

Unexpected properties of supported Copper catalysts

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Abstract: Supported Cu/SiO₂ shows unusual acidic activity in same reaction. This acidity can be combined with the hydrogenation activity of the metal to set up bifunctional processes, also in water as solvent, of interest for the valorization of platform molecules coming from renewables or from agro-industry waste. The Lewis acid activity of the Cu nanoparticle is linked to the presence of low coordination sites in turn due to very high dispersion generated by the catalyst preparation method.

Keywords: Cu catalysts, Lewis acids, Bifunctional processes.

1. Introduction

Metal dispersion has long been recognized to play a pivotal role in determining catalytic activity, high dispersion being usually pursued to improve effective utilization of active species. Moreover, in some case an inert metal such as gold can turn out to be extremely active for many reactions only when metal particles are small enough¹.

Here we wish to report that not only a particular preparation method can promote the activity of Cu catalysts in hydrogenation reactions by increasing metal dispersion, but also that both supported CuO and supported Cu particles may acquire acidic activity when their size and morphology are suitable. This activity can be added to hydrogenation activity in the case of the reduced catalyst thus leading to a bifunctional catalyst where two activities rely on the same site

2. Experimental

Catalysts were prepared by the chemisorption–hydrolysis (CH) method by adding the support to an aqueous [Cu(NH₃)₄]²⁺ solution at pH 9 and diluting the slurry, held in an ice bath at 0 °C, with water. The solids, dried overnight at 120°C and calcined at 350°C were characterized by several techniques and in particular acidic properties were deduced from FT-IR Spectra of Adsorbed Probe Molecules (Pyridine and GVL).

In a typical test for the synthesis of pentyl-valerate GVL (4 g, 40 mmol), 1-pentanol (200 mmol) and catalyst (400 mg) were loaded in a Parr reactor under 10 atm H₂ at 250 °C for 10 h. Mixtures were analyzed by GC-MS.

3. Results and discussion

TPR, XRD, DRUV, TEM and STEM analysis together with FT IR of adsorbed CO put in light that the catalyst preparation method used in our lab allows one to obtain high dispersion of the CuO phase due to the electrostatic interaction taking place between the [Cu(NH₃)₄]²⁺ solution and the acidic support. In turn, high dispersion of the CuO phase translates into formation, after ex situ pre-reduction, of small Cu crystallites with suitable morphology to effectively activate H₂. In this way unexpected high activity in hydrogenation reactions of polyunsaturated compound can be obtained.²

However the less awaited consequence of high dispersion is the low acidity of supported CuO. FT IR spectra of adsorbed pyridine evidenced the presence of Lewis acid sites,³ in agreement with the acidic behavior shown by this material in epoxide ring opening⁴ and even Friedel Craft acylation⁵ reactions where materials with the same Cu content but lower dispersion were found to be inactive. This kind of acidity is even increased when the catalyst is pre-reduced, thus allowing one to design a bifunctional catalyst where both acidic and hydrogenation activity can be ascribed to the same site.

This was found to be the case when carrying out the one pot synthesis of pentyl-valerate from GVL. The Cu/SiO₂ catalyst showed the same catalytic activity of a Cu catalyst supported on acidic material, namely a silica zirconia mixed oxide, but much higher selectivity due to the absence of Bronsted acidic sites

FT IR spectra of adsorbed pyridine show the presence of bands ascribable to Lewis acid sites while HRTEM analysis is in agreement with the presence of cuboctahedron Cu particles in a fcc crystal structure. By comparing turnover frequencies calculated for both catalysts with respect to total surface atoms, high coordination sites and low coordination sites according with a cuboctahedron model, as well as Lewis acid sites as evaluated from pyridine adsorption we found that the ratio between the two values calculated for low coordination sites and for Lewis acid sites are close to 1, clearly showing that Lewis behavior is linked with low coordination sites on the metal particle.⁶

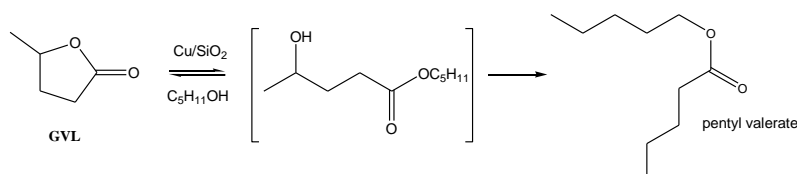


Figure 1. One pot conversion of GVL into pentyl-valerate requiring both acidic and hydrogenation sites

The Lewis acid sites also survive in water as shown by the FTIR spectra reported in Fig.2, thus allowing to carry out interesting bifunctional reactions in water, such as the hydrogenation of lactose to sorbitol and dulcitol.⁷

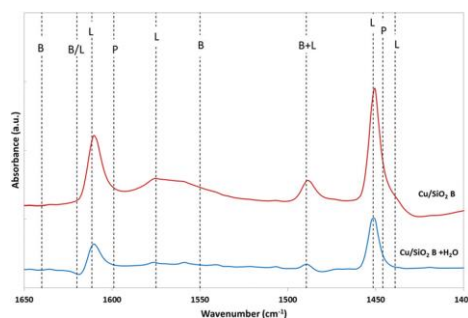


Figure 2. FT-IR spectra of adsorbed pyridine over Cu/SiO₂ and over water-saturated Cu/SiO₂.

4. Conclusions

The chemisorption hydrolysis preparation method leads to high dispersion of CuO in supported Cu catalysts, that in turn leads to very active catalysts in hydrogenation reactions after reduction to the metallic phase. The very small particle size enhances surface defectivity of the CuO phase accounting for Lewis acid activity of this material. Reduction of CuO promotes an increase of the Lewis acid character linked to low coordination sites on the metal particle.

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