

Title: The role of spinel in copper nanoparticle formation

Michelle Hammerton, David Martin, Moniek Tromp (University of Amsterdam)
m.hammerton@uva.nl

1. Introduction

Copper chromite spinel (CuCr_2O_4) based materials are industrially proven hydrogenation catalysts, exhibiting both chemical and mechanical stability under reaction conditions. However, besides the main Cr(III) component, these catalysts can contain carcinogenic Cr(VI), so alternative Cr-free catalysts are currently being sought. This research seeks to gain a more fundamental understanding of how the structure of these Cr-free oxides affects the activation to the hydrogenation catalyst by reduction in hydrogen to form Cu nanoparticles (NP), thought to be the active site of catalysis.

2. Experimental methods

Cu K-edge (8979 eV) and Cr K-edge (5989 eV) x-ray absorption spectroscopy (XAS) measurements were conducted in-situ during catalyst activation up to $K = 16$ Angstroms. XANES data were analysed using Linear Combination Fitting (LCF) of reference components to determine the changing composition of the catalyst during reduction. EXAFS were modelled using scattering paths generated from crystallographic data. The model of the reduced catalyst was used to estimate the average coordination number (N) of the first shell of copper atoms in the metal NP formed on the catalyst surface. This coordination number was used to calculate the NP size in terms of number of atoms and diameter.

3. Results and Discussion

Cu(II) in CuO and spinel phases was observed to undergo reduction in one step to predominantly Cu(0) and a small percentage of Cu(I), with very little Cu(II) remaining in spinel in the reduced catalysts. Catalysts with greater spinel character were reduced at higher temperatures compared to those consisting of different mixed crystalline and amorphous oxide phases. Cr(III) was not reduced under these conditions XANES measured before and after activation were very similar.

The copper NP formed by reduction in hydrogen were measured between 80 and 360 atoms, or 1.4 and 2.4 nm. However, this method of estimating NP size is only accurate below 200 atoms, as the correlation between N and the number of atoms (n) becomes less pronounced whereas the error remains large at high n. Pure CuAl_2O_4 spinel was observed to produce the smallest nanoparticles, whereas the industrial $\text{CuO.CuCr}_2\text{O}_4$ (copper oxide on copper chromite spinel) catalyst produced the largest.

Catalysts with spinel as the majority phase before reduction were observed to form smaller NP on reduction. However, where a CuO phase was present or Cu(II) was not observed in a spinel structure, larger Cu NP were observed. After reduction, smaller NP were observed in Cr-free than in Cr-containing catalysts, although similar levels of Cu(0) were formed. The majority of Cu(II) in $\text{CuO.CuCr}_2\text{O}_4$ was not observed have spinel local structure, whereas Cr(III) was predominantly coordinated by spinel. It is likely that this catalyst consists of a complex mixture of different copper oxide phases, and therefore resulted in the largest NP size.

4. Conclusions

The size of metal NP in activated copper spinel based hydrogenation catalysts seems to depend on the amount of spinel character of the catalyst before it is reduced. Cr-free catalysts have greater spinel character than the industrial $\text{CuO.CuCr}_2\text{O}_4$ catalyst and form, smaller but likely more numerous NP. The difference in the NP:spinel interfacial area between Cr containing catalysts and Cr-free alternatives could explain differences in catalyst activity.

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