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Effect of the acid–base properties of the support on the performance of Pt catalysts in the partial hydrogenation of citral

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ABSTRACT

In this work, the effect that mesoporous solid materials, with different acid–base properties (Pt-1 wt%/acid or base) have over the product distribution during the partial hydrogenation of citral was evaluated. It was found that basic materials were the most active catalysts reaching a 100% citral conversion after 1 h of reaction. Regarding selectivity, in basic materials (Pt/MgAl-c and Pt/MgAl-r) citronellal was the main product, while nerol and geraniol were produced in acid solids (Pt/SiO_2; Pt/SiO_2–TiO_2 and Pt/SiO_2–ZrO_2). The formation of unsaturated alcohols is related to the strength and density of the acid sites of the catalyst and in this sense the Pt/SiO_2–ZrO_2 gave a yield of 80%. The acidity trend is: Pt/SiO_2–ZrO_2 > Pt/SiO_2–TiO_2 > Pt/SiO_2 > Pt/MgAl-c.

1. Introduction

Citral (3,7-dimethyl-2,6-octadienal) is a terpene present in lemon grass (65–85 wt%) responsible for the citric aromas and flavors. It is a molecule with three sites susceptible to be hydrogenated: a carbonyl group (—C═O), a double bond (C═C) conjugate to the carbonyl and an isolated double bond (C═C). Products from the partial hydrogenation (geraniol–nerol and citronellal) are used in flavor, pharmaceutics and cosmetics industries [1]. In this way, the design and synthesis of heterogeneous catalysts to drive the citral hydrogenation by a specific route is an attractive task [2].

It is well known that the hydrogenation of the carbonyl group is thermodynamically less favourable than the C═C double bond conjugate to the carbonyl present in citral. Several research groups have directed some efforts to develop catalysts for the selective hydrogenation of the carbonyl [2]. The product distribution during citral hydrogenation is affected by different factors such as type of metal, promoter addition, the physicochemical properties of the support and reaction conditions. In this sense, Cordier et al. [3] examined the effect of active metal, support, reaction conditions, solvent and the addition of promoters on the selectivity to unsaturated alcohols in the hydrogenation of α,β unsaturated aldehydes. Gallezot and Richard [4] produced a review on the chemioselective hydrogenation of α,β unsaturated aldehydes, pointing out the effect of different solid catalysts on the selectivity in hydrogenation. In the case of the metallic phase, it has been demonstrated that transition metals provide specific selectivities to unsaturated alcohols in selective hydrogenation reactions. Singh and Vannice [5] studied the hydrogenation of citral on several Group VIII metals supported on silice and showed the activity has the following trend: Pd > Pt > Ir > Os > Ru > Rh > Ni > Co > > Fe, with Os, Ru and Co producing unsaturated alcohols, nerol and geraniol, whereas Rh, Ni and Pd were selective to citronellal and isopulegol.

On the other hand, the high electron density of the conjugate C═C and the oxygen of the carbonyl group induces polarity to the citral molecule. This electronic condition affects the way the citral molecule interacts with the catalytic surface, being influenced by the acid–base nature of the catalyst surface. In this sense, materials with Lewis acid sites induce the adsorption of α,β unsaturated aldehydes through the carbonyl (C═O), which allows the increase of selectivity towards unsaturated alcohols [4]. These Lewis sites can be produced by: (a) the modification of the hydrogenating metal with the addition of a second metal (Pt–M bimetallic catalysts, where M = Sn, Ge, Co) [3,6–9], (b) the use of reducible metal oxides [10–13] or the synthesis of mixed oxides as supports[14]. However, in the case of bimetallic catalysts it has been reported that the addition of electropositive promoters to the metallic active phase brings a decrease of the activity due to the decoration effect of the metallic particles [15–19].

Regarding the effect of basic species, Satagopan et al. [20] reported an increase in selectivity to unsaturated alcohols upon the addition of alkaline compounds to the reaction mixture. Such effect

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has been attributed to the formation of Lewis sites as result of the interaction of cationic species (Na^+, K^+, etc.) with the support [4,21]. In contrast, basic mixed oxides derived from hydrotalcites (LDH) of the type Mg^{2+}/Al^{3+} and modified by Ni^{2+}, Mg^{2+}, Co^{2+} [22], and Rh/MgO [23] catalysts were evaluated in the citral hydrogenation. In both cases, the main product was citronellal.

Based on this information, it is clear that upon the modification of the acidity or basicity of the catalytic support the interaction of a citral molecule with the catalytic surface would be affected due to its polarity. The nucleophilic zone of citral (—C=O) would be oriented towards Lewis acid sites appearing on the formation of Si—O—M species, so that the unsaturated alcohols nerol and geraniol would be obtained. On the other hand, on basic sites, the support would induce citral to adsorb and hydrogenate the conjugate C=C bond allowing the formation of citronellal.

In this work a study has been performed to evaluate the effect of acid–base properties of the support on the catalytic behavior of Pt catalysts in the hydrogenation of citral in liquid phase.

2. Experimental

2.1. Catalyst synthesis

Acid supports pure SiO_2; SiO_2–TiO_2 (95:5 wt%) and SiO_2–ZrO_2 (90:10 wt%) were synthesized by the sol–gel method. In order to obtain materials, the hydrolysis and condensation were performed using a two-stage process: acid (HNO_3) and basic (NH_4OH). The molar ratios used in the synthesis were those employed by Tamayo et al. [24]: solvent/alkoxide = 30 for Si and Si–Ti, or 40 for Si–Zr; water/alkoxide = 8; acid/alkoxide = 0.2 and base/alkoxide = 0.2. After drying at room temperature, the xerogels were calcined 4 h at 773 K under air flow. Supports were labeled as: SiO_2–AB (synthesized as reference); SiO_2–TiO_2 and SiO_2–ZrO_2.

In the case of basic materials, hydrotalcite (LDH) samples Mg_3AlO were prepared by coprecipitation from an aqueous solution of magnesium and aluminum cations (solution A) and a highly basic carbonate solution (solution B). Solution A containing $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3){\cdot}9H_2O$ dissolved in deionized water. Solution B was prepared by dissolving appropriate amounts of Na_2CO_3 and NaOH in deionized water, the concentration of Na_2CO_3 being equal to 1 M. NaOH concentration was adjusted to obtain pH 10. The synthesis procedure was similar to that reported in the literature [25,26]. Precipitates were aged for 72 h at pH 10 and 333 K, the solids were filtered, washed with deionized water until pH 7 and calcined at 773 K.

Alcoholic solutions (H_2PtCl_6/C_2H_5OH) were used in the wet impregnation method to obtain Pt (1 wt%) on the supports. After platinum impregnation all materials were calcined and reduced at 773 K under H_2 atmosphere just before used as catalysts. The synthesized (Pt/MgAl-c) was considered as a Lewis basic material. Part of the reduced Pt/MgAl-c was rehydrated by directly adding deionized water (100 wt% with respect to the sample Pt/MgAl-c), and aged for 6 h, in order to restore the LDH structure and obtain Brönsted basic sites, before being used as catalyst and named Pt/MgAl-r.

2.2. Materials characterization

The BET specific surface areas were obtained with an Autosorb-1 Quantachrome equipment. The samples were pretreated in vacuum (<10^{-2} Pa) at 373 K prior to N_2 adsorption. The solids crystalline structure was characterized by X-ray diffraction (XRD) with a Siemens D-500 diffractometer using Cu Kα radiation with $\lambda = 1.5406$ Å. NH_3 and CO_2 thermodesorption tests were performed using an ISRI RIG-110 automatic reactor with thermal conductivity detector equipment. Samples (0.1 g) were loaded into a quartz reactor and pretreated for 1 h at 773 K under helium atmosphere, then cooled at room temperature. Samples were saturated using pulses of Ammonia or CO_2. After saturation, ammonia (or CO_2) was replaced with helium, and the sample was heated to 773 K at a rate of 10 K min^{-1}. To identify the acid type sites of the mixed oxides FTIR-Py thermodesorption experiments were carried out in an IR-PerkinElmer equipment for a wide wavelength of 2000–400 cm^{-1}. FTIR measurements were performed using self-supporting pressed discs (12 mg/cm^2 thickness). Samples were outgassed at 523 K (10^{-6} Torr) for 1 h. Pyridine was then adsorbed, and evacuated for 30 min at room temperature. Spectra were taken every 100 K temperature increase. The FTIR instrument was typically operated at a scan speed of 0.1 $cm^{-1}\,s^{-1}$ and a resolution of 2 cm^{-1} collecting 20 scans per spectrum. High resolution images were obtained in a High Resolution Electron Microscopy-JEOL-JEM-2100 (resolution 0.19 nm at 200 kV accelerating voltage). Samples powder was deposited in a vial with ethanol; a drop of the solution was taken with a glass capillary and deposited in a copper carbon covered grid.

2.3. Catalytic activity

Catalytic tests were performed in a Parr reactor at 200 psi of H_2 at 373 K and 1000 rpm. A citral/isopropanol 0.1 M solution (130 mL) and 16 wt% of catalysts (catalyst particle size = 50 μm) respect to citral were used. After reduction the catalyst was handled under nitrogen atmosphere and loaded to the reactor. Reaction samples were taken at regular periods and products were analyzed by an Agilent 6890N chromatograph (HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm)) coupled to an Agilent 5973 mass spectrometer with a selective mass detector. At the end of the reaction, after cooling, the reaction mixture was filtered; the catalyst was washed and recovered. The catalytic tests were done in a kinetic regime, without mass transfer resistances. Calculations following Weiz-Pratter and Mears criteria confirmed the absence of external or intraparticle mass transfer limitations.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the diffraction spectra of all synthesized materials, prepared by sol–gel (SiO_2–AB, SiO_2–ZrO_2 and SiO_2–TiO_2), calcined at 773 K and the Mg_3AlO calcined at 773 K and rehydrated. The diffraction patterns of the silica-based materials present only a typically broad reflection peak at 22° that corresponds to a 3.9 Å interplanar distance. All these materials are amorphous solids. On the other hand the temperature treatment of the LDH material (Mg_3AlO) at 773 K causes the hydrotalcite structure destruction and a mixed oxide of low crystallinity was obtained (Fig. 1D). It is important to remark that during these thermal events, structural transformations take place due to dehydration, dehydroxilation and decarboxylation processes.

Once the calcined Mg_3AlO is rehydrated, by the addition of deionized water, the hydrotalcite structure restoration takes place. This phenomenom occurs gradually, until complete restoration of the hydrotalcite-like structure (Fig. 1E) after 6 h of aging. The XRD pattern of MgAl-r sample corresponds to the Mg_3AlO hydrotalcite phase structure (JCPDS 22-700) with sharp and symmetric (0 0 3) reflections below 30 $2\Theta/°$, and asymmetric (0 0 6) reflections at higher $2\Theta/°$ values. Specifically, the reflection peaks at 2Θ of 11°, 23°, 35°, 39° and 47° attributed to the (0 0 3), (0 0 6), (0 1 2), and (0 1 5) crystal planes [27] provide a clear evidence for the formation of LDH structure. This result confirms the memory effect characteristic of the LDH materials.