Alkynes hydrogenation over Pd-supported catalysts

N. Marin-Astorga, G. Pecchi, J.L.G. Fierro, and P. Reyes

Departamento de Fisicoquímica, Facultad de Ciencias, Universidad de Concepción, Casilla 160-C, Concepción, Chile

Instituto de Catalálisis y Petroquímica, CSIC, Cantoblanco, 28049 Madrid, Spain

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The selective half hydrogenation of alkynes is a particularly important type of reaction in the context of fine chemical manufacture. The acetylenic group readily participates in substitution reactions enabling the formation of new carbon–carbon bonds and hydrogenation leading to alkene or alkane species, among others. The use of synthetic alkynes has been exploited in the synthesis of biologically active compounds, e.g., insect sex pheromones (pest control) and vitamins [1].

Palladium catalysts used for the selective hydrogenation of alkenes in industrial scale contains a low palladium loading (0.01–0.03 weight%) in a highly dispersed state. The effect of metal dispersion, carbon deposits, and the use of promoters and additives on the catalytic performance during alkynes hydrogenation have also been reported [2–4]. Attempts have been made to relate the activity of palladium catalysts during the partial hydrogenation of superior alkynes with the nature and porosity of the support substrate. The use of the new materials of the M41S family opened new opportunities to analyze the performance of palladium catalysts. These materials appear specially interesting because their mesoporous may allow an easy access of the large molecules, as that usually involved in the production of fine chemicals, to the active sites. The preparation of this type of solids was initiated by Pinnavaia [5–6], and it has been widely developed by other authors [7–8]. Mastalir et al. [9] pointed out that the porosity of the support may significantly affect the performance of Pd/montmorillonite catalyst for the hydrogenation of 1-phenyl-1-pentyne, which allows a high selectivity to the cis-alkene. The high cis-isomer stereoselectivity and the limit of overhydrogenation at such low palladium contents is attributed to the porosity of the support.

This work was undertaken with the aim to study the influence of the support, and also the poisoning of the palladium sites with lead, on the activity and selectivity in the stereoselective hydrogenation in liquid phase of the phenyl alkyl acetylenics. A commercial silica, an MCM-41 type, and a silylated MCM-41 substrate have been used as supports of the palladium catalysts. Specific surface area was evaluated from the nitrogen adsorption–desorption isotherms, metal dispersion from H2 and CO chemisorption, XRD, XPS, and TEM.

KEY WORDS: palladium; MCM-41; phenyl alkyl acetylenics; hydrogenation; stereoselectivity.

1. Introduction

The selective half hydrogenation of alkynes is a particularly important type of reaction in the context of fine chemical manufacture. The acetylenic group readily participates in substitution reactions enabling the formation of new carbon–carbon bonds and hydrogenation leading to alkene or alkane species, among others. The use of synthetic alkynes has been exploited in the synthesis of biologically active compounds, e.g., insect sex pheromones (pest control) and vitamins [1].

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2. Experimental

2.1. Preparation

Three different supports were used: a commercial SiO2 (BASF D11-11), S BET = 85 m2/g, r p = 80 Å, V p = 0.16 cc/g; a mesoporous material type MCM-41, S BET = 984 m2/g, r p = 22 Å, V p = 0.89 cc/g; and a silylated MCM-41, S BET = 1016 m2/g, r p = 24 Å, V p = 0.72 cc/g. The synthesis of MCM-41 was performed using a standard procedure [10]. The resulting synthetic gel of composition SiO2:CTABr:TMAOH:H2O = 1:0.15:0.26:24.3. An aliquot of this solid was silylated using 1,1,1,3,3,3 hexamethyldisilazane (HMDS

To whom correspondence should be addressed.
E-mail: preyes@udec.cl
as a silylating agent. A solution of HMDS: toluene = 1 : 20 was added to the calcined samples after vacuum. The mixture was refluxed for 2 h at 393 K with magnetic stirring under argon. The volatiles were stripped on a refrigerant and the dry powder was washed two or three times with toluene, dried and calcined as described above.

The catalysts were prepared by impregnation using a slight excess of solution required to fill the pore volume of the supports with a solution of Pd(acac)$_2$ in toluene, in the required amount to get 1 wt% of palladium. The solids were dried at 373 K and calcined at 673 K under airflow for 4 h. The solids were labeled as Pd/SiO$_2$, Pd/MCM-41, and Pd/MCM-41-Si. An aliquot of the previously prepared catalysts was poisoned by adsorption of a solution of Pb(C$_2$H$_3$O$_2$)$_2$·3H$_2$O in toluene, in the required amount to get 1 wt% of lead, followed by drying and calcination step at 373 and 673 K, respectively. Three new catalysts were obtained according to the previous procedure: Pb-Pd/SiO$_2$, Pb-Pd/MCM-41, and Pb-Pd/MCM-41Si. All catalysts were reduced in situ in hydrogen at 573 K for 1 h before their characterization or catalytic evaluation.

2.2. Characterization

Specific area and porosity were obtained with an automatic Micromeritics apparatus Model ASAP 2010 using nitrogen gas as adsorbate at the liquid nitrogen temperature in the 0.05–0.995 relative pressure range. The dispersion of the metal was determined by H$_2$ and CO chemisorption at 343 K in the same equipment. Hydrogen chemisorption was carried out at 298 K in the pressure range of 1 to 100 mm Hg. Once the hydrogen isotherm was obtained, the sample was outgassed at room temperature and a second hydrogen isotherm was determined at the same temperature. The hydrogen uptake was evaluated from the irreversible amount of adsorbed CO as difference between the first (total) and the second (reversible) isotherm within the pressure range of 1 to 4 mm Hg. Thermogravimetric analysis (TGA) of the supports was carried out in a Mettler Toledo TGA/SDTA851e apparatus in a temperature range of 273 to 873 K. TPR experiments were carried out in a TPR/TPD 2900 Micromeritica system provided with a thermal conductivity detector. The reducing gas was a mixture of 5% H$_2$/Ar (40 cm$^3$/min) and a heating rate of 10 K/min was employed. X-ray diffraction patterns were obtained on a Rigaku diffractometer using a Ni-filter and Cu K$_{\alpha 1}$ radiation. Intensity was measured by scanning steps in the 20 range, first between 3 and 70° at 1°/min, and then the region between 20 and 50° was rescanned at 0.25°/min. TEM micrographs were obtained in a Jeol Model JEM-1200 EXII system. The samples were prepared by the extractive replica procedure.

Photoelectron spectra (XPS) were recorded using an Escalab 200R spectrometer provided with a hemispherical analyzer, operated in a constant pass energy mode and Mg K$_\alpha$ X-ray radiation ($h\nu = 1253.6$ eV) operated at 10 mA and 12 kV. The system was provided with a reaction cell that allows pretreatment at high temperatures. The samples were pressed in a hydraulic die to form thin, smooth discs and placed in the cell. The catalysts were reduced in situ in hydrogen at 573 K for 1 h and then transported to the analysis chamber without contact with air. The surface Pd/Si, Pb/Si ratios were estimated from the integrated intensities of Pd 3d$_{5/2}$, Pb 4f$_{7/2}$, and Si 2p lines after background subtraction and corrected by the atomic sensitivity factors [11]. The line of Si 2p at 103.4 eV was used as an internal standard. Palladium and lead peaks were decomposed into several components assuming Gaussian–Lorentzian shapes.

2.3. Catalytic activity

The hydrogenation in liquid phase of the phenyl alkyl acetylenic compounds (1-phenyl-1-propyne, 1-phenyl-1-butyne, and 1-phenyl-1-pentyne) (ALDRICH 99% of purity) was carried out in a batch reactor at 298 K and 1 bar H$_2$ pressure using 25-mg catalyst. A phenyl-alkyl-acetylenics/Pd molar ratio of 5000 was used, similar to that employed for Mastalir et al. [12] for these kind of reactions. Prior to reaction, the sample was reduced at 573 K during 1 h in H$_2$ flow and cooled to the reaction temperature. Then, the solvent (dried THF) was injected and the phenyl-alkyl-acetylenics were fed under constant stirring. Samples were taken at different reaction times and analyzed by a gas chromatograph Star VARIAN 3400-CX provided with a capillary column DB-Wax (0.53 mm: 30 m) and flame ionization detector (FID).

3. Results and discussion

XRD analysis of the samples allowed to confirm that the mesoporous MCM-41 material was obtained. The peaks corresponding to (100), (110), (200), and (210) planes of a hexagonal structure with symmetry P6$_3$ for the reflection planes (hk0) were found. On the other hand, the values of the parameter “a$_0$” of the hexagonal pore arrangement for MCM-41 (noncalcined), MCM-41 (calcined), and MCM-41-Si substrates were 50, 46, and 47 Å respectively and were in good agreement with those previously reported by Beck et al. [10]. TG analysis of the MCM-41 support showed three weight-loss peaks associated with exothermic processes. The former between 298 and 403 K corresponds to the desorption of physisorbed water on the surface. The second and third steps, at 403–593 K and above 593 K, are mainly attributed to the decomposition and oxidation of the organic matter associated with condensation of silanol.