Hydrodeoxygenation of phenol over Pd on oxophilic supports

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Introduction

During the last few years, catalytic hydrodeoxygenation (HDO) has been extensively investigated for a number of molecules to represent the different families of biomass-derived compounds [1]. Phenol is an important model compound that is present in the bio-oil as well as it is an intermediate produced during HDO of different molecules. According to the literature, the HDO of phenol is a bifunctional reaction that requires a metallic site and an acid site [2]. The metal particles are responsible for hydrogenation/dehydrogenation reactions while the oxo-compound is adsorbed on the Lewis acid sites of the support, which also catalyzes the alklylation and polymerization reactions. Therefore, the support plays a key role in the HDO of phenol. The goal of this work is to further compare the product distribution of HDO of phenol over Pd catalysts supported on different oxides. The analysis of reaction pathways combined with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements might shed some light on the reaction mechanism.

Materials and Methods

SiO₂ (Hi-Sil 915) and Al₂O₃ (Puralox) used as supports were obtained from PPG Industries, Inc. and Sasol, respectively. The ZrO₂ support was synthesized by the precipitation method. Pd/SiO₂, Pd/Al₂O₃ and Pd/ZrO₂ catalysts with a nominal Pd loading of 2.0 wt. % were prepared by incipient wetness impregnation of the supports with an aqueous solution of Pd(NO₃)₂ (Merck). After impregnation, the powder was calcined in air at 673 K for 3 h (2 K/min). The samples were characterized by optical emission spectroscopy (ICP-OES), N₂ physisorption, X-ray diffraction (XRD), CO chemisorption, diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed pyridine and DRIFTS in-situ experiments under similar conditions to those employed in the HDO reaction. The vapor-phase conversion of the oxygenate compound of interest (phenol, cyclohexanol, or cyclohexanone) was carried out in a fixed-bed quartz reactor, operating at atmospheric pressure of H₂ and 573 K.

Results and Discussion

The DRIFTS spectra of pyridine absorbed showed that both Brönsted and Lewis acid sites exist on the surface of the Pd/Al₂O₃ catalyst while Pd/ZrO₂-N shows predominantly Lewis acid sites. Pd/SiO₂ does not exhibit any measurable acidity. Thus, the following order of density of acid sites is observed: Pd/Al₂O₃ > Pd/ZrO₂-N > Pd/SiO₂.

The performance of Pd catalysts supported on SiO₂, Al₂O₃, and ZrO₂ for the hydrodeoxygenation (HDO) of phenol has been compared in the gas phase, at 300°C and 1 atm on a fixed bed reactor. Figure 1 shows the phenol conversion and product yield as a function of W/F for Pd/SiO₂ and Pd/ ZrO₂ catalysts. Pd/ZrO₂ was much more active than the Pd/SiO₂ and Pd/Al₂O₃ catalysts, which exhibited approximately the same conversion. The TOF over Pd/ZrO₂ catalysts was about two times higher than that over Pd/SiO₂ and Pd/Al₂O₃, which suggests that ZrO₂ support enhance the deoxygenation activity. While Pd supported on SiO₂ and Al₂O₃ exhibits high selectivity to cyclohexanone, when supported on an oxophilic support such as ZrO₂, it favors the selectivity towards benzene, reducing the formation of ring hydrogenated products, cyclohexanone and cyclohexanol. DRIFTS experiments support the participation of a keto-tautomer intermediate (2,4-cyclohexadienone) in the reaction. This intermediate can be hydrogenated in two different paths. If the ring is hydrogenated, cyclohexanone and cyclohexanol are dominant products, as in the case of Pd/SiO₂ and Pd/Al₂O₃ catalysts. By contrast, if the carbonyl group of the keto-intermediate tautomer is hydrogenated, benzene is directly formed via rapid dehydration of the unstable cyclohexadienol intermediate. This is observed in the case of Pd/ZrO₂ catalyst. These results demonstrate that the selectivity for HDO of phenol can be controlled by using supports of varying oxophilicity.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Phenol conversion and products distribution as a function of W/F over: (A) Pd/SiO₂; (B) Pd/ZrO₂. Reaction conditions: Temperature: 573 K, atmospheric pressure, H₂/phenol molar ratio = 60.

**Significance**

The evaluation of Pd/SiO₂, Pd/ZrO₂ and Pd/Al₂O₃ catalysts in the reaction of the phenol HDO will allow better understanding of the effect of the support on the reaction mechanism. In general, this contribution will help the development of catalysts with high activity and stability in the process of HDO bio-oil, facilitating the production of liquid fuels from renewable sources.

**References**