Hydrodeoxygenation of phenol over niobia supported Pd catalyst

Adriana M. Barrios[a,b], Camila A. Teles[a,b], Priscilla M. de Souza[a], Raimundo C. Rabelo-Neto[a], Gary Jacobs[c], Burtron H. Davis[c], Luiz E.P. Borges[b], Fabio B. Noronha[a,b,*]

[a] National Institute of Technology, Catalysis Division, Rio de Janeiro 20081-312, Brazil
[b] Military Institute of Engineering, Chemical Engineering Department, Praça Gal. Tiburcio 80, Rio de Janeiro 22290-270, Brazil
[c] Center for Applied Energy Research, University of Kentucky, 2540 Research Park Dr., Lexington, KY 40511, USA

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ABSTRACT

This work investigates the performance of Pd supported on SiO_2 and Nb_2O_5 for the HDO of phenol reaction at different temperatures using a fixed-bed reactor. The type of support significantly affects activity and product distribution. The reaction rate for HDO of phenol over Pd/Nb_2O_5 was 90-fold higher than that observed for silica supported catalyst. Cyclohexanone was the dominant product for Pd/SiO_2, whereas benzene was mainly formed on Pd/Nb_2O_5. The high activity and selectivity to deoxygenated products of Pd/Nb_2O_5 for HDO of phenol is likely due to the strong interaction between the oxophilic sites represented by Nb^{5+}/Nb^{4+} cations and the oxygen from the phenol molecule. This promotes hydrogenation of the carbonyl function, resulting in the formation of 2,4-cyclohexadienol, which is dehydrated to benzene. For Pd/SiO_2 catalyst, the hydrogenation of the ring is the main reaction pathway observed. The reaction pathway was also affected by the reaction temperature, the hydrogenation of the carbonyl group being favored at high temperature.

1. Introduction

The global energy demand, in particular for renewable energy, is continuously increasing due to depletion of fossil fuel and environmental concerns. Lignocellulosic biomass has been identified as an attractive feedstock towards producing biofuels and chemicals. Among the different technologies for biomass conversion, fast pyrolysis has received greater attention because it is able to transform low density biomass solid into a denser liquid, which is easily storable and transportable [1,2]. However, the liquid generated via biomass pyrolysis (bio-oil) has poor quality and is thermally and chemically unstable due to the high content of oxygenated species and water in its composition [3]. Therefore, the bio-oil cannot be used directly as a transportation fuel without prior treatment. The hydrodeoxygenation (HDO) process is considered to be the most efficient technology for improving the quality of bio-oil by removal of oxygen from oxygenated functions of aromatic compounds [1]. The catalytic treatment of pyrolysis vapors at atmospheric pressure would eliminate most of the adverse properties of bio-oil, making it miscible with petroleum, non-corrosive, higher heating value, lower viscosity and more chemically stable [4]. Due to the complex chemical composition of bio-oil, model molecules that are representative of families of compounds derived from biomass have been studied such as phenolic model compounds (guaiacol, anisol, cresol and phenol) which derive from pyrolytic 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 H_2 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.

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 that 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(sp^2)–OH bond [7]. However, this reaction route may occur in the presence of oxophilic metals such as Ru as well as supports like TiO_2, 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

* Corresponding author at: National Institute of Technology, Catalysis Division, Rio de Janeiro 20081-312, Brazil.
E-mail address: fabio.bellot@int.gov.br (F.B. Noronha).

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) plays a key role on the tautomerization mechanism, improving the deoxygenation activity. The oxophilic sites may favor the activation of the C=O bond, the chemoselective C=O bond hydrogenation and the production of deoxygenated 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 deoxygenation of phenolic compounds such as phenol and cresol [10,13,14]. The high selectivity to deoxygenated 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_2O_3, SiO_2-Al_2O_3, C, TiO_2, Nb_2O_5) was tested for the HDO of lauric acid [15]. Pt/Nb_2O_5 exhibited the highest activity followed by Pt/TiO_2. An increase in activity with an increase in the reduction temperature of Pt/Nb_2O_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_2O_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_2O_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_2O_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_2O_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 $Pd(NO_3)_2\cdot2H_2O$ (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 ($\approx$ 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_6H_{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 2θ 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 λ = 1.0332 Å was selected by a double-crystal Si (111) monochromator. λ and the distance of the sample to the detector were calibrated using Si (SRM 640d) and Al_2O_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