Structure effects of supported silver catalysts prepared via melt infiltration in the selective hydrogenation of cinnamaldehyde

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Silver catalysts are industrially used amongst others to produce formaldehyde from methanol, and to selectively oxidize ethylene to ethylene oxide [1]. Moreover, silver has promising catalytic properties for the selective hydrogenation of α,β-unsaturated aldehydes [2]. Supported silver catalysts are generally synthesized using precipitation or impregnation routes. As an alternative technique we explore melt infiltration: we heat a physical mixture of silver nitrate and a porous support, in this case SBA-15, above the melting point of silver nitrate, which then enters the pores as a result of capillary forces. Advantages are that catalysts with high metal loadings can be obtained and dissolution of the precursor salt is not needed [3].

The narrow pore size distribution of the chosen ordered mesoporous silica support, SBA-15, allowed us to study the infiltration process using differential scanning calorimetry, by measuring the heat loss or gain during phase transitions. Subsequently, the silver nitrate was decomposed to obtain supported silver nanoparticles or nanorods. The well-defined pore structure, and hence absence of support irregularities, allowed control over the silver size and shape. Both transmission electron microscopy and in-situ X-ray diffraction were used to follow the decomposition process. By varying the decomposition conditions (temperature and atmosphere), either long silver nanowires or small spherical silver particles inside the mesopores of the SBA-15 were obtained, while a few large silver particles were present on the external surface area.

We investigated the influence of structure and size in Ag-catalyzed liquid phase hydrogenation of cinnamaldehyde. In this α,β-unsaturated aldehyde, both the C=O and the C=C bond can be hydrogenated. We found that the silver wires are more selective towards the hydrogenation of the C=O bond, which gives the desired cinnamyl alcohol, than spherical silver particles. Claus et al. reported the structure sensitivity of silver particles in the hydrogenation of a similar α,β-unsaturated aldehyde, crotonaldehyde, by using gas phase reactions [2]. Similar to their findings, we propose that also in liquid phase catalysis, silver shows a higher selectivity towards the hydrogenation of the C=O bond on the silver wires, which are proposed to expose more Ag(111) surfaces, than spherical particles with more edge sites.

Transmission electron microscopy images of the silver catalysts obtained after reduction of the silver nitrate in hydrogen.


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