Effect of precursor on the acetic acid conversion over palladium supported catalysts

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Introduction

Human economic activities and the world’s population growth have resulted in the high consumption of fossil fuels. Energy requirements and environmental concerns have led to increased interest in substituting fossil fuels with alternatives such as biomass. Hydrogen is one of the most widely accepted new energy vectors, and its production from bio oil that is derived from fast pyrolysis of biomass is today a promising option and afterwards for its application in fuel cells. Acetic acid is one of the molecules that comprise bio-oil in higher amount and for this reason it is commonly chosen as a model compound [1]. In this work, the decomposition of acetic acid (HOAC) was carried out to investigate the influence of Pd precursor in two different supports.

Materials and Methods

All the catalysts (1 wt% Pd) were prepared by the incipient wetness technique using palladium acetylacetonate solution (Merck99%), palladium chloride (Aldrich 99%) or palladium nitrate (Merck99%) as precursors. After impregnation, the catalysts were dried at 120 °C for 15h and calcined at 500 °C for 3h. The catalysts Pd/Al2O3-Aca, Pd/Al2O3-Cl, Pd/Al2O3-Ni, Pd/TiO2-Aca, Pd/TiO2-Cl and Pd/TiO2-Ni were characterized by N2 physisorption, XRD, H2-TPR, XPS and CO-DRIFTS. The BET surface area, average pore diameter and pore volume were determined in a Micromeritics ASAP 2020 device. XRD patterns were recorded in a Rigaku Miniflex diffractometer (10°-90°). The H2-TPR experiments were performed under 5% H2/He flow. The XPS analyses were obtained in an ESCALAB 250Xi Thermo Scientific. CO-DRIFTS were collected with a FTIR spectrometer (Bruker) equipped with a diffuse reflectance cell with Praying Mantis geometry and a reaction chamber with ZnSe windows (Harrick). Acetic acid decomposition tests were carried out using an apparatus with a mass flow controller, a tubular reactor and the analysis system was constituted by a gas chromatograph (Varian CP3800) equipped with two capillary columns (Carboxen 1010 plot and CP-PoraBond Q).

Results and Discussion

Table 1 shows BET surface area, the pore volume and diameter for the several catalysts. The adsorption isotherms of Pd/Al2O3-Aca, Pd/Al2O3-Cl and Pd/Al2O3-Ni catalysts were type IV isotherms with ‘ink bottle’ type pores. Pd/TiO2-Aca, Pd/TiO2-Cl and Pd/TiO2-Ni catalysts presented type V isotherms with ‘slit-like’ pores [2]. XRD results showed two crystalline forms of TiO2 (Anatase and Rutile). Typical diffraction peaks of γ-Al2O3 were observed for Al2O3 supported catalysts. The TPR profiles showed that the peak at room temperature matches to PdO reduction. TiO2 supported catalysts showed TPR peaks in the range of 70-90°C which are attributed to desorption of weakly adsorbed hydrogen from the Pd surface and the decomposition of Pd hydride (β-H2Pd), formed at room temperature [3]. There were also peaks assigned to the reduction of the support and relative to the interaction between Pd and TiO2. The XPS results of reduced catalysts indicate that Pd species exists in the forms of Pdº and Pd2+ (minor intensity). These results are supported by the results of FTIR spectra of CO adsorption where a strong band at 1925 cm-1 is assigned to bridge-bonded CO on Pd (111) [3]. H2 selectivity over all the catalysts at temperatures between 300-800 ºC is depicted in Figure 1.

Table 1. BET surface area (S_BET), average pore size (D_V) and pore volume (V_p) obtained for all the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd/Al2O3 Aca</th>
<th>Pd/Al2O3 Cl</th>
<th>Pd/Al2O3 Nit</th>
<th>Pd/TiO2 Aca</th>
<th>Pd/TiO2 Cl</th>
<th>Pd/TiO2 Nit</th>
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<tbody>
<tr>
<td>S_BET(m²/g)</td>
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<td>190</td>
<td>193</td>
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<td>56</td>
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<td>D_V(Å)</td>
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<td>131</td>
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<td>142</td>
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<tr>
<td>V_p(cm³/g)</td>
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<td>0.47</td>
<td>0.47</td>
<td>0.19</td>
<td>0.21</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Figure 1. Selectivity towards hydrogen production over all the catalysts for acetic acid decomposition.

Maximum H2 selectivity was obtained at 700°C (52%) for the Pd/Al2O3-Aca catalyst. H2 was detected only at temperatures between 600 to 800 ºC. At lower temperatures the main products of the reaction were CO2, H2O, CH4 and CO. Catalysts prepared with palladium acetylacetonate as precursor were more active.

Significance

Pd/Al2O3-Aca was the most active and selective catalyst for decomposition of HOAC reaction due to better dispersion, good thermal stability and weak support interaction.

References