

Preparation of Cu-Zn/SiO₂ catalysts by co-impregnation – Evidence for Cu-Zn interactions through the reaction of selective hydrogenation of crotonaldehyde

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Introduction

Cu-Zn based catalysts are used in the reactions of steam reforming, methanol synthesis and ester hydrogenolysis. The key point for their catalytic performance is the presence of Cu-Zn interactions. The goal of this study is to show that for a model catalyst prepared by a very simple method of preparation, i.e., Cu-Zn/SiO₂ prepared by co-impregnation of the nitrates (10-10 wt% Cu-Zn), the way the catalysts are dried and activated has drastic consequences on the Cu-Zn interactions.

The presence of Cu-Zn interactions is not easy to point out, but a simple and definitely sensitive test reaction can be used. The selective hydrogenation of crotonaldehyde (CH₃CH=CHCHO) was chosen, knowing that the C=O/C=C hydrogenation ratio is very sensitive to any modifier in metal catalysts, e.g., copper modified by sulfur [1] or platinum modified by zinc [2]. We can expect that the changes in the metallic properties of Cu induced by the interaction with Zn will lead to changes in the selectivity of this reaction and favors the selective hydrogenation of the C=O bond instead of that of the C=C bond which is thermodynamically favored.

Results and Discussion

First, we show that the temperature of drying (25 or 90°C) has a strong influence on the nature of the supported Cu^{II} and Zn^{II} species. Indeed, Cu/SiO₂ (reference catalyst) and Cu-Zn/SiO₂ dried at 25°C contain copper nitrate and a mixture of copper and zinc nitrates, respectively, well dispersed on the silica surface (amorphous in XRD). In contrast, drying at 90°C leads to the respective formations of copper hydroxynitrate and a mixed compound of copper hydroxynitrate-type containing Zn^{II} ions in substitution in the Cu(OH)₂ brucitic layers (Table 1).

After calcination at 450°C, the Cu-Zn/SiO₂ systems «keep the memory» of the drying step. Indeed, the XRD pattern of the calcined 90°C-dried sample reveals the presence of CuO and traces of ZnO whereas the calcined 25°C-dried sample is amorphous. TPR of the calcined 25°C-dried sample shows that the Cu^{II} species (CuO_x) is reducible in two steps, but its nature has not been identified yet. As for the zinc species, if one refers to a former work on Zn/SiO₂ [3], it is as an amorphous zinc silicate of hemimorphite-type (Zn₄SiO₇(OH).H₂O). It may be noted that part of Zn is probably also a zinc silicate in the calcined 90°C-dried sample. In addition, the comparison of the XRD patterns of the calcined 25°C-dried Cu/SiO₂ (CuO detected) and Cu-Zn/SiO₂ (no CuO detected) samples evidences the drastic effect of zinc addition on the CuO particle size.

After reduction by TPR of the calcined samples up to 330 °C, which leads to the reduction of Cu^{II} and not to that of Zn^{II}, the Cu⁰ particles also «keep the memory» of the size of the CuO particles before reduction, since large CuO particles give large Cu⁰ particles after reduction, detected by XRD (Table 1).

In contrast, when the samples are directly reduced after drying, the results are different. The 25 °C-dried Cu/SiO₂ and Cu-Zn/SiO₂ samples which contain well-dispersed nitrates, give small Cu⁰ particles non detected by XRD, whereas the 90 °C-dried samples which contain ill-dispersed hydroxynitrate, give large particles detected by XRD. Metal particle measurements by electron microscopy are under progress.

The catalysts were tested in the reaction of hydrogenation of crotonaldehyde. The Cu-Zn/SiO₂ calcined then reduced at 400°C are less active (2-3 times less) but more selective in crotyl alcohol than the Cu/SiO₂ catalysts (≈20 % instead of 5 %). This indicates the modifier effect of Zn and the presence of Cu-Zn interactions. The activity of Cu-Zn/SiO₂ previously dried at 25 °C is higher than that of the catalyst dried at 90 °C because of the smaller metal particles, but the selectivities in crotyl alcohol are the same (≈20 %). The decrease in activity due to zinc addition is more dramatic (more than 10 times) when the catalysts are directly reduced. However, direct reduction of Cu-Zn/SiO₂ dried at 90 °C leads to the highest selectivity in crotyl alcohol (29 %). One can deduce that under this thermal treatment of drying at 90 °C followed directly by reduction, Cu-Zn interactions are most favored probably because the formation of the mixed Cu-Zn hydroxynitrate at 90 °C favors the interdispersion of the Cu and Zn elements, interdispersion which is suppressed if the sample is calcined before reduction because of segregation of the Cu^{II} and Zn^{II} species.

Table 1: Characteristics of the Cu/SiO₂ et Cu-Zn/SiO₂ samples after the various steps of preparation

samples	drying T (°C)	Nature of the copper and zinc species		
		after drying	after calcination	after reduction
Cu/SiO ₂	25	amorphous Cu nitrate	CuO (small particles*) + CuO (large particles*)	Cu ⁰ (large particles)
			—	Cu ⁰ (small particles)
Cu-Zn/SiO ₂	25	amorphous mixture of Cu and Zn nitrates	CuO _x + amorphous zinc silicate	Cu ⁰ (small particles)
			—	Cu ⁰ (small particles)
Cu/SiO ₂	90	crystallized Cu hydroxynitrate	CuO (large particles)	Cu ⁰ (large particles)
			—	Cu ⁰ (large particles)
Cu-Zn/SiO ₂	90	crystallized mixed Cu-Zn hydroxynitrate	CuO (large particles) + traces of ZnO + amorphous zinc silicate	Cu ⁰ (large particles)
			—	Cu ⁰ (large particles)

* “large particles” means that they are detected by XRD while “small particles” means means that they do not lead to XRD pattern. Metal particle measurements by TEM are under progress.

References

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