

Tailoring supported Co catalysts for the selective hydrogenation of citral

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Introduction

Selective catalytic hydrogenation of α , β unsaturated aldehydes is an important step in the preparation of various fine chemicals products. In fact, the obtained unsaturated alcohols are important intermediates in organic synthesis in several industries, such as flavour, fragrance and pharmaceutical industry. However, the hydrogenation of the C=C bond is thermodynamically more favourable than the C=O hydrogenation. Among the α , β unsaturated carbonyl compounds, citral is a particularly attractive molecule, because it possesses an isolated C=C bond in addition to the conjugated C=O and C=C bonds (Figure 1).

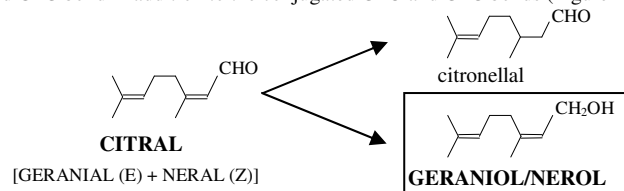


Figure 1. Simplified reaction scheme for citral hydrogenation.

Nevertheless, concerning the liquid phase hydrogenation of citral, no investigation is reported over monometallic Co catalysts. To our knowledge, the present study is the first direct evidence that Co-supported monometallic catalyst can lead to high unsaturated alcohol selectivity for this reaction. This study was aimed at establishing for the first time correlations between the surface properties of Co catalyst, the sorption characteristics for hydrogen and the catalytic activity in the hydrogenation of citral.

Materials and Methods

Monometallic Co catalysts with different metal loadings were prepared:

- either by wet impregnation of the supports using an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Four different supports were used: SiO_2 with a low-surface-area (Aldrich, $4 \text{ m}^2 \cdot \text{g}^{-1}$, denoted LS), SiO_2 with a high-surface-area (Degussa, $200 \text{ m}^2 \cdot \text{g}^{-1}$, denoted HS), $\gamma\text{-Al}_2\text{O}_3$ (AXENS, $210 \text{ m}^2 \cdot \text{g}^{-1}$) and TiO_2 (Degussa, $50 \text{ m}^2 \cdot \text{g}^{-1}$).
- or by a water-in-oil (w/o) microemulsion method using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and tetraethyl orthosilicate (TEOS) as a SiO_2 source.

The catalysts were dried at 120°C for 48 hours and then reduced at 450°C (heating rate = $2^\circ\text{C} \cdot \text{min}^{-1}$) in flowing pure hydrogen for 12 hours. The resulting materials were tested for the selective hydrogenation of citral at 70°C and at constant pressure of 7 MPa. They were characterized by transmission electron microscopy (TEM), electron diffraction spectroscopy (EDS), X-ray diffraction (XRD) and by cyclohexane dehydrogenation.

Results and Discussion

Among the Co materials, the catalysts prepared by microemulsion showed the highest activity and selectivity to the unsaturated alcohols (U.A.) (Figure 2). The characterization of these catalysts by temperature-programmed desorption of hydrogen (H_2 -TPD) indicated that the samples with the highest unsaturated alcohol selectivities present particular H-Co species, labeled β [1, 2]. Electron diffraction and XRD measurements revealed that these β -species would be linked to the presence of the Co^0 hexagonal phase. According to the results obtained by TEM and cyclohexane dehydrogenation, these two properties would be combine on large Co particles ($\geq 100 \text{ nm}$).

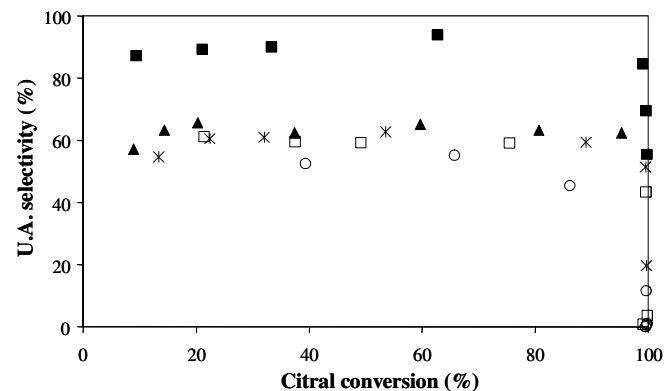


Figure 2. Unsaturated alcohols selectivity as a function of citral conversion for (■) 28 wt% Co / SiO_2 prepared by microemulsion and (▲) 30 wt% Co / SiO_2 -LS, (□) 30 wt% Co / SiO_2 -HS, (○) 30 wt% Co / Al_2O_3 , (*) 10 wt% Co / TiO_2 prepared by wet impregnation.

Significance

On supported-Co catalysts, three factors were found to be crucial to achieving high selectivity to unsaturated alcohols in the course of citral hydrogenation. These factors include a particular H-Co species, the Co^0 hexagonal phase and a large size of particles.

References

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2. E.L. Rodriguez and J.M.C Bueno, *Appl. Catal. A: General* 257 (2004) 201.