Hydrodeoxygenation of phenol over niobia supported Pd catalyst

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ded by the reaction mechanism. Different reaction pathways have been proposed for the HDO of phenol: (i) hydrogenation/dehydration; (ii) direct deoxygenation (DDO); and (iii) tautomerization. The preferred pathway and product distribution depends on the catalyst properties and reaction conditions used.

Bifunctional catalysts are able to promote route (i), with the metal site providing the hydrogenation function for hydrogenating the phenolic aromatic ring, producing the saturated alcohol compound (which is dehydrated on acid sites [5,6]). When catalysts do not have sufficient acidity, the dehydration step is hindered, such that the deoxygenated compound must be formed by others routes.

Under mild reaction conditions, direct deoxygenation has been questioned by many authors due to the high-energy dissociation of the C(sp²)–OH bond [7]. However, this reaction route may occur in the presence of oxophilic metals such as Ru as well as supports like TiO₂, whose strong interaction with the oxygen atom reduces the energy barrier for the direct cleavage of the C–O bond of the aromatic ring [8].

Recently, our group proposed by DRIFTS experiments and DFT calculations that the HDO of phenolic compounds should involve the decomposition of the lignin fraction of woody biomass. The main challenge is to design an optimal catalyst, which should be active, stable and selective, allowing C–O bond scission with minimal H₂ consumption and carbon loss. Therefore, the development of an appropriate catalyst for HDO of model compounds such as phenol requires an understanding of the reaction mechanism. Different reaction pathways have been proposed for the HDO of phenol: (i) hydrogenation/dehydration; (ii) direct deoxygenation (DDO); and (iii) tautomerization. The preferred pathway and product distribution depends on the catalyst properties and reaction conditions used.

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formation of an unstable ketone intermediate with preliminary tautomerization step [9–12]. In this case, when the C=O group of this unstable ketone is hydrogenated, a very reactive unsaturated alcohol is formed and dehydration occurs easily. The oxophilic sites (represented by unreduced metals and metal oxide cations from the support) play a key role on the tautomerization mechanism, improving the deoxygénation activity. The oxophilic sites may favor the activation of the C=O bond, the chemoselective C=O bond hydrogenation and the production of deoxygénated aromatic compounds. The oxophilic metal reduces the energy barrier for C=O scission through a strong interaction of the oxophilic metal with the oxygen of the aromatic compound [13]. ZrO$_2$ and TiO$_2$ supports have demonstrated superior performance for deoxygénation of phenolic compounds such as phenol and cresol [10,13,14]. The high selectivity to deoxygénated products over TiO$_2$ and ZrO$_2$ supported catalysts is likely due to the oxophilic sites of these supports represented by incompletely coordinated Ti$^{4+}$/Ti$^{3+}$ and Zr$^{4+}$/Zr$^{3+}$ cations near the perimeter of the metal particles. A stronger interaction between the oxygen atom in phenolic molecule with the metal oxide cation promotes the selective hydrogenation of the carbonyl function of the tautomer intermediate produced or the cleavage of the aromatic C=O bond. Like zirconia and titania, niobia is also a reducible support but it has been scarcely used for HDO of model molecules representatives of lignin. Niobia was used as a catalyst support for the HDO of fatty acids and triglycerides [15,16] and alcohol [17]. Pt supported over various oxides (SiO$_2$, MgO, CeO$_2$, ZrO$_2$, Al$_2$O$_3$, SiO$_2$-Al$_2$O$_3$, C, TiO$_2$, Nb$_2$O$_5$) was tested for the HDO of lauric acid [18]. Pt/Nb$_2$O$_5$ exhibited the highest activity followed by Pt/TiO$_2$. An increase in activity with an increase in the reduction temperature of Pt/Nb$_2$O$_5$ was observed from 100 to 300 °C. Infrared spectroscopy results of adsorbed CO revealed that the increase in the reduction temperature led to a blockage of bridged adsorbed CO on the surface of Pt due to the partial decoration of Pt by NbO$_x$ species formed. The authors associated the high activity of Pt/Nb$_2$O$_5$ and Pt/TiO$_2$ catalysts to a cooperation between Pt and NbO$_x$ (or TiO$_x$) species at the perimeter sites, an effect promoted by the SMSI state (strong metal-support interaction). Thus, hydrogen is dissociated on the Pt surface and carboxylic acid is activated by NbO$_x$ species. The increase in activity with the increase of reduction temperature was attributed to the increase in the Pt-NbO$_x$ perimeter due to the migration of NbO$_x$ patches onto the Pt surface. However, there are no experimental studies about HDO of phenol over niobia supported catalysts.

Therefore, the aim of this work is to investigate the performance of Pd supported on SiO$_2$ and Nb$_2$O$_5$ for HDO of phenol reaction. The changes in catalyst structure with the reduction temperature were monitored by in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) experiments. The role of the support on the activation of carbonyl group was studied by DRIFTS experiments of adsorbed cyclohexanone.

2. Experimental

2.1. Catalyst synthesis

SiO$_2$ and Nb$_2$O$_5$ were used to prepare supported Pd catalysts. SiO$_2$ (silica gel, Aldrich, 7631-86-9) was calcined under air flow (50 mL/min) at a heating rate of 5 K/min up to 1073 K, remaining at this temperature for 5 h. Nb$_2$O$_5$ was obtained by calcination of niobic acid (CBMM, PR0043/0000000111) under air flow (50 mL/min) at 5 K/min up to 673 K for 4 h. Pd catalysts were prepared by incipient wetness impregnation of the support with 0.179 mL/g of an aqueous solution of Pd(NO$_3$_)$_2$·2H$_2$O (solution of 20% Pd in nitric acid, Umicore, 1846366) in order to obtain 2 wt% of Pd. After impregnation, the powder was dried in air at 293 K for 12 h and then calcined under synthetic air flow (50 mL/min) at 673 K for 3 h (2 K/min). Then, the samples were sieved between 150 and 270 mesh.

2.2. Catalyst characterization

Specific surface areas of the samples were measured on a Micromeritics ASAP 2020 analyzer by $N_2$ adsorption at 77 K. The density of acid sites of the catalysts was measured by temperature-programmed desorption of ammonia (NH$_3$-TPD). The samples (400 mg) were reduced under a flow of 60 mL/min of a mixture 10% H$_2$/He at a heating rate of 10 K/min up to 573 or 773 K, for 1 h, and then purged in He flow (30 mL/min) for 30 min. After reduction, the sample was cooled to 423 K and the feed composition was switched to a mixture containing 4% NH$_3$ in He (30 mL/min) for 30 min. The physisorbed ammonia was flushed out with flowing He (30 mL/min) for 1 h. Then, the catalyst was heated under He at 20 K/min to 773 K.

In order to titrate the oxophilic sites, infrared spectroscopy using DRIFTS of adsorbed cyclohexanone was performed using a Nicolet Nexus 870 spectrometer equipped with a DTGS-TEC detector. A Thermo Spectra-Tech cell (P/N 0030-102) capable of high pressure/high temperature operation and fitted with ZnSe windows served as the reaction chamber for in-situ adsorption and reaction measurements. Scans were taken at a resolution of 4 cm$^{-1}$ to give a data spacing of 1.928 cm$^{-1}$. The number of scans taken was typically 512 (~15 min). The sample (40 mg) was reduced in 100 mL/min of H$_2$ mixed with 100 mL/min of He at 573 or 773 K for 1 h and cooled to 323 K in 100 mL/min of He, and a background spectrum was recorded. He (60 mL/min) was flowed through a saturator containing the cyclohexanone at 323 K for 5 min prior to starting the first scan. Then the sample was purged with 100 mL/min of He for 15 min and a spectrum was obtained. The temperature was raised to 373, 423 and 473 K and additional spectra were recorded at those temperatures in 100 mL/min flowing He.

The dehydrogenation of cyclohexane was used as an insensitive structure reaction to determine the metallic dispersion of supported Pd catalysts [10]. In this case, a calibration curve between the cyclohexane dehydrogenation rate and the dispersion of palladium catalysts measured by CO chemisorption was used to determine the Pd dispersion of the catalysts of this study. Cyclohexane dehydrogenation was performed in a fixed-bed reactor at atmospheric pressure. Fresh samples (10 mg) were reduced at 573 or 773 K (10 K/min) for 1 h under a flow of 60 mL/min of pure H$_2$ and then cooled to the cyclohexane dehydrogenation reaction temperature (543 K) under hydrogen. The reaction mixture (WHSV = 170 h$^{-1}$) was fed into the reactor after bubbling H$_2$ (60 mL/min) through a saturator containing cyclohexane kept at 285 K (H$_2$/C$_6$H$_{12}$ = 13.2). The exit gases were analyzed using a GCMS (Agilent 7890A/5975C) equipped with an HP-Innowax capillary column and a flame-ionization detector (FID).

In situ X-ray powder diffraction measurements were performed at the beamline XRD1-D12A [18] of the Brazilian Synchrotron Light Laboratory (LNLS), Campinas, Brazil. The sample was loaded into a quartz capillary of 1.0 mm diameter between two quartz wool beds. The capillary was placed in a reaction cell connected to a 3-circle Heavy Duty diffractometer from Newport and oriented horizontally and perpendicularly to the X-ray beam. A Yaskawa-Motoman robotic arm was used to hold a hot air blower above the sample to control the temperature during the experiment. The diffraction patterns in a 20 range between 10 and 120° with an acquisition time of 5 s were obtained using an array of 24 Mythen detectors, installed in the delta circle at a distance of 760 mm from the sample. The wavelength of $\lambda = 1.0332 \, \text{Å}$ was selected by a double-crystal Si (111) monochromator. $\lambda$ and the distance of the sample to the detector were calibrated using Si (SRM 640d) and Al$_2$O$_3$ (SRM 676a) powders NIST standards. The measurements were carried out while the sample underwent the following treatments: (i) under a flow of He (8 mL/min) at 298 K; (ii) under a flow of 5% H$_2$/He mixture (8 mL/min) at 298 K, and (iii) under a flow of 5% H$_2$/He mixture (8 mL/min) from 298 to 773 K at a heating of 10 K/min, remaining at this temperature for 1 h. The average crystallite size of metallic Pd under different treatments was calculated.