Catalytic conversion of glycerol with reduced Co_2AlO_4 nanoparticles produced by flame spray pyrolysis

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Keywords: flame spray pyrolysis, Co, Al_2O_3, Co catalyst, activation
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Biodiesel is currently one of the most important biofuels (Martino et al., 2008). However, about 10-wt% of glycerol is formed as a by-product during the transesterification process of vegetable oil to biodiesel (Zhou et al., 2008). Therefore the catalytic conversion of glycerol to added value chemicals has been intensively studied.

The catalytic-alumina particles are typically prepared in a solution followed by thermal treatments in air (Dumond et al., 2007). However, the thermal treatments are likely to induce migration of cobalt into alumina forming an aluminate spinel that cannot be reduced below 800 ºC. Co_3O_4 and γ-Al_2O_3 also have isotype crystal structures which enables the migration of ions from cobalt oxide into the underlying support. The optimization of dispersion and degree of reduction is therefore demanding.

In the current study Co_2AlO_4 nanoparticles were synthesized using flame spray pyrolysis (FSP). In order to activate Co particles the produced powder was reduced using a temperature programmed reduction (TPR) at 850 ºC for 1h. The catalytic activity of the powder was then tested for glycerol hydrogenolysis using a quartz fixed bed down flow reactor at 573 K for 6h. The properties of the powder were characterized before and after the reduction using electron microscopy and X-ray diffraction. The surface characterization was carried out using X-ray photoelectron spectroscopy.

According to BET analysis the total surface area of the as-synthesized Co_2AlO_4 powder was around 174 m^2/g with a mean pore diameter of 10 nm. Figure 1A show a TEM images of the produced particles. The particles were spherical with the particle size between 50 nm and 200 nm. The particle surface consists of Co, Al and O. The atomic ratio of Co/Al on the surface is 0.27 which is lower than ratio of nominal $CoAl_2O_4$ (0.5).

A TEM image of the reduced powder is shown in Figure 1B. The appearance of Co nanoparticles with sizes between 3 and 8 nm can be observed, as well as the formation of shell-like. The reduction also caused a significant decrease in Co/Al atomic ratio down to 0.11. This indicates the reduction of exposed Co atoms in the aluminate to metallic Co.

Based on the TPR profile the reduction of $CoAl_2O_4$ is a two stage process. At temperatures between 200 and 250 ºC Co_3O_4 is first reduced to CoO which is then further reduced to metallic Co. The second stage of the reduction takes place at temperatures between 500 and 800 ºC. At this temperature range the oxidized cobalt species (Co^{2+} and Co^{3+}) which are strongly interacting with the support are reduced to metallic Co (Arnodly and Moulijin, 1985).

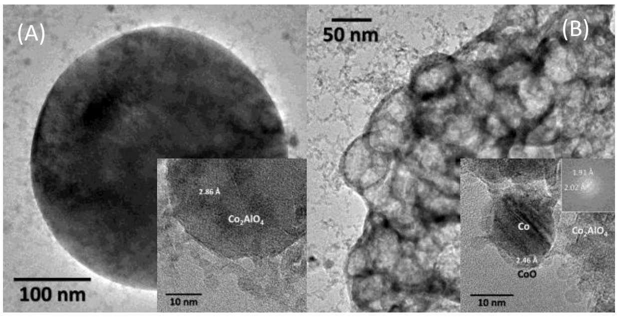

Figure 1. TEM images of the Co_2AlO_4 particles (A) as-synthesized and (B) after the reduction.

The reduced Co_2AlO_4 consisting of Co and Al_2O_3 was observed to promote dehydration and dehydrogenation of glycerol. The main products were hydroxyacetone, lactic acid, and lactide. However, the glycerol conversion dropped from 80 % to around 35 % after 4 h of reaction, indicating deactivation of the catalyst. The deactivation is most likely due to the deposition of carbon species on the surface of the catalyst powder during the dehydration reactions.

This work was supported by the strategic funding of the University of Eastern Finland (Namber).

P. Arnoldy and J.A. Moulijn (1985) *J. Catal.* **93**, 38.
F. Dumond et al. (2007) *J. Phys. Chem. C* 111, 4780.
D.S. Martino et al. (2008) *Energy Fuels* **22**, 207-217.
C.H. Zhou et al. (2008) *Chem. Soc. Rev.* **37**, 527-549.