Manganese promoter effects in copper-based ester hydrogenation catalysis

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Abstract: Promoted copper-based catalysts are widely applied for the industrial hydrogenation of various oxygenates, however the promoter effects are not yet fully understood. Manganese oxide was studied as an efficient promoter for the catalytic hydrogenation of ethyl acetate to ethanol. We developed a method to deposit well-defined and highly dispersed copper-manganese-oxide nanoparticles onto graphitic carbon supports. Similar particle sizes could be obtained over a wide range of manganese concentrations. These catalysts are being used to investigate the effects of promoter loading upon catalytic activity. Using carbon as an inert support will allow in-depth studying of the promoter effects for this important reaction.

Keywords: Ester hydrogenation, Cu-based catalysts, Promoter effects.

1. Introduction

Catalytic ester hydrogenation is an important industrial process for the bulk production of various alcohols. Examples of particular current interest include the formation of ethylene glycol, methanol and ethanol as versatile platform chemicals. Copper-based catalysts are widely applied for these hydrogenation reactions. Addition of promoters is often crucial to enhance catalytic activity, selectivity and stability. Promoters may induce structural and electronic effects or create a new type of active sites.[1] Manganese oxide (MnO_x) is proposed as a more environmentally-friendly replacement for the widely used chromium promoter.[2] However, the MnO_x promoter effects are not yet fully understood.

In this project, we study the MnO_x promoter effects for Cu-based hydrogenation catalysis. A strong tool is the use of inert graphitic carbon supports, which have a tunable surface chemistry and a weak interaction with the active metals, facilitating characterization and fundamental studies.[3] We present the preparation of well-defined $CuMnO_x$ nanoparticles on carbon supports, with various amounts of promoter and are currently evaluating their performance in the catalyst hydrogenation of ethyl acetate to ethanol.

2. Experimental

$CuMnO_x$ nanoparticles were deposited using co-impregnation of the graphitic carbon support (~ 500 $nm^2\ g^{-1}$ BET surface area, ~ 0.7 mL g^{-1} total pore volume) with a mixed aqueous solution of $Cu(NO_3)_2$ and $Mn(NO_3)_2$, followed by drying and heat treatment under H_2-containing flow to 400 °C. Catalysts were mainly characterized by (scanning) transmission electron microscopy ((S)TEM), energy-dispersive X-ray spectroscopy (EDX) and temperature-programmed reduction (TPR). The performance of the $CuMnO_x$ catalysts is being investigated for the gas-phase hydrogenation of ethyl acetate to ethanol, at 30 barg reaction pressure and 180–210 °C reaction temperature.

3. Results and discussion

A method was developed to prepare highly dispersed, well-defined $CuMnO_x$ nanoparticles using facile and scalable co-impregnation of the graphitic carbon supports with the mixed metal precursor aqueous solution, followed by drying and thermal treatment to decompose the metal precursors (Fig. 1 A). With constant Cu loading and increasing Mn loadings, we achieved similar $CuMnO_x$ nanoparticle sizes over a

wide range of Mn concentrations (Fig. 1 B). Analyses by TPR and STEM-EDX indicate close contact between Cu and MnO_x, essential to efficiently induce the promoter effects (Fig. 1C).

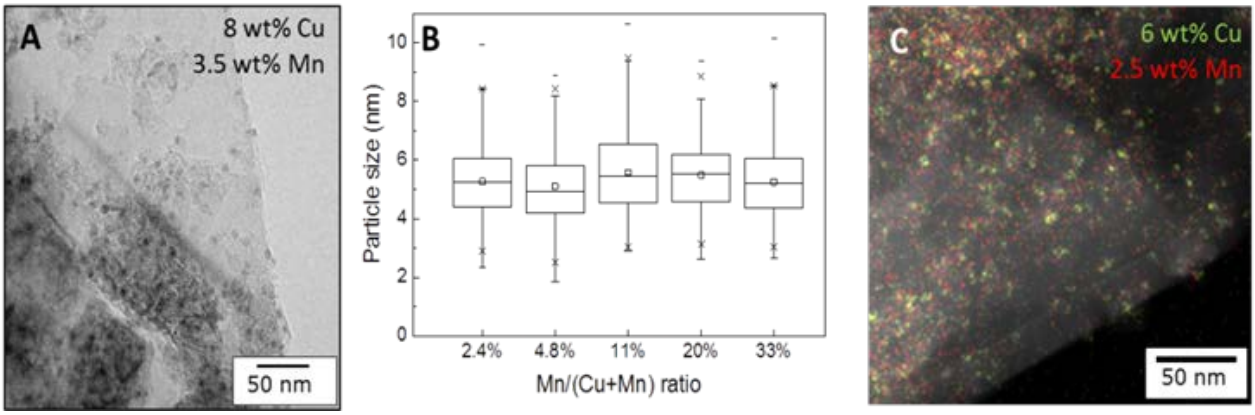

Fig. 1: *(**A**) TEM image of well-defined $CuMnO_x$ nanoparticles; (**B**) Particle size distribution from TEM analysis of Cu-based catalysts with increasing Mn promoter concentrations; (**C**) STEM-EDX image of Cu (green) and Mn (red) distributions on carbon.*

The influence of MnO_x promoter concentrations is currently being investigated for the catalytic hydrogenation of ethyl acetate to ethanol. Preliminary results showed a strong effect of increasing Mn concentrations upon catalytic performance. The nature of the MnO_x promotor effects for activity and stability over time for this important hydrogenation reaction will be presented at the conference.

4. Conclusions

Well-defined and highly dispersed carbon-supported $CuMnO_x$ nanoparticles were prepared *via* a facile impregnation method. The Mn loading could be varied over a wide range, for the same final $CuMnO_x$ particle size. The correlation between Mn concentration and catalytic activity is currently being studied. Using carbon as an inert support allows us to further study the promoter effects on the nanometre scale. These findings may contribute to implementing MnO_x as an efficient promoter for a range of different hydrogenation reactions.

References

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