

Hydrogenation of citral on IrAu/TiO₂ catalysts. Effect of the preparation method.

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Introduction

The selective hydrogenation of α,β -unsaturated aldehydes to their corresponding unsaturated alcohols is of importance in fine chemical manufacture [1]. Catalysts based on noble metals deposited on an inert support display a very low selectivity towards the unsaturated alcohol. An important enhancement in selectivity may be obtained by using reducible supports, by the addition of promoters (second metal, oxides or cationic species), modifying the metal particle size, etc. [2-4]. In a previous paper it was shown that Ir/TiO₂ catalysts are very active and selective in the hydrogenation of citral [4], and also that the addition of cationic promoters as Fe(III) and Ge(IV) ions, are able to enhance both, the activity and selectivity. In the present work, the effect of the preparation method of bimetallic IrAu/TiO₂ on the activity and selectivity in the citral hydrogenation was studied.

Materials and Methods

Degussa P-25 TiO₂ was used as support. Ir/TiO₂ catalyst (1 wt.%) was prepared by deposition-precipitation with urea (Ir DPU) and calcined at 673 K. Ir-Au/TiO₂ catalyst (total metal loading 2 wt.%, atomic ratio Ir/Au=1) was prepared by two methods: co-impregnation following the modified incipient wetness impregnation (MIWI) method proposed by Delannoy et al. [5] to prepare Au supported catalysts (IrAu C-MIWI), and a combined DPU-MIWI method. In the latter, Ir was first incorporated using the DPU method followed by calcination at 673 K and reduction at 573 K. Then Au was impregnated using the MIWI method and reduced at 573 K (IrAu S-DPUMIWI). Particle size distribution before reaction was determined using electron microscopy techniques (HAADF). The citral was Merck (>98%, mixture of E- and Z-isomers). Reactions were done in a homemade batch reactor at a constant stirring rate (1000 rpm). Prior to the experiment, the catalyst (0.2 g) was reduced in situ under hydrogen flow (20 mL/min) at atmospheric pressure and temperature of 573 or 773K (LTR or HTR, respectively). For all reactions, 50 ml of a 0.1 M citral solution in n-heptane was used. The reaction temperature was fixed at 363 K and the total pressure to 6.2 bar. Citral conversion and selectivity towards all the possible products were followed by GC-MS as a function of time. Ir/TiO₂ catalyst prepared by wet impregnation [4] was used as reference.

Results and Discussion

Characterization by electron microscopy showed for Ir DPU and the Ir/TiO₂ reference catalyst a mean particle size of 3 and 2.6 nm, respectively. In the case of bimetallic samples; IrAu C-MIWI sample presented a mean particle size of 1.5 nm while for IrAu S-DPUMIWI catalyst it was 2 nm. Figure 1 shows the citral conversion as a function of time

displayed by catalysts reduced at high temperature (773K). The citral conversion after 1h reaction was around 12% for Ir/TiO₂ prepared by DPU and IrAu DPU-MIWI catalysts (initial activity, $0.47 \mu\text{mol s}^{-1}\text{g}^{-1}$), while only 2 % conversion was obtained for the same reaction time in the IrAu C-MIWI sample (initial activity $0.06 \mu\text{mol s}^{-1}\text{g}^{-1}$). After 7 hours reaction, the IrAu DPU-MIWI catalyst was the most active (35% conversion). A lower activity was observed for all samples reduced at low temperature (573 K). The Ir/TiO₂ catalyst prepared by wet impregnation at low and high reduction temperature used as reference presented about 6% conversion after 1 h reaction. Concerning the selectivity, the only detected products in all catalysts, Ir DPU, IrAu C-MIWI and IrAu S-DPUMIWI, reduced at low (573K) and high (773K) temperature, were geraniol and nerol. At this respect, the reference Ir/TiO₂ catalyst produced besides geraniol and nerol, citronellal and citronellol products. The addition of gold to Ir DPU and prepared by sequential deposition, practically had no effect in the initial activity for citral hydrogenation. Also the selectivity to the desired products (geraniol and nerol) was about the same as in Ir DPU. However, a noticeable effect in the activity is observed as a function of time. For bimetallic catalysts prepared by coimpregnation, the LTR and HTR samples were less active compared to the catalysts prepared using a sequential deposition. Moreover, in these samples the LTR catalyst was more active than the HTR one.

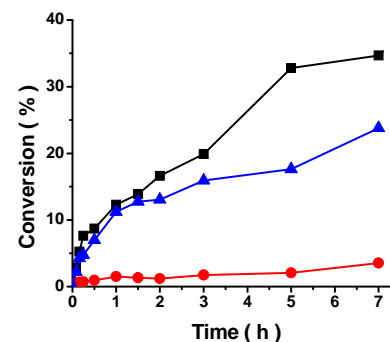


Figure 1. Evolution of the citral conversion as a function of time displayed by HT (773K) reduced catalysts. Reaction temperature 363K, P=6.2 bar. (▲) Ir DPU, (●) IrAu C-MIWI, (■) IrAu S-DPUMIWI.

Significance

Results concerning active and selective Ir-based catalysts with potential interest for fine chemical manufacture.

References

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