

Enhancing the Stability of Copper Chromite Catalysts for the Selective Hydrogenation of Furfural Via ALD Overcoating

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Introduction

Copper chromite ($\text{CuCr}_2\text{O}_4 \cdot \text{CuO}$), due to its mild catalytic reduction properties, has been used extensively for years in various industrial processes such as the partial hydrogenation of vegetable oils and fatty acids [1]. The advantage of this catalyst for hydrogenation reactions stems from its ability to selectively hydrogenate carbonyl bonds while leaving unsaturated C=C bonds virtually untouched. This catalyst has also been used for the reduction of furfural due to its high activity and selectivity to furfuryl alcohol [2]. Unfortunately, copper chromite catalysts suffer severe deactivation under the normal working conditions. Our recent results have shown that coke formation along with chromite migration over the active sites of Cu is the major cause for deactivation of the Cu-chromite catalyst in the gas phase reduction of furfural [3].

Recently, Dumesic [4] and coworkers found that atomic layer deposition (ALD) Al_2O_3 overcoating can suppress the deactivation of Cu caused by sintering and leaching of the metal under trickle bed conditions. In this work, *in situ* and operando X-ray absorption methods were used to elucidate the mechanism of alumina ALD overcoating of Cu nanoparticles and the effect of ALD overcoatings against vapor phase furfural reduction reactions over Cu-chromite. Different numbers of ALD Al_2O_3 cycles were performed on the Cu catalysts to vary the thickness of the protective overcoats and evaluate the effect of thickness on the Cu reduction and the furfural hydrogenation reaction. XANES analysis shows that $\text{Cu}^{1+}/\text{Cu}^0$ are the active species for this reaction.

Materials and Methods

ALD Coating. ALD was performed in a viscous flow reactor. 0.5 g Cu-chromite powder was spread uniformly onto a stainless steel sample plate with a mesh top to contain the powder. The Cu-chromite catalyst was coated with 10, 20, 30 and 45 ALD cycles of Al_2O_3 . The Al_2O_3 ALD used alternating exposures to trimethyl aluminum (TMA) and deionized water at 200°C.

XAFS Measurements. *In situ* x-ray absorption measurements at Cu K-edge (8,980.48 eV) were conducted at the Materials Research Collaborative Access Team (MRCAT) 10ID (insertion device) and 10BM (bending magnet) at the Advanced Photon Source (APS) at Argonne National Laboratory. Cu-K edge XAS spectra were collected in transmission mode with minimum data point interval of 0.5 eV.

Results and Discussion

During furfural hydrogenation, each catalyst created only two products: furfuryl alcohol (the desired product) and 2-methyl furan (a known by-product). Lower activity for furfural hydrogenation resulted in higher selectivity to furfuryl alcohol. Severe catalyst

deactivation was observed for the commercial Cu-chromite [3]. Furfural conversion dropped from 100% initially to 30% within 3 hours. Compared to the uncoated Cu-chromite, all of the ALD overcoated catalysts exhibited improved stability for furfural hydrogenation. As expected, the catalytic activities decreased with increasing ALD Al_2O_3 coating thickness. However, the ALD coated catalysts remained more active with time on stream. The stability of the ALD Cu-chromite-10c (10 ALD cycles of Al_2O_3) is much higher than that of the Cu-chromite. More interestingly, addition of 45 ALD cycles of Al_2O_3 resulted in zero deactivation within the 5 h run time. The improved stability of the ALD catalysts may be due to the unique microporosity properties within the ALD Al_2O_3 layers, which has proven to be effective for minimizing coke formation [5].

Figure 1 shows the H_2 -TPR profile for the Cu-chromite and ALD Cu-chromite-45c samples. The uncoated Cu-chromite can be fully reduced to Cu^0 below 250 °C, much lower

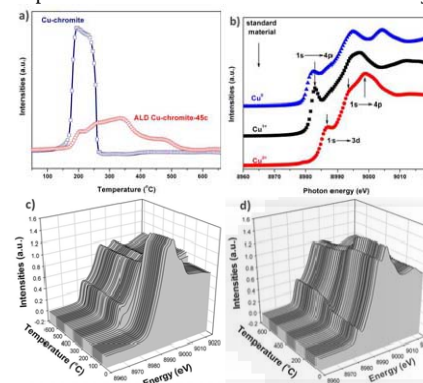


Figure 1. (a) TCD signal trace during the H_2 -TPR of Cu-chromite and ALD Cu-chromite-45c; (b) XANES spectra of standard Cu^{2+} , Cu^{1+} and Cu^0 ; stacked normalized Cu K-edge XANES spectra of (c) Cu-chromite and (d) ALD Cu-chromite-45c collected during the *in situ* H_2 -TPR.

completely reduced until about 650 °C (figure 1d) providing further evidence for the formation of copper aluminate at the interface. The different concentrations of Cu^{2+} , Cu^{1+} and Cu^0 between the ALD catalysts and the bare Cu-chromite catalyst after reduction influences the activation energy of the reaction while the formation of copper aluminate may retard the deactivation of Cu-chromite during the reaction.

References

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