modified calcium aluminate samples with mayenite stoichiometry were prepared using the aerogel technique. The surface area of resorcinol-containing aerogels after the autoclave drying was as high as 490 m^2/g.
✓ A stabilization of the porous structure of the resorcinol-modified samples after treatment at 900°C and 1100°C in an argon flow was observed
✓ The formation of the amorphous carbon coating through resorcinol pyrolysis was confirmed by TEM.

Literature

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[2] E.V. Ilyina, Y.Y. Gerus, S.V. Cherepanova, A.F. Bedilo. Synthesis of C12A7 calcium aluminate aerogels. *Mater. Lett.* 293 (2021) 129699.
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