Report ÅForsk

Dopningsmekanismer i nanoporösa material

Proj. nr. 18-566

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Summary of results:

The project aimed to synthesize mesoporous silica of SBA-15 type doped with catalytically active elements, such as Zr and Zn and study the formation process in situ. The results show that substituting Si with other materials is a difficult task and even though Zr can be added up to a Zr/Si molar ratio of 0.1, doping with Zn and other elements such as Ni, Co, Cr and Fe only provide trace amounts of the active element. Cu can however be doped into the material with approximately Cu/Si molar ratio of 0.02. Various synthesis parameters, such as metal salt concentration, salt addition time, type of salt, and mixing rate were tested. However, it was not possible to increase the Cu concentration further. The formation of the materials were studies using in situ attenuated total reflectance. It was observed that the addition of a metal salt slightly decreases the material formation rate, but no changes in the silica structure could be observed. Doped mesoporous silica films were successfully grown on silicon wafers using the Direct Growth method.

Project organization

The project was carried out at within the Nanostructured Materials division at Linköping University by Dr. Emma Björk (P.I, project design, materials synthesis and characterization, data analysis and interpretation) with the support of postdoc Bernhard Baumann (experiments with Cu, data analysis).

Project results

The fundamental research question in this project was how the metal ions are integrated into the mesoporous silica framework. The aim was to find the incorporation mechanisms and study how they affect the catalytic activity of the material.

Deviation from the project plan

The project aimed to study the formation of mesoporous silica doped with Zr and Zn, in order to understand how the formation process affects the catalytic activity. The doping with Zr had been performed earlier and the reports from Atakan et al were followed. However, substituting the Zr with other metals was not a trivial task. Several metals were tested, e.g. Ni, Fe, Co, Cr, etc. but this this only resulted in trace amounts of metals as detected with EDX. Cu could however be introduced with a Cu/Si molar ratio of 0.02, and this metal was used to study the doping process.

Main research results

Doping mesoporous silica of SBA-15 type is a limited process. Cu could be doped into SBA-15 to a Cu to Si molar ratio of 0.02. Different types of salts ($CuCl_2$, $Cu(NO_3)_2$, $CuSO_4$, and $Cu(CH_3COO)_2$ were used. Electron microscopy (SEM and TEM) showed that the particle morphology and pore structure remained unaffected by the doping, and that the particles had a platelet shaped morphology with hexagonally ordered pores running between the large flat surfaces. The specific surface area of the material increased from ~800 m^2/g to ~850 m^2/g when a Cu salt concentration corresponding to a Cu/Si molar ratio of 0.2 was used. The specific surface area was further increased to > 900 m^2/g when the Cu/Si molar ratio increased to > 0.7. At the same time the pore size increased from 9.1 nm to ~10.5 nm when Cu was introduced. This indicates that the Cu affect the formation of the silica. The salt addition time was altered between 30 min prior to the addition of the silica precursor and to 30 min after the addition of the silica precursor, as well prior to the hydrothermal treatment when the silica structure is completed. The largest amount of Cu was observed when the salt was added 10 min prior to the addition of the silica precursor. Elemental mapping in TEM showed a homogenous Cu distribution in the silica particles.

The formation of the Zr and Cu doped materials was studied with in situ ATR. No change in the final spectra of the materials could be observed, i.e. there is no change in the silica structure upon addition of a metal salt, and no new bands are visible. However, there is a decrease in the formation rate when the metal salts were added. The same trend can be observed for all types of metal salts. The decrease in formation rate can be the reason for the increased surface area, as the decreased condensation rate enables a higher degree of interaction between of the hydrophilic parts of the micelles and small silica clusters prior to the formation of the less flexible silica network.

Finally, the doped materials were grown on silicon wafers and Ti-foil. The usage of Ti-foil enabled elemental analysis of the films using EDX without additional Si signal from the substrate. It was observed that the films have the same chemical composition as the powders, and we can therefore conclude that it is possible to grow doped films using the direct growth method.

Continuation

As the doping of mesoporous silica of SBA-15 type was not successful, and therefore other mesoporous silica system can be studied to observe if pH or other types of surfactants (e.g. cationic or anionic) can benefit the doping process. The work on studying the formation process of undoped MCM-41 synthesized at basic conditions with a cationic surfactant and KIT-6 which is a less acidic synthesis compared to SBA-15 is currently ongoing.