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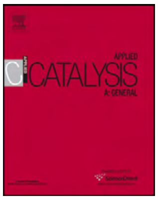

Support and solvent effects on the liquid-phase chemoselective hydrogenation of crotonaldehyde over Pt catalysts

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ABSTRACT

A study of the selective reduction of crotonaldehyde to crotyl alcohol over Pt catalysts supported on various partially reducible solids including Fe_2O_3, Fe_3O_4, ZrO_2, ZnO, TiO_2 and SnO_2 was conducted. The catalysts were characterized by thermal programmed reduction (TPR) and reduced at temperatures that were selected as a function of the presence of specific reduction peaks for Pt in the TPR profiles. The reduced catalysts were studied by XRD spectroscopy and TEM, and used for the liquid-phase hydrogenation of crotonaldehyde. As a rule, low reduction temperatures led to catalysts providing high yields in the unsaturated alcohol (2-butenol). Such yields were substantially increased by the addition of water in mixtures with dioxane to the medium, whether the medium was acid, neutral or basic. The highest selectivity towards crotyl alcohol was obtained with the solid Pt/ZnO reduced at 175 °C. This may have resulted from the presence of ZnO_xCl_y species forming around Pt particles, which were detected by XPS and might have acted as Lewis acid sites facilitating anchoring of crotonaldehyde via its carbonyl double bond. The optimum working conditions, which included a reaction temperature of 30 °C and an initial hydrogen pressure of 0.414 MPa, afforded a selectivity higher than 90% for crotyl alcohol at conversions in the region of 40%.

1. Introduction

The selective hydrogenation of unsaturated aldehydes to unsaturated alcohols over heterogeneous catalysts has aroused considerable attention as a result of its usefulness for the flavor, fragrance and pharmaceutical industries [1]. The most challenging class of these chemoselective hydrogenation reactions is the reduction of α,β-unsaturated aldehydes to allyl alcohols. This chemoselective hydrogenation of carbonyl compounds over heterogeneous catalysts has been recently reviewed [2]. The activity and unsaturated alcohol selectivity of unpromoted catalysts is dependent on the particular type of metal they contain. Unpromoted Ir and Os catalysts are known to be highly selective, those of Ru and Co moderately selective, and those of Pd, Rh and Ni unselective towards the formation of the unsaturated alcohol [3].

The performance of unpromoted catalysts can be improved by using an appropriate promoter. Thus, ionic metal promoters increase alcohol selectivity by coordinating with and polarizing the aldehyde group, thereby enhancing its activity [4]. Recently, the addition or Zn and/or Fe to a Pt catalyst was found to have a substantial promoting effect on its activity and alcohol selectivity in the hydrogenation of cinnamaldehyde; the effect was ascribed to electron transfer from Zn and Fe to Pt particles (reflected in XPS analyses) and the formation of electrophilic sites for the carbonyl group to anchor [5]. Also, the electron density of the catalytic metal was found to be increased by the effect of its alloying with a more electropositive metal [6,7] or the use of an electron-rich support [8,9]. Thus, gold supported on various oxides considerably altered the selectivity towards hydrogenation of the conjugated C=O bond in benzalacetone [10], which was highly correlated with the reducibility of the support. Their correlation was ascribed to electron transfer from the reduced support to the metal leading to the formation of electron-enriched gold particles facilitating C=O hydrogenation on their surface [10]. Other reducible oxides in addition to those of iron have been found to contribute to changes in catalytic activity and selectivity in the hydrogenation of unsaturated carbonyl compounds over Pt catalysts; such oxides include TiO_2 [11], SnO_2 [12], Nb_2O_5 [13], Y_2O_3 [14], ZrO_2 [15], ZnO [16] and CeO_2 [17].

The selective hydrogenation of crotonaldehyde over Pt supported catalysts can be used as a probe reaction sensitive to metal–support interactions [18–20]. In other words, when the metal is not modified by the support, the C=C bond is selectively hydrogenated; otherwise, the carbonyl bond is the selective target

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with the metal in an SMSI state. However, the origin of the specific behavior of Pt in such a state remains a controversial subject for some supports. Thus, the SMSI effect on the selective reduction of the C=O bond in α,β-unsaturated carbonyl compounds might be related to (a) the formation of an alloy between Pt and the reduced metal in the support [18]; (b) an electronic effect of Pt particles due to partial reduction of the support [21]; or (c) the decoration of Pt particles with patches of partially reduced support [17].

In addition to the active metal, the activity and selectivity for the reduction of the C=O bond in unsaturated carbonyl compounds is influenced by additional factors including the metal precursor [12,16], solvent [2,22–25], metal particle size [2,26], synthetic procedure for the catalytic system [23,26], use of additives [27], various reaction conditions such as temperature and hydrogen pressure, and whether the process is conducted in the gas or liquid-phase [26]. Additionally, the change in metal particle size can affect the electronic and geometrical properties of the metal particles. The smaller metal particles are known to be more electron deficient than larger ones. Furthermore, the number of edges and corners, which could have different activities and selectivities is increased in the smaller particles [2].

Singh and Vannice reviewed the solvent effects on heterogeneously catalysed reactions [23]. The most salient effects on the hydrogenation of α,β-unsaturated aldehydes are solvent polarity, hydrogen solubility, catalyst–solvent interactions and reactant solvation in the bulk liquid-phase. Although rationalizing solvent effects is very difficult owing to the lack of systematic experimental data, recent trends regarding solvent polarity suggest that polar solvents boost the hydrogenation of C=O bonds and raise the selectivity towards the unsaturated alcohol whereas non-polar solvents favor hydrogenation of the non-polar C=C bond [2,28,29]. Also, the addition of water has been found to increase the selectivity for the unsaturated alcohol in both Pd/C and Pt/C catalysts [29]. Some authors have noted that the hydrophilic nature of the C=O bond facilitates its selective hydrogenation in pure water [22] and water/organic solvent mixtures [30].

Most of the papers published on the Pt catalysed selective hydrogenation of crotonaldehyde deal with gas-phase reactions. In this sense, recently, Rynkowski et al. [31] summarized the activity and selectivity obtained for different Pt/support catalysts in selective hydrogenation of crotonaldehyde in the gas phase. However, as far as liquid-phase selective hydrogenation of crotonaldehyde over Pt catalysts is concerned, the published works are relatively scarce. Bartok et al. reported the activity and selectivity for several Pt/support catalysts in the liquid-phase providing TOF (s^{-1}) values in the 10^{-1} to 10^{-2} range with selectivities to crotyl alcohol between 7 and 43% [28].

In this work, we explored the liquid-phase Pt-catalysed selective hydrogenation of crotonaldehyde as a test reaction for analysing the effect of various reducible supports including Fe_2O_3, Fe_3O_4, ZrO_2, TiO_2, ZnO and SnO_2, and examining the solvent effect on activity and selectivity towards the unsaturated alcohol.

2. Experimental

2.1. Synthesis of Pt supported catalysts

The catalysts studied were obtained from an aqueous solution containing 8% (w/w) chloroplatinic acid (Sigma–Aldrich Ref. 262587) as metal precursor and the following metal oxides as supports: tin (IV) oxide (Sigma–Aldrich Ref. 549657), zirconium (IV) oxide (Sigma–Aldrich Ref. 544760), zinc (II) oxide (Sigma–Aldrich Ref. 544906), iron (II,III) oxide (Sigma–Aldrich Ref. 637106), iron (III) oxide (Sigma–Aldrich Ref. 544884) and titanium (IV) oxide (Degussa, P-25).

The synthetic procedure was as follows: a volume of 6.57 mL of chloroplatinic acid solution was diluted to 200 mL with Milli-Q water and adjusted to pH 7 by adding 0.1 M NaOH (FLUKA Ref. 43617). Then, an amount of 4.75 g of support was added and the mixture readjusted to pH 7 with NaOH for acid supports or HCl for basic supports. The solution containing the support was refluxed at 80 °C under vigorous stirring for 2 h. Then, a volume of 10 mL of isopropanol was added, the temperature raised to 110 °C and refluxing continued for 30 min, after which the mixture was vacuum filtered and the filtrate washed with three portions of 25 mL of water each. The resulting solid was dried in a muffle furnace at 110 °C for 12 h, ground and calcined at 400 °C for 4 h. After calcination, the solid was ground again, sieved through a mesh of 0.149 mm pore size and stored in a topaz flask. The nominal proportion of Pt in the catalyst thus obtained was 5 wt%. Finally, the catalyst was reduced under a hydrogen stream flowing at 30 mL/min at selected temperatures for 2 h. Reduction temperature was chosen according to significant features observed in the temperature-programmed reduction profiles. The solid names used included the metal, its support and the reduction temperature used (*e.g.* Pt/ZnO-175).

2.1.1. Characterization of catalysts

The textural properties of the solids calcined at 400 °C (*viz.* specific surface area, pore volume and mean pore radius) were determined from nitrogen adsorption–desorption isotherms obtained at liquid nitrogen temperature on a Micromeritics ASAP-2010 instrument. Surface areas were calculated with the Brunnauer–Emmett–Teller (BET) method. All samples were degassed to 0.1 Pa at 110 °C prior to measurement.

Elemental analysis of Pt containing samples was performed by the staff at the Central Service for Research Support (SCAI) of the University of Córdoba, using inductively coupled plasma mass spectrometry (ICP-MS). Measurements were made on a Perkin–Elmer ELAN DRC-e instrument following dissolution of the sample in a 1:1:1 $H_2SO_4/HF/H_2O$ mixture. Calibration was done by using PE Pure Plus atomic spectroscopy standards, also from Perkin–Elmer.

Transmission electron microscopy (TEM) images were obtained at the SCAI of the University of Córdoba by using a Philips CM-10 microscope for low magnification samples and a JEOL JEM 2010 microscope for high magnification samples. All samples were mounted on 3 mm holey carbon copper grids.

EDX measurements were made with a JEOL JSM-6300 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) detector.

X-ray patterns for the samples were obtained with a Siemens D-5000 diffractometer equipped with a DACO-MP automatic control and data acquisition system. The instrument was used with CoK_α radiation and a graphite monochromator.

Temperature-programmed reduction (TPR) measurements were made with a Micromeritics TPD-TPR 2900 analyser. An amount of 200 mg of catalyst was placed in the sample holder and reduced in a 5:95 H_2/Ar stream flowing at 40 mL/min. The temperature was ramped from 0 to 850 °C at 10 °C min^{-1}; by exception, the upper limit for solids Pt/ZnO and Pt/SnO_2 was 500 °C.

X-ray photoelectron spectroscopy (XPS) data were recorded on 4 mm × 4 mm pellets 0.5 mm thick that were obtained by gently pressing the powdered materials following outgassing to a pressure below about 2×10^{-8} Torr at 150 °C in the instrument pre-chamber to remove chemisorbed volatile species. The main chamber of the Leibold-Heraeus LHS10 spectrometer used, capable of operating down to less than 2×10^{-9} Torr, was equipped with an EA-200 MCD hemispherical electron analyser with a dual X-ray source using AlK_α (hv = 1486.6 eV) at 120 W, at 30 mA, with C(1s) as energy reference (284.6 eV).