Cluster-derived, heterogeneous, single-site nanoparticle catalysts for production of second generation hybrid biofuels

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Introduction

Traditional methods for making fuels from biomass come in two forms – biological (using enzymes) or chemical (mainly thermochemical using metal catalysts at high temperatures). Biomass-derived ethanol is a liquid biofuel (perhaps the best known in the transportation sector) that is produced via enzymatic methods whereas synthetic diesel and 'syn-gas' are produced using a thermochemical approach. Given the limitations of ethanol as a biofuel (low energy density and affinity for water) and the significant enthalpy generated in the partial oxidation of biomass (which diminishes almost half of the carbohydrate's energy value), the challenge of producing biofuels from biomass is finding the right approach for breaking down long carbohydrate chains to smaller (usable) molecules while simultaneously removing oxygen atoms and minimizing the loss of energy value of the original biomass. Furanic compounds offer viable alternatives and are produced by the acid-catalysed dehydration of hexoses. Our present study (see Figure 1) focuses on the synthesis of 2,5-dimethylfuran (DMF), which is conventionally produced by the hydrogenation of 5-hydroxymethylfurfural (HMF) in the gas phase.[1]
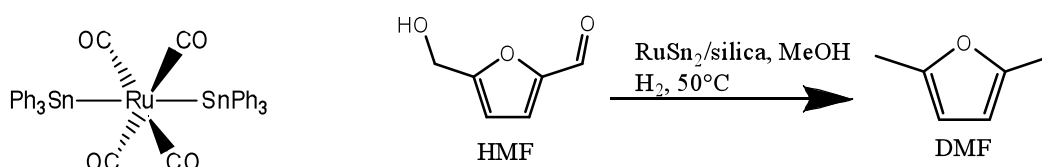

Figure 1: Cluster precursor formula and reaction scheme for hydrogenation of HMF to DMF

The single-site catalysts that we have employed for this purpose are mixed-metal nanoparticles supported on mesoporous silica, which are generated from molecular cluster precursors, by gentle thermolysis under vacuum. Previous work has shown that inclusion of oxophiles such as tin in the precursor compounds have a synergistic effect leading to improved selectivities towards less-hydrogenated species in multiple hydrogenation reactions. We have shown that ruthenium-tin nanoparticles derived from the cluster $Ru(CO)_4(SnPh_3)_2$ display good selectivities for DMF, in the *liquid-phase* hydrogenation of HMF.

Experimental

Cluster precursors were prepared according to reported procedures. The precursor compounds were anchored (3 % metal loading) on mesoporous silica (Davisil 923) by stirring a hexane- dichloromethane solution for 18 hours. The catalyst was activated by heating the as-synthesized anchored cluster under vacuum for two hours. FTIR spectra of self-supporting wafers were recorded with a Bruker IFS88 spectrometer. The samples, after the decomposition of cluster precursors, were outgassed and heated up to 200°C *in vacuo*. NO

and CO were adsorbed at room temperature. Catalysis was performed in a 160ml Parr pressure reactor with temperature control unit and a magnetically-driven stirrer. For all catalytic tests, the conditions were as follows: 0.4g HMF, 40g methanol, 0.4g 1-chlorobutane (GC internal standard), 20bar H_2, 50mg catalyst, 50°C. Product analysis was performed by gas chromatography and GC-mass spectrometry was employed for product identification.

Results and discussion

Initial findings have indicated a 50% DMF yield after 18 hours at 50°C. Further details on the catalysis will be reported at the conference. The synergistic effects of other cluster combinations and optimization of process variables are currently being evaluated.

The nature of the active sites was studied by FTIR spectroscopy using CO and NO as probe molecules. Upon CO adsorption (Figure 2), the Ru/SiO_2 catalyst, shows bands at 2134, 2066 cm^{-1} assigned to the symmetric and asymmetric stretches of two CO molecules in gem-dicarbonyl on RuO_x species or on low coordination edge and corner metal atoms. The band at 1995 cm^{-1} is plausibly due to atop Ru sites.[2]. These features suggest the presence of highly dispersed and un-coordinated Ru° sites that are able to dissociate CO and coordinate to two CO molecules [2]. On $RuSn/SiO_2$ a blue shift of the CO adsorbed bands is observed (Figure 2) indicating that the bond strength between CO and Ru sites is higher in this sample with respect to Ru/SiO_2. This suggests that more isolated Ru sites are present in this catalyst and that the presence of Sn possibly helps attain a better dispersion of Ru active sites. No spectroscopic contribution due to CO bound to tin was observed.
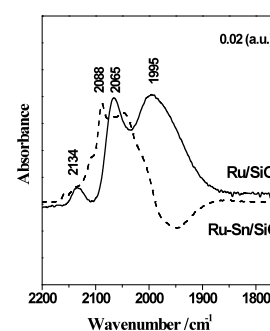

Fig 2: FTIR spectra of CO adsorbed on Ru and Ru-Sn/SiO$_2$.

Conclusions

We have shown that supported cluster-derived, tin-containing, mixed metal nanoparticles have tremendous potential as catalysts for the hydrogenation of HMF to DMF in the liquid-phase at ambient conditions. The presence of tin has a synergistic effect in enhancing the efficiency of the reaction and also play a major role in facilitating the site isolation of the active sites thereby leading to greater catalytic turnover.

Acknowledgements

References

[1] Roman-Leshkov, Y., Barrett, C.J., Liu, Z.Y., Dumesic, J.A., Nature, Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. 447(7147), (2007), 982-U5.
[2] Guglielminotti, E., Boccuzzi, F., Manzoli, M., Pinna, F., Scarpa, M., Journal of Catalysis, Ru/ZrO2 catalysts I. O-2, CO, and NO adsorption and reactivity. 192(1), (2000), 149-157.