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Crotonaldehyde hydrogenation on supported gold catalysts

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Abstract

Au/Nb_2O_5 and Au/CeO_2 catalysts were studied for the selective hydrogenation of crotonaldehyde, both in liquid (batch reactor, 4 atm, 60 °C, solvent: isopropanol) and in gas (flow microreactor, 120 °C, atmospheric pressure) phases. Samples were characterized by TPR and XRD and tested for the CO oxidation reaction. Large differences in support reducibility between both catalysts were determined from the TPR results. The XRD and CO oxidation results demonstrated that the gold particles were lower than 5 nm. The dependence of the selectivity towards crotyl alcohol and of the conversion on time on stream was measured. The niobia-supported catalyst was mainly unselective, the selectivity towards crotyl alcohol value being 20% for both liquid and gas phases. The Au/CeO_2 catalyst is highly selective in gas phase (78% of selectivity towards crotyl alcohol). Under liquid phase conditions, a high selectivity level was not reached mainly due to secondary reactions.

Keywords: Gold catalyst; Ceria; Niobia; Selective hydrogenation; Crotonaldehyde

1. Introduction

The control of the selective hydrogenation of α,β-unsaturated compounds has been extensively studied over a large variety of catalysts. The desired product, from an industrial viewpoint, is the unsaturated alcohol, which is an important reactant in the synthesis of cosmetic and pharmaceuticals products.

In the following scheme, the possible hydrogenation products of crotonaldehyde are shown (Scheme 1).

It is very difficult to preferentially hydrogenate the C=O bond over the C=C bond using classical hydrogenation catalysts based on Ni, Pd or Pt. Lately, several research groups have reported that the selectivities to the unsaturated alcohol are quite high when gold-supported catalysts are employed [1–7], showing that gold is peculiarly selective towards hydrogenation of the conjugated C=O bond. In addition, there seems to be a certain influence of the nature of the support in the activity and selectivity. For example, Milone et al. [1] studied Au/Fe_2O_3 and Au/Al_2O_3 as catalysts to selectively hydrogenate the C=O bond of *trans*-4-phenyl-3-buten-2-one (benzalacetone) and 4-methyl-3-penten-2-one, 3-penten-2-one. The authors concluded that the reducibility of the support plays an important role: the higher the reducibility of the support the higher is the catalytic performance of gold. Claus and coworkers [3a,3b] investigated the selective hydrogenation of acrolein and of crotonaldehyde over Au/SiO_2, Au/TiO_2, Au/ZrO_2, Au/ZnO and Au–In/ZnO. They found that the selectivity to unsaturated alcohol was in the 23–63% range. They concluded that the support would play a role only in the determination of the morphology of the particles. They suggested that the edges of gold crystallites are the active sites for C=O hydrogenation. In this way, the support would participate indirectly on selectivity, by determining the morphology of the particles.

In the present work, Au/CeO_2 and Au/Nb_2O_5 are studied as catalysts for the hydrogenation of crotonaldehyde, both in liquid and in gas phases. The results obtained in gas phase reactions are important for evaluating the catalysts from a fundamental point of view. On the other hand, tests in liquid phase are more appropriate to evaluate the catalysts under operational conditions more suitable for industrial applications.

Ceria was selected as a support due to its redox properties as well as the fact that it promotes a high metal dispersion [8]. In a previous work, some of us have studied Au/HSA–CeO_2 [9]. In this work it was concluded that gold supported on high-surface

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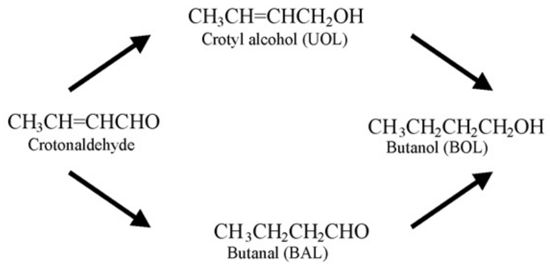

Scheme 1. Hydrogenation of crotonaldehyde.

ceria is highly selective for the hydrogenation of crotonaldehyde in gas phase. Niobia was chosen considering the possibility of achieving a gold catalyst in the SMSI state. Noronha et al. [10] measured a promotional effect of Nb_2O_5 on the catalytic properties of Pd. Yoshitake and Iwasawa [11] reported that the selectivity towards the allylic alcohol, in acrolein hydrogenation over Pt/Nb_2O_5, was higher for the catalysts in the SMSI state than for those reduced at lower temperature.

Finally, it is important to state that the reactions were carried out under the same experimental conditions corresponding to previous studies on Pt-based samples [12], in order to perform a comparison between Au and Pt catalysts.

The samples were characterized by XRD and TPR measurements and they were tested for the CO oxidation reaction.

2. Experimental

2.1. Catalyst preparation

Ceria (240 m^2/g) was from Rhône Poulenc, while niobia (52 m^2/g) was kindly provided by CBMM, Brazil. Previous to gold introduction both supports were calcined, ceria at 300 °C and niobia at 800 °C.

Au/CeO_2 was prepared by deposition–precipitation method using sodium bicarbonate. At 70 °C approximately 5 g of support were contacted with 500 ml of an aqueous solution of $HAuCl_4$ (10^{-3} M). The pH of the solution was kept at 8 by adding a 0.1 M solution of Na_2CO_3 drop by drop. Afterwards, the solid was filtered and the catalyst precursor was washed with a 4 M NH_3 solution and with hot water in order to eliminate Cl^- and Na^+ ions. Finally, the solid was dried at 100 °C for 12 h and then calcined under air at 300 °C (1 °C/min) for 4 h.

Au/Nb_2O_5 was prepared following the method developed by Ivanova et al. [13]. Approximately 5 g of the support were contacted with an aqueous solution of $HAuCl_4$ (10^{-3} M) at 70 °C. The suspension was vigorously stirred for 2 h. Then, a concentrated solution of NH_3 was added and 30 min later, the solid was filtered and washed with hot water in order to eliminate Cl^- and NH_4^+ ions. The catalyst was then dried at 100 °C for 12 h and calcined under air at 300 °C (1 °C/min) for 4 h.

Caution/safety note: the contact of ammonia with a gold solution could provoke the formation of gold ammonia complexes which are explosive [14]. The use of this procedure is not dangerous if the gold complexes are strongly attached to the support. The assurance that there remains no gold in the solution prior to the introduction of ammonia is a pre-requisite.

The Au loading in the catalysts was determined by atomic absorption spectroscopy.

2.2. Catalysts characterization

An X-ray diffraction (XRD) analysis of the Au/Nb_2O_5 and Au/CeO_2 catalysts reduced at 120 °C, was carried out on a Siemens D 5000 polycrystalline diffractometer using Cu Kα radiation.

The reducibility of the catalysts was studied by temperature-programmed reduction (TPR) in a homemade apparatus.

The activity of the catalysts was tested using the CO oxidation reaction. Tests were carried out in a fixed bed quartz microreactor, at atmospheric pressure. The catalyst mass was 50 mg, while the reactive mixture was 1.5 and 5.0% of CO and O_2, respectively, diluted in He. The concentration of CO and CO_2 were measured by Rosemount infrared detectors. The reaction temperature was in the 20–300 °C range. The temperature required to obtain a 50% conversion, T_{50}, was taken as a relative measurement of the size of gold particles. It is well known that the gold crystallites in nanometric range lead to low reaction temperatures for CO oxidation [13,15].

2.3. Crotonaldehyde hydrogenation in gas and liquid phases

The reaction in gas phase was carried out in a quartz microreactor, at atmospheric pressure. In a typical run, the sample (200 mg) was reduced *in situ* at 120 °C for 1 h. The crotonaldehyde (Fluka puriss, 100–200 μl) was introduced in a trap, set before the reactor tube, and was maintained at 0 °C to achieve a constant crotonaldehyde partial pressure of 1.6 kPa. Two catharometers, inserted in the line at the input and output of the reactor, respectively, measure the reactant pressure all along the experiment. When crotonaldehyde was injected, the reactor was kept closed to avoid air contamination. Approximately 20 min later, the reactor was opened. If no adsorption occurs on the catalyst, the output signal should recover to its initial level in about 30 s, the time for gas to reach the catharometer.

The reaction products were analyzed each 20 min by gas chromatography with a FID detector and a DB-Wax column operating at 40 °C.

The reaction in liquid phase was carried out in a Parr reactor, operating in batch conditions at 60 °C and 4 atm of H_2. In a typical experiment, a sample of 100–150 mg was reduced *ex situ* at 300 °C and then introduced to the reactive mixture (crotonaldehyde in isopropanol, 0.1 M) in H_2 flow. Then, the reactor was pressurized at 4 atm of H_2. Finally, the stirring rate was set at 500 rpm and the reaction was considered to be started. Samples of the reactive mixture were taken from the reactor at 20 min intervals. Crotonaldehyde and product concentrations were measured by gas chromatography, using a FID detector and a Chrom PAW column operating at 35 °C.