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Hydrodeoxygenation of phenol over Pd catalysts. Effect of support on reaction mechanism and catalyst deactivation

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Abstract

This work investigates the effect of the type of support (SiO₂, Al₂O₃, TiO₂, ZrO₂, CeO_2 and $CeZrO_2$) on the performance of Pd-based catalysts for the hydrodeoxygenation of phenol at 573 K using a fixed bed reactor. Product distribution is significantly affected by the type of support. Benzene was the major product over Pd/TiO_2 and Pd/ZrO_2 ; on the other hand, cyclohexanone was a major product over Pd/SiO₂, Pd/Al₂O₃, Pd/CeO₂ and Pd/CeZrO₂. A reaction mechanism based on the tautomerization of phenol was proposed based on DRIFTS experiments and catalytic tests with the intermediate products. The high selectivity to benzene over Pd/TiO₂ and Pd/ZrO₂ catalysts is likely due to the oxophilic sites of this support represented by incompletely coordinated Ti⁴⁺ and Zr⁴⁺ cations in close proximity to the periphery of metal particles. The greater interaction between oxygen in the keto-tautomer intermediate with oxophilic sites promotes the selective hydrogenation of C=O. Pd/SiO₂, Pd/Al₂O₃, Pd/TiO₂ and Pd/ZrO₂ catalysts significantly deactivated during TOS. However, Pd/CeO₂ and Pd/CeZrO₂ were more stable and only slight losses in activity were observed. Carbon deposits were not detected by Raman spectroscopy after reaction. DRIFTS experiments under reaction conditions revealed a build-up of phenoxy and intermediate species during reaction. These species remained adsorbed on the Lewis acid sites, blocking those sites and inhibiting further reactant adsorption. The growth of Pd particle size and the reduction in acid site density during HDO of phenol were the primary routes of catalyst deactivation. The higher stability of Pd/CeO2 and Pd/CeZrO2 catalysts is likely due to the higher amount of oxygen vacancies of these supports.

Keywords: Phenol; Bio-oil; Hydrodeoxygenation; Stability; Pd catalysts; Oxophilic sites.

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1. Introduction

The hydrodeoxygenation (HDO) of bio-oil process is a fundamental step in the production of biofuels and chemicals from lignocellulosic biomass.^{1, 2, 3} In recent years, HDO has been explored for a number of molecules that are representative of families of compounds derived from biomass.⁴ One important molecule is phenol, which is not only present in the bio-oil, but is also an intermediate produced during HDO of different molecules.

According to the literature, HDO of phenol is a bifunctional reaction that requires a metallic site and an acid site.^{5,6} The metal particles are responsible for hydrogenation/ dehydrogenation reactions, whereas alkylation and polymerization reactions are catalyzed by the Lewis acid sites. Then, the design of the proper catalyst for HDO of phenol requires an understanding of the reaction pathways.

Various reaction routes have been suggested for phenol HDO. Direct deoxygenation (DDO) involves hydrogenolysis of the relatively stable C(sp²)–O bond, whose scission is difficult due to ring stabilization. Thus, under conventional conditions, the probability that this path occurs is low.⁴ However, the reaction may happen on 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.^{7,8} Another proposal is the metal-catalyzed successive ring hydrogenation (HYD), which reduces the energy for C–O bond scission. After hydrogenation, acid-catalyzed cyclohexanol dehydration takes place on the acid sites.⁹⁻¹² This pathway proceeds on catalysts containing sufficient acidity. Recently, we proposed that phenol conversion likely involves tautomerization, producing cyclohexadienone as an intermediate.¹³ Due to lack of stability, this intermediate may be hydrogenated to produce 2-cyclohexen-1-one, which is converted by hydrogen addition to the ketone, and then the

alcohol. In contrast, hydrogen addition to the carbonyl functional group of the cyclohexadienone intermediate assisted by the metal produces 2,4-cyclohexadienol, which dehydrates to benzene on the acid sites. Thus, in this case, the mechanism depends on the support. For supports containing oxophilic sites such as zirconia (incompletely coordinated Zr^{4+} or Zr^{3+} cations), the carbonyl group is selectively hydrogenated on metal sites at the metal-support interface, increasing the probability for benzene formation. It is clear that the type of support may drive the reaction by different pathways.

Different catalysts and operating conditions have been used for HDO of phenol.¹⁴⁻ ²⁵ An optimal catalyst for upgrading of bio-oil should exhibit high activity for deoxygenation as well as stability under reaction conditions.²⁶

Catalyst deactivation is currently one of the main challenges facing catalyst developers for the HDO reaction and it is mainly due to carbon deposition or sintering of metal particles.²⁷ Carbon formation occurs via polymerization and polycondensation reactions on the acid sites of the support, producing polyaromatic species that may block the active sites.²⁸ Therefore, the density and the nature of acid sites of the support play an important role on catalyst deactivation during HDO of bio-oil. To date, only few studies have been dedicated to catalyst deactivation during HDO of guaiacol, anisol and m-cresol.^{29,30} Gao et al.²⁹ investigated the mechanism of deactivation of carbon supported catalysts for HDO of guaiacol. Pd/C, Rh/C and Ru/C strongly deactivated during 300 min of time on stream (TOS) whereas Pt/C remained quite stable during reaction. Metal crystallite growth was ruled out using TEM images. Thermogravimetric analysis (TGA) showed that the amount of carbon deposits was the same on both catalysts. However, the type of carbon was different. Ru/C deactivation was attributed to a relatively higher concentration of naphthalene. Gonzalez-Borja and Resasco³⁰ studied the performance of Pt, Sn and PtSn catalysts for HDO of guaiacol and anisole. Deactivation was observed over

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Inconel supported catalysts and depended on the molecule. Guaiacol caused a more severe catalyst deactivation than anisole, consistent with pulse experiments that revealed stronger adsorption of guaiacol than anisole. Therefore, guaiacol is retained adsorbed on the surface, hindering the deoxygenation sites and causing catalyst deactivation. However, to date, there have been no studies reported concerning the deactivation of catalysts during HDO of phenol.

This work aims at investigating the mechanism of catalyst deactivation during HDO of phenol using supported Pd on various oxide carriers (SiO₂, Al₂O₃, TiO₂, ZrO₂, CeO₂ and CeZrO₂). The investigation of reaction pathways in combination with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements, Raman spectroscopy and model reactions were carried out to determine the causes of catalyst deactivation.

2. Experimental

2.1 Catalyst synthesis

SiO₂, Al₂O₃, TiO₂, ZrO₂, CeO₂ and CeZrO₂ were used to prepare supported Pd catalysts. SiO₂ (Hi-Sil 915), Al₂O₃ (Puralox) and TiO₂ (Aeroxide TiO₂ P25) supports were provided by PPG Industries, Sasol and Evonik, respectively. Al₂O₃ was calcined at 1273 K at a rate of 10 K/min for 5 h. ZrO₂, CeO₂ and CeZrO₂ were synthesized by precipitation or co-precipitation method. For ZrO₂, a 2.0 M solution of 35 wt.% ZrO(NO₃)₂ (Sigma-Aldrich) was added to a solution containing 4.0 M NH₄OH (Vetec) at room temperature. It was stirred vigorously for half an hour. The precipitate formed was collected by filtration and rinsed with distilled H₂O until the pH was neutral. The preparation of CeO₂ followed the same procedure as previously described for ZrO₂ but using ammonium cerium (IV) nitrate ((NH₄)₂Ce(NO₃)₆, Sigma-Aldrich) as the precursor salt. CeZrO₂ mixed oxide with a

Ce/Zr molar ratio = 1 was prepared by co-precipitation using zirconyl nitrate and ammonium cerium (IV) nitrate solutions. The precipitates were dried for 12 h at 383 K and calcined under flowing air at 773 K for 6 h and the ZrO_2 , CeO₂ and CeZrO₂ supports were obtained. The 2 wt. % Pd catalysts (Pd/SiO₂, Pd/Al₂O₃, Pd/TiO₂, Pd/ZrO₂, Pd/CeO₂ and Pd/CeZrO₂) were prepared by incipient wetness impregnation of the supports using an aqueous solution of palladium nitrate (Pd(NO₃)₂, Umicore). The powder was then dried at 393 K for a period of 12 h followed by calcination at 673 K for 3h in 50 mL/min of flowing air.

2.2. Catalyst characterization

The chemical composition of each sample was determined by X-ray fluorescence (XRF) in wavelength dispersive mode (S8 Tiger Bruker Spectrometer, Rh tube, 4 kW). The samples (300 mg) were analyzed by a semi-quantitative method (QUANT-EXPRES/Bruker). Surface areas were measured using a Micromeritics ASAP 2020 instrument by nitrogen adsorption at 77 K. X-ray diffraction (XRD) was carried out in a Rigaku Miniflex instrument with Cu K α radiation using the following parameters: $2\theta = 10-80^\circ$; scan rate = 0.04 °/step; and scan time = 1 s/step. The Raman spectra were recorded using a Horiba LabRam HR-UV800/Jobin-Yvon Spectrometer, equipped with He-Ne laser ($\lambda = 632$ nm) with 10 mW of intensity, a CCD detector and an Olympus BX41 microscope with objective lens of 100^{\times} . The acid properties of the catalysts was investigated by temperature-programmed desorption of ammonia (NH₃-TPD). The samples (350 mg) were reduced at 573 K for 1 h under a flow of H₂ of 60 mL/min and then purged in He flow for 30 min. After reduction, the sample was cooled to 423 K and the feed composition was switched to a mixture containing 4% NH₃ in He (30 mL/min) for 30 min. The physisorbed ammonia was flushed out with flowing He for 1 h. Then, the catalysts was heated at 10

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K/min under He to 773 K. The density of acid sites of the catalysts before and after HDO of phenol was measured by the cyclohexanol dehydration reaction.³¹ This probe reaction was performed using a fixed-bed reactor made of quartz at 1 atm and 543 K. The fresh catalyst was previously reduced with hydrogen (60 mL/min) at 573 K for a period of 1 h. The reactant mixture was obtained by flowing He (30 mL/min) through a saturator containing cyclohexanol, which was maintained at 336 K. A GCMS (Agilent 7890A/5975C) with capillary column (HP-Innowax) and flame ionization detector was used to analyze the products of the reaction. The dehydration rate was calculated by the sum of cyclohexene, cyclohexane and benzene yields. The nature of acid sites was determined by DRIFTS of adsorbed pyridine using a Nicolet Nexus 870 instrument with a DTGS-TEC detector and a Thermo Spectra-Tech reaction chamber with ZnSe windows. To reduce the sample, H₂ was flowed at 573 K for a period of 1 h and the temperature was decreased to 373 K while He was flowed to record a spectrum for use as a background. Pyridine adsorption involved bubbling He (30 mL/min) through a saturator for 30 min, followed by a He purge. The scan resolution was 4 cm⁻¹ and 512 scans were taken. For DRIFTS of adsorbed CO, each sample was subjected to the same H₂ reduction treatment. After cooling the catalyst to 473 K, a 1.3 % CO in He mixture was flowed for 25 min. Spectra were recorded in flowing CO/He to measure formate band intensities by reaction with defect-associated OH groups with CO. For DRIFTS of adsorbed cyclohexanone, the samples underwent the same H₂ reduction treatment previously described. Then, the catalyst was cooled to 323 K and He was flowed through a bubbler containing cyclohexanone at 60 ml/min and spectra were recorded at 323, 373, 423, and 473K. Peak fitting was performed on the band corresponding to adsorbed cyclohexanone by using Gaussian peaks and the nonlinear generalized reduced gradient (GRG) algorithm. The dehydrogenation of cyclohexane was used as an insensitive structure reaction to determine

the metal dispersion of supported Pd catalysts.³² For Pd/CeO₂ and Pd/CeZrO₂ catalysts, more traditional techniques such as H₂ or CO chemisorption are not recommended for these catalysts due to the possibility of adsorption of both gases on ceria.^{33,34} In addition, the determination of Pd particle size by transmission electron microscopy (TEM) is challenging due to the low contrast between the Pd and CeO₂ and CeZrO₂ supports. Therefore, Pd dispersion of Pd/SiO₂, Pd/Al₂O₃ and Pd/ZrO₂ catalysts of this work was determined by chemisorption of carbon monoxide. Prior to chemisorption, the catalysts (50 mg) were activated with H_2 (60 ml/min) at 573 K for 1h, and then the temperature was decreased to room temperature. The catalysts were purged in helium for 30 min. Pulses of a mixture containing 5%CO in He were injected until the saturation of the surface. The gasses were analyzed by quadrupole mass spectrometry using an MKS Cirrus 200 instrument. Dispersion of Pd was calculated considering that the Pd:CO ratio was unity. Then, a direct relationship between the cyclohexane dehydrogenation rate and the dispersion of palladium was established and used to determine the Pd dispersion of the other catalysts of this study. In order to validate this methodology, the Pd dispersion of Pd/ZrO₂ catalyst was also obtained by high resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) analyses.³⁵ The results obtained by both techniques were quite close, revealing that this procedure can be used for the determination of metal dispersion. This procedure enables the measurement of the Pd dispersion of fresh and used catalysts (after HDO of phenol for 24 h). A fixed-bed reactor was used to carry out the dehydrogenation of cyclohexane reaction over fresh and used catalysts. The fresh samples (10 mg) were first reduced at 573 K for 1 h and then cooled to the cyclohexane dehydrogenation reaction temperature (543 K). The reaction mixture (WHSV = 170 h^{-1}) was fed into the reactor after bubbling H₂ through a saturator containing cyclohexane maintained at 285 K ($H_2/C_6H_{12} = 13.2$). For the used catalysts, after HDO of

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phenol for 24 h, the saturator containing phenol was bypassed and hydrogen was allowed to flow through the catalyst for 30 min at 573 K, which removed hydrocarbons that remained adsorbed on the surface. The reactor was cooled to 543 K under hydrogen. Then, a cyclohexane/H₂ mixture was passed through the reactor. The effluent was analyzed by GCMS (system previously described). To probe the reaction mechanism, experiments were conducted in the in-situ DRIFTS cell previously described for acidity measurements using conditions representative of HDO. The sample (40 mg) was reduced under H₂ (60 ml/min) at 573 K and the temperature was decreased to 323 K to record a background spectrum. Hydrogen was passed through a saturator containing phenol at 60 ml/min and spectra were recorded at 373, 473, 573, 673 and 773 K. Scan resolution was 4 cm⁻¹ and 1024 scans were recorded at each point. The DRIFTS cell has a very small system volume, and the residence time inside the chamber is only 3.4 s, such that steady state is achieved very rapidly. To study catalyst deactivation, spectra were taken for 6h at steady state under reaction conditions at 573 K using a H₂ flow of 60 ml/min passing through the phenol saturator as previously described.

2.3. Catalytic activity

A fixed bed reactor made of quartz was used for the gas phase conversion of the various oxygenate compounds (i.e., phenol, cyclohexanone, or cyclohexanol). The reactor was operated at 1 atm and 573 K. Preliminary tests were carried out following the same criteria proposed by Madon and Boudart (1982) to ensure that external and internal mass transfer limitations were eliminated.³⁶ The powder catalysts (53-106 μ m range) were diluted with inert material (m_{SiC}/m_{catalyst} = 3/1) to avoid localized overheating. Before reaction, the catalyst was activated in H₂ (60 mL/min) for 1 h at 573 K. Hydrogen was

passed through a bubbler containing the reactant (phenol, cyclohexanol, cyclohexanone), which was kept at the temperature needed to achieve H_2 /reactant molar ratio of 60.

Two different series of experiments were performed to determine the initial phenol conversion and to study catalyst deactivation. In the first series, each catalyst was tested at various W/F values by changing the amount of the catalyst (2.5 to 120 mg). W/F is catalyst mass (g) divided by mass flow rate (g/h) of the organic feed. The initial phenol conversion was taken after 5 min of TOS in order to avoid catalyst deactivation. In the second series, 60 mg of catalyst and a total flow rate of 60 mL.min⁻¹ were used for all catalysts in order to observe catalyst deactivation within 24 h TOS. To avoid condensing the gas, the tubing was heat traced to 523 K. The GCMS used for analysis was previously described. Product yield and selectivity were defined as:

$$yield(\%) = \frac{mol \ of \ product \ produced}{mol \ of \ phenol \ fed} \times 100 \tag{1}$$

Selectivity (%) =
$$\frac{mol \ of \ product \ produced}{mol \ of \ phenol \ consumed} \times 100$$
 (2)

3.1- Results and discussion

3.1 Catalyst characterization

As shown in Table 1, Pd content varied from 1.83 to 2.46 wt.% and was close to the expected value (2 wt.%). Pd/SiO₂ and Pd/Al₂O₃ samples exhibited the highest specific surface areas (172 and 134 m²/g, respectively), while the smallest ones were observed for Pd/CeO₂ and Pd/TiO₂ (51 and 54 m²/g, respectively).

Table 1. Pd loading, BET surface area, reaction rate of dehydrogenation of cyclohexane (DHO), Pd dispersion, reaction rate of dehydration of cyclohexanol (DHA) of fresh catalysts and total amount of ammonia desorbed.

Catalyst	wt % Pd	BET (m²/g)	Rate of DHO (mmol.g ⁻¹ _{Pd} .min ⁻¹)	D ^[a] (%)	Rate of DHA (mmol.g ⁻¹ _{cat} .min ⁻¹)	Ammonia desorbed (µmol/g _{cat})
Pd/SiO ₂	1.92	172	0.22	15.9	1.4	8
Pd/Al ₂ O ₃	2.28	134	0.25	18.4	83.0	339
Pd/TiO ₂	1.83	54	0.91	63.3	31.4	225
Pd/ZrO ₂	2.24	84	0.57	40.4	12.6	114
Pd/CeO ₂	2.44	51	0.62	43.6	1.9	27
Pd/CeZrO ₂	2.46	82	0.55	38.7	1.2	56

^[a] Pd dispersion of the fresh catalyst.

The diffractograms of Pd-based catalysts are provided in Figure S1 (Supporting Information). With the exception of the Pd/SiO₂ catalyst, the lines characteristic of PdO were not observed, which could be attributed to their overlapping by the diffraction lines of the supports or the small PdO particle size. The Pd/SiO₂ catalyst also exhibited a broad peak at 22.7° corresponding to amorphous SiO₂. The diffractogram of Pd/Al₂O₃ presented diffraction lines corresponding to various phases of Al₂O₃: θ -Al₂O₃ (JCPDS 35-0121), δ -Al₂O₃ (JCPDS 46-1131), γ -Al₂O₃ (JCPDS 10-0425). The diffractogram of Pd/TiO₂

revealed lines characteristic of both anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) titania phases. For Pd/ZrO₂ catalyst, the diffractogram has the diffraction lines of two zirconia phases, tetragonal ZrO₂ (JCPDS 17-0923) and monoclinic (JCPDS 37-1484). Pd/CeO₂ and Pd/CeZrO₂ catalysts showed the diffraction pattern of the cubic fluorite structure (JCPDS 34-0394) typical of ceria. However, for Pd/CeZrO₂ catalyst, the lines in the diffractogram are shifted to higher 20 positions, suggesting that a CeO₂/ZrO₂ solid solution was formed.³⁷

The Pd dispersion calculated by the cyclohexane dehydrogenation reaction depended on the support (Table 1). The Pd/TiO₂ catalyst had the highest Pd dispersion whereas the lowest values were observed for Pd/SiO₂ and Pd/Al₂O₃ catalysts. Pd/ZrO₂, Pd/CeO₂ and Pd/CeZrO₂ exhibited approximately the same dispersion.

The nature of acid sites was studied by DRIFTS of adsorbed pyridine (Figure 1). For Pd/Al₂O₃, the band at 1593 cm⁻¹ is assigned to the vibrations of pyridine coordinated to octahedral Al³⁺ sites, whereas the band at 1615 cm⁻¹ corresponds to pyridine adsorption on tetrahedral Al³⁺ cations. The bands at 1500 and 1449 cm⁻¹ can be attributed to physically adsorbed pyridine.³⁸



Figure 1. DRIFTS spectra of adsorbed pyridine at 373 K over (a) Pd/Al₂O₃; (b) Pd/TiO₂; (c) Pd/ZrO₂; (d) Pd/CeZrO₂; (e) Pd/CeO₂.

The infrared spectrum after pyridine adsorption on Pd/TiO₂ catalyst showed bands at 1446, 1475, 1487, 1583, and 1602 cm⁻¹. These bands can be attributed to physically adsorbed pyridine (1446, 1475, 1487, 1583 cm⁻¹), and pyridine adsorbed on unsaturated Ti⁴⁺ cations (1602 cm⁻¹). The DRIFTS spectra of adsorbed pyridine on Pd/ZrO₂, Pd/CeO₂ and Pd/CeZrO₂ were quite similar to that of the Pd/TiO₂ catalyst. The main difference was that the bands were shifted to lower wavenumber in the presence of Ce.

The DRIFTS spectra for adsorption of pyridine are dominated by Lewis acid sites. Slight features that might indicate a minor contribution from Bronsted acid sites (range of $1500 - 1550 \text{ cm}^{-1}$) might be present on Pd/ZrO₂ and Pd/TiO₂, but the features were within

the experimental limits of detection. Therefore, only the Lewis acid sites were considered to explain the results on HDO of phenol.

The titration of acid sites of the catalysts was measured by two different methods: temperature-programmed desorption of NH₃ (NH₃-TPD) and the cyclohexanol dehydration reaction. Table 1 reports the amount of desorbed ammonia calculated from the NH₃-TPD profiles. Pd/Al₂O₃ catalyst exhibited the highest number of acid sites (339 μ mol/g_{cat}) whereas Pd/SiO₂, Pd/CeO₂ and Pd/CeZrO₂ catalysts showed the lowest values.

The dehydration of cyclohexanol reaction was also used to measure the number of acid sites of the supports. Martin and Duprez³¹³¹ proposed to investigate the acid-base properties of oxides using the dehydration of cyclohexanol reaction. They reported that the dehydration of cyclohexanol to cyclohexene would likely be catalyzed by the acid sites. In our work, the reaction rate of dehydration of cyclohexanol for fresh catalysts is listed in Table 1. Pd/Al₂O₃ exhibited the highest rate of dehydration of cyclohexanol, suggesting a higher density of acid sites. Pd/ZrO₂ showed a reaction rate 10-fold higher than Pd/SiO₂, Pd/CeO₂ and Pd/CeZrO₂ catalysts. The following order was observed for the density of acid sites in agreement with the NH₃-TPD experiment. In fact, both techniques revealed that the density of acid sites is low and approximately the same for Pd/SiO₂, Pd/CeO₂ and Pd/CeZrO₂ catalysts.

3.2 HDO of phenol over Pd-based catalysts

The HDO of phenol was performed over all supports. The supports displayed insignificant activity in the W/F range studied. Thus, activity can be ascribed to the metal

surface and/or the metal-support junction. The phenol conversion and product yield versus W/F for HDO of phenol at 573 K over all catalysts are shown in Figure S2.

Among the catalysts, Pd/TiO₂ and Pd/ZrO₂ were the most active, whereas Pd/SiO₂, Pd/Al₂O₃, Pd/CeO₂, and Pd/CeZrO₂ exhibited approximately the same conversion at the conditions of the study. Regarding product distributions, benzene, cyclohexanone (ONE), cyclohexanol (OL) and C₁₂ hydrocarbons such as biphenyl and cyclohexylbenzene were the main products observed. Cyclohexane and C₁₂ O-containing hydrocarbons (2phenylphenol, 2-cyclohexylcyclohexan-1-one and 2-cyclohexylphenol) were also detected in trace amounts at high conversion on some catalysts. However, product distribution significantly depended on the support.

Cyclohexanone was mainly formed at low conversion for Pd/Al₂O₃, Pd/SiO₂, Pd/CeO₂ and Pd/CeZrO₂ catalysts. Higher formation of benzene only occurred at high conversions. Minor production of cyclohexanol was also observed for the Pd/SiO₂, Pd/CeO₂ and Pd/CeZrO₂ catalysts. On the other hand, benzene was the dominant product over the entire W/F range for Pd/TiO₂ and Pd/ZrO₂. In this case, only small amounts of cyclohexanone and C₁₂ hydrocarbons were observed. C₁₂ hydrocarbons were formed on all catalysts, except Pd/SiO₂. The highest yield of C₁₂ hydrocarbons was obtained on Pd/Al₂O₃ and Pd/TiO₂ catalysts. C₁₂ hydrocarbons were likely the product of alkylation through the reaction of cyclohexanone with phenolic / aromatic rings over Lewis acid sites.^{28,39} These C₁₂ hydrocarbons are quite interesting as a fuel due to their high cetane number.⁴⁰

The reaction rate of HDO of phenol was calculated and the selectivity of all catalysts was compared at low phenol conversion (around 10%), as shown in Table 2.

Catalyst	Conversion Rate of HDO			Selectivity(%)					
	(%)	(mmol.min ⁻¹ .g _{cat} ⁻¹)	BZ	ONE	OL	C ₁₂			
Pd/SiO ₂	7.0	0.09	8.1	88.9	3.0	0.0			
Pd/Al_2O_3	7.5	0.13	11.4	84.1	2.0	2.8			
Pd/TiO ₂	7.0	0.72	66.8	33.2	0.0	0.0			
Pd/ZrO ₂	12.6	0.59	29.9	68.7	1.3	0.0			
Pd/CeO ₂	9.0	0.14	4.9	85.8	9.4	0.0			
Pd/CeZrO2	12.4	0.09	4.6	84.4	11.0	0.0			

Table 2. Reaction rate of HDO of phenol and product distribution at low conversion.

BZ: benzene; ONE: cyclohexanone; OL: cyclohexanol; C₁₂: bicyclic compounds.

 Pd/TiO_2 and Pd/ZrO_2 exhibited the highest reaction rates, whereas the other catalysts showed basically the same values. However, for Pd/TiO_2 this value was about 1.2-fold higher than that of Pd/ZrO_2 . The reaction rates displayed the following trend: $Pd/TiO_2 > Pd/ZrO_2 > Pd/Al_2O_3 \approx Pd/CeO_2 \approx Pd/SiO_2 \approx Pd/CeZrO_2$.

The dependency of the product selectivity on the support is remarkable. Pd/TiO₂ and Pd/ZrO₂ exhibit a higher selectivity to benzene, whereas the other catalysts showed a higher selectivity to cyclohexanone. For instance, Pd/ZrO₂ catalyst showed selectivity to benzene that was 6-fold higher than that of either Pd/CeO₂ or Pd/CeZrO₂ catalysts. Thus, the type of support significantly impacts not only the activity for deoxygenation but also the distribution of products.

The HDO reaction of cyclohexanol and cyclohexanone (potential intermediate products) was also conducted on supports and catalysts to investigate the effect of support on the reaction pathways. In addition, DRIFTS spectra were also obtained under reaction at different temperatures.

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3.3. Cyclohexanol and cyclohexanone conversion over Pd-based catalysts

Table 3 reports the yields of products for phenol, cyclohexanol or cyclohexanone HDO at the same conversion over Pd catalysts. When cyclohexanone was used as the feed, phenol was the dominant product formed, although minor quantities of cyclohexanol and benzene were also produced over all catalysts. This result indicates that benzene is a secondary product from HDO of phenol. For Pd/Al₂O₃, Pd/TiO₂ and Pd/ZrO₂, significant formation of C₁₂ hydrocarbons was also observed. Nimmanwudipong et al. also observed a high yield of C₁₂ hydrocarbons for the reaction of cyclohexanone over Pt/Al₂O₃ catalysts.²⁸ This result was attributed to the Lewis acid sites of this support and indicates that C₁₂ hydrocarbons are preferentially formed via conversion of cyclohexanone during HDO of phenol. The conversion of cyclohexanol yielded predominantly phenol and cyclohexanone over Pd/SiO₂, Pd/ZrO₂, Pd/CeO₂ and Pd/CeZrO₂ catalysts. Significant formation of cyclohexane and cyclohexane was observed for Pd/Al₂O₃ and Pd/TiO₂ catalysts, whereas benzene was only produced over alumina supported catalyst.

This result suggests that the cyclohexanol dehydration to cyclohexene may occur when Al_2O_3 and TiO_2 are used as supports. To study the role of the support on the dehydration of cyclohexanol, this reaction was performed over the pure supports at the same reaction conditions used for the HDO of phenol over the supported Pd catalysts. SiO_2 , ZrO_2 , CeO_2 and $CeZrO_2$ supports showed low conversion of cyclohexanol to cyclohexene, which suggests that the activity of the supports for this reaction is not significant. On the other hand, Al_2O_3 and TiO_2 supports were very active for cyclohexanol dehydration. However, benzene cannot be formed via the dehydration of cyclohexanol on Pd/TiO_2. In contrast, the formation of benzene by cyclohexanol dehydration cannot be ruled out over Pd/Al_2O_3.

3.4. DRIFTS of HDO of phenol over Pd-based catalysts

The DRIFT spectra of experiments performed using the mixture of phenol and hydrogen over Pd/SiO₂ did not reveal the presence of significant bands over the entire temperature range studied, indicating that the adsorption of phenol or intermediates on the catalyst is very low. For Pd/Al₂O₃ catalyst, the DRIFT spectra obtained under reaction conditions at different temperatures are shown in Figure 2. The vibrational modes of the various species formed from phenol adsorption were obtained from the open literature.⁴¹⁻⁴⁶

At 373 K, phenol is dissociatively adsorbed over metal oxide cations with bands attributed to modes of vibration of unidentate or bidentate phenoxy species (1289, 1495, 1595, 3034, and 3065 cm⁻¹). These bands are related to the following vibrational mode assignments: v(CO) stretching (1289 cm⁻¹); v(C=C_{ring}) (1495 and 1595 cm⁻¹); and v(C–H) stretching (3034 and 3065 cm⁻¹).

As discussed previously¹³ from experiments with probe molecules, the bands at 2942, 2857 and 1687 cm⁻¹ likely correspond to 2-cyclohexen-1-one species. In this case, the band typical of the v(C=O) is shifted to 1687 cm⁻¹ (from 1715 cm⁻¹), which is caused by conjugation of the carbonyl with the unsaturated bond of the ring.

Table 3.	Performance comparison	of Pd/SiO ₂ ,	Pd/Al_2O_3 ,	Pd/TiO ₂ ,	Pd/ZrO ₂ ,	$Pd/CeO_2 \ and$
Pd/CeZrO	2 catalysts under different	feeds.				

Catalyst	W/F	Feed			Yield %)			Х
	(h)		ANE+ENE	ΒZ	ONE	OL	Phenol	C ₁₂	(%)
	0.053	Phenol	-	2.9	16.8	1.6	-	-	21.3
Pd/SiO ₂	0.024	ONE	-	0.3	-	0.9	27.2	-	28.4
	0.098	OI	-	2.9	7.6	-	13.3	-	23.8
SiO ₂	0.160	OL	3.0	-	-	-	-	-	3.0
	0.160	Phenol	0.1	6.6	17.5	-	-	4.0	28.2
Pd/Al ₂ O ₃	0.092	ONE	1.2	2.6	-	-	9.5	8.4	21.6
	0.006	OI	11.8	13.1	2.1	-	-	-	27.1
Al_2O_3	0.160	OL	100	-	-	-	-	-	100
	0.053	Phenol	0.1	13.3	5.3	-	-	4.0	22.7
Pd/TiO ₂	0.046	ONE	3.0	1.3	-	1.1	9.0	7.0	21.4
	0.012	OI	14.2	-	5.8	-	0.3	-	20.6
TiO ₂	0.160	OL	94.7	-	-	-	-	-	94.7
	0.026	Phenol	-	8.7	10.1	0.4	-	0.4	19.6
Pd/ZrO ₂	0.023	ONE	-	1.2	-	2.2	9.7	9.0	22.1
	0.024	OI	0.4	4.0	9.3	-	5.6	-	19.3
ZrO ₂	0.160	OL	3.8	-	-	-	-	-	3.8
	0.026	Phenol	-	1.0	17.1	3.1	-	-	21.2
Pd/CeO ₂	0.005	ONE	-	0.2	-	4.7	14.3	-	19.2
	0.006	OI.	0.3	0.4	16.3	-	9.9	-	26.8
CeO_2	0.160	OL	3.3	-	-	-	-	-	3.3
	0.053	Phenol	-	1.7	21.1	6.0	-	-	28.9
Pd/CeZrO ₂	0.011	ONE	0.1	0.3	-	3.9	21.1	-	25.4
	0.012	OI	0.8	1.1	11.8	-	9.8	-	23.6
CeZrO ₂	0.160	UL	4.0	-	-	-	-	-	4.0

ANE + ENE: cyclohexane + cyclohexene; BZ: benzene; ONE: cyclohexanone; OL: cyclohexanol; C₁₂: bicyclic hydrocarbon



Figure 2. DRIFTS spectra under HDO of phenol over Pd/Al_2O_3 (H₂/phenol = 60) at (a) 373 K, (b) 473 K, (c) 573 K, (d) 673 K, (e) 773 K.

Increasing the temperature to 473 K, band intensities characteristic of phenoxy species and 2-cyclohexen-1-one species diminished. In addition, the appearance of a new band at 1459 cm⁻¹ and the increase in the intensity of the bands at 2937 and 2863 cm⁻¹ suggests that phenoxy species reacted, producing cyclohexanol species. Further increasing temperature to 773 K resulted in a decrease in band intensities of phenoxy and cyclohexanol species, which is indicative of facile desorption from the surface.

For Pd/TiO₂, the IR spectrum at 373 K exhibited bands positioned at 1283, 1491, 1591 and 3064 cm⁻¹ that are attributed to the phenoxy vibrational modes (Figure 3).



Figure 3. DRIFTS spectra under HDO of phenol over Pd/TiO₂ (H₂/phenol = 60) at (a) 373 K, (b) 473 K, (c) 573 K, (d) 673 K, (e) 773 K.

The bands at 1454, 1666, 2859 and 2937 cm⁻¹ indicate the presence of both cyclohexanol and 2-cyclohexen-1-one species. Raising temperature to 473 K caused the intensities of all bands to diminish, and they were no longer observed at 573 K.

DRIFTS spectra of the phenol/ H_2 mixture over Pd/ZrO₂ catalyst (Figure 4) showed some different features from those of the Pd/Al₂O₃ catalyst.



Figure 4. DRIFTS spectra under HDO of phenol over Pd/ZrO_2 (H₂/phenol = 60) at (a) 373 K, (b) 473 K, (c) 573 K, (d) 673 K, (e) 773 K.

Bands characteristic of the vibrational modes of phenoxy species were detected (3064, 3025, 1592, 1494, 1291 cm⁻¹), as well as bands positioned at 2931, 2852, 1697 (shoulder), 1457 and 1049 cm⁻¹, demonstrating that adsorbed phenol reacted to produce cyclohexen-1-one and cyclohexanol species. Additional bands at 1559, 1417 and 1342 cm⁻¹ were also observed, and may be assigned to v(OCO) of phenol adsorbed on the support, analogous to carboxylates formed by ethanol adsorption.⁴⁷ In this case, the v(OCO) vibration produced by the bonding of carbon from the aromatic ring to oxygen from the phenoxy molecule as well as oxygen from the support. Increasing temperature to 573 K

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resulted in increases in band intensities associated with phenol adsorbed at defect sites. Further increasing in temperature to the 673 - 773 K range significantly decreased the band intensities.

The DRIFTS spectra obtained under HDO of phenol over Pd/CeO₂.were shown in Fig. 5. At 373 K, the reaction of phenol in the presence of hydrogen leads to bands positioned at 2934, 2856, 1423, and 1055 cm⁻¹ ascribed to cyclohexanol. However, intense bands located at 1591 and 1491 cm⁻¹ correlate well with the v(C=C) aromatic ring modes of phenoxy species, with 1262 cm⁻¹ being consistent with the v(CO) monodentate mode of phenoxy species as well. The band at 1687 cm⁻¹ is due to the presence of 2-cyclohexen-1-one. However, as we previously observed with Pd/ZrO₂, there is an intense band at close to 1560 cm⁻¹ that is too low to be consistent with an aromatic ring mode. Rather, it correlates very well with an asymmetric v(OCO) stretching mode of a vibration that resembles that of carboxylate species (e.g., similar to adsorbed formate or acetate). The band at ~1330 cm⁻¹ may be the symmetric v(OCO) stretching mode. Considering the tautomerization of phenol, the result provides further confirmation for the coordination of the carbonyl species of 2-cyclohexadienone to the defect site, which results in carboxylate-like modes of vibration as the C of the carbonyl is now bonded to both O which came from the carbonyl functional group, as well as oxygen adjacent to the defect site.



Figure 5. DRIFTS spectra under HDO of phenol over Pd/CeO₂ (H₂/phenol = 60) at (a) 373 K, (b) 473 K, (c) 573 K, (d) 673 K, (e) 773 K.

When temperature was raised to 473 and 573 K, band intensities attributed to coordination of phenol to defect sites increase, while those of cyclohexanol decrease. In addition, there is the development of a broad band between 1930 and 1750 cm⁻¹. Further increases in temperature diminished all band intensities. Figure 6 displays the DRIFTS spectra of experiments carried out with the mixture of phenol and hydrogen using Pd/CeZrO₂. Qualitatively, the trend is nearly identical to that of Pd/CeO₂.



Figure 6. DRIFTS spectra under HDO of phenol over Pd/CeZrO₂ (H₂/phenol = 60) at (a) 373 K, (b) 473 K, (c) 573 K, (d) 673 K, (e) 773 K.

3.5- Effect of support on the reaction mechanism for HDO of phenol

Our DRIFT spectra revealed that phenol adsorbs dissociatively over metal oxide cations of the support. In addition, DRIFT spectra also revealed the formation of 2,4-cyclohexadien-1-one, which is the keto tautomer of phenol. This result indicates that after adsorption, phenol is tautomerized to 2,4-cyclohexadien-1-one, which may follow two different routes of reaction, and depends on support type. Ring hydrogenation of this keto-tautomer intermediate led to the production of 2-cyclohexen-1-one that further hydrogenates to cyclohexanone. The catalytic tests with different feeds showed that

cyclohexanone is rapidly converted to cyclohexanol, or it may alkylate the phenolic ring producing bicyclic compounds. This is the main reaction pathway for Pd/SiO₂, Pd/Al₂O₃, Pd/CeO₂ and Pd/CeZrO₂ catalysts. In the case of Pd/Al₂O₃ catalyst, the dehydration of cyclohexanol to benzene may also take place due to the high density of acid sites of this support, as revealed by cyclohexanol dehydration test and temperature-programmed desorption of NH₃ (NH₃-TPD). However, there is no correlation between the selectivity to deoxygenated products and the density of acid sites. The cyclohexanol dehydration tests and NH₃-TPD experiments showed that Pd/Al₂O₃ catalyst exhibited the highest density of acid sites whereas the highest selectivity to benzene was observed with Pd/ZrO₂ and Pd/TiO₂ catalysts. Mortensen et al.^{Errort Bookmark not defined.} also proposed that the density of acid sites of the support does not affect the activity for liquid phase phenol HDO using supported nickel.

Therefore, the formation of benzene should proceed by another route on Pd/ZrO_2 and Pd/TiO_2 , which do not have sufficient acidity. In this case, hydrogenating the CO functional group of the keto-tautomer intermediate results in the formation of 2,4cyclohexadienol and further conversion to benzene. This reaction pathway is favored over Pd/ZrO_2 and Pd/TiO_2 catalysts.

There are some studies in the literature that suggested the oxygen vacancies play a key role in the HDO of molecules like guaiacol. Schimming et al.⁴⁸ investigated the HDO of guaiacol over ceria-zirconia catalysts. They reported a linear correlation between the concentration of oxygen vacancies and the conversion of guaiacol at 573 K, indicating that the HDO of guaiacol occurs on paired oxygen vacancies. In order to unveil the role of the oxygen vacancies for the HDO of phenol, the IR of CO was used to measure the amount of oxygen vacancies and the reaction was also carried out after reduction of Pd/CeZrO₂ catalyst at 773 K.

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The IR bands after reduction of Pd-based catalysts at 573 K and CO adsorption at 473 K are shown in Figure 7.



Figure 7. DRIFTS spectra of adsorbed CO at 473 K over supported Pd catalysts.

The bands at 2062 and 1960 cm⁻¹ are assigned to linear and bridge CO adsorption on metallic Pd particles. The bands between 1700 - 1200 cm⁻¹ are due to the different vibrational modes of monodentate and bidentate formate species: 1570 and 1361 cm⁻¹ (v(OCO) symmetric and asymmetric); 1381 cm⁻¹ (δ (CH)). The shoulder at 1531 cm⁻¹ and the bands at 1623, 1420 and 1336 cm⁻¹ could be due to the formation of hydrogen carbonate and carbonate species. Formates are formed by the reaction between CO and defect-associated hydroxyl groups. Therefore, the ratio between the intensities of the formate bands and the carbonyl bands on the metallic particles provides information about

the density of oxygen vacancies on the Pd-based catalysts. This ratio is highest for the Pd/CeZrO₂ catalyst and decreases in the following order: $Pd/CeZrO_2 > Pd/CeO_2 > Pd/ZrO_2 > Pd/Al_2O_3 > Pd/TiO_2$. This result is in agreement with the literature, since the addition of zirconia to ceria structure improves the formation of oxygen vacancies. ⁴⁹ However, Pd/ZrO₂ catalyst exhibited much higher activity to deoxygenation and selectivity to benzene than Pd/CeZrO₂ and Pd/CeO₂ catalysts. This result reveals that there was no clear correlation between the concentration of oxygen vacancies and the deoxygenation activity of phenol over these Pd-based supported catalysts.

Table 4 shows a comparison between the selectivities obtained for HDO of phenol over Pd/CeZrO₂ catalyst after reduction at 573 and 773 K.

Table 4. Distribution of products for phenol HDO over Pd/CeZrO2 activated at 573 and773K.

Reduction	Conversion	W/F		Selecti	vity(%)		
temperature (K)	(%)	(h)	BZ	ONE	OL	C ₁₂	
573	33.0	0.16	15.3	63.1	21.1	0.2	
773	35.3	0.80	12.0	63.7	23.7	0.2	

Increasing the reduction temperature of Pd/CeZrO₂ catalyst did not impact the distribution of products for phenol HDO. However, the reduction at high temperature increases the formation of oxygen vacancies, which is simultaneously followed by the conversion of Ce^{4+} to Ce^{3+} to compensate for oxygen removal. Therefore, the higher amount of oxygen vacancies formed after reduction at 773 K did not affect the selectivity to deoxygenated products that remained unchanged in comparison to the catalyst reduced at 573 K. Furthermore, the oxophilicity of Ce^{4+} and Ce^{3+} cations should be similar and low,

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since the selectivity to deoxygenated products was the same, regardless of the reduction temperature.

Recently, it has been proposed in the literature that oxophilic sites (represented by unreduced metals and metal oxide cations from the supports) promote the deoxygenation pathway.^{7,50,51} The strong bond between the oxygen from the phenol molecule and the oxophilic site might favor the hydrogenation of the carbonyl function or even the direct cleavage of the C-O bond. Newman et al.⁵² also investigated the effect of the support on liquid phase phenol HDO using Ru/SiO₂, Ru/Al₂O₃, Ru/TiO₂, and Ru/C catalysts. The highest selectivity to benzene was shown by Ru/TiO2. This was attributed to the strong interaction between the Ti³⁺ sites (created during the reduction) with the oxygen from the phenol molecule, which weakens the aromatic C-O bond and promotes the cleavage of this bond. Griffin et al.⁸ also observed a higher selectivity to toluene over Pt/TiO₂ than Pt/C for gas phase m-cresol HDO at 623 K. They performed DFT calculations to study the most energetically favorable reaction pathway over Pt(111) and anatase TiO₂ (101) surfaces. 3methylcyclohexanone and 3-methylcyclohexanol were mainly formed by the hydrogenation of the ring over Pt(111) surface. For TiO₂ (101) surface, tautomerization and direct deoxygenation to toluene were also energetically favorable routes. In this case, the reaction takes place at oxygen vacancy defects. This could explain the higher selectivity to toluene observed for Pt/TiO₂ catalyst.

In the present work, the high selectivity to benzene over Pd/TiO_2 and Pd/ZrO_2 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 periphery of metal particles. Stronger interactions between oxygen in phenol with metal oxide cations favors the selective hydrogenation of the CO function of the tautomer intermediate, which is assisted by the

metal function. However, the direct deoxygenation over TiO_2 or ZrO_2 supports to benzene may not be ruled out.⁵⁰

For Pd/SiO₂, Pd/CeO₂ and Pd/CeZrO₂ catalysts, the weak interaction between the oxygen from carbonyl group and the metal cations of the support, could be responsible for the preferential hydrogenation of the aromatic ring, producing mainly cyclohexanol and cyclohexanone as the main products. Pd/Al₂O₃ catalyst has enough acidity to promote cyclohexanol dehydration to cyclohexene, as demonstrated by the dehydration of cyclohexanol tests over supports and catalysts.

In order to measure the strength of the interaction between the oxygen from the carbonyl group and the oxophilic site, we used an experimental procedure proposed by Corma et al.^{53,54} They used the adsorption of cyclohexanone to probe the strength of the interaction of the carbonyl oxygen with the active sites of Si-, Sn-, Ti-, Al- and V-beta zeolites. The IR spectra of Sn-beta showed that the carbonyl band shifted of 48 cm⁻¹ to lower wavenumbers after desorption at 373 K. This result was attributed to the formation of an adduct between the tetrahedral Sn in the beta framework and the oxygen from the carbonyl group. The position of the band corresponding to the carbonyl group was shifted of 32cm⁻¹ (Ti) and 25cm⁻¹ (V), which suggests a weaker interaction of between the oxygen from carbonyl group with Ti and V than with Sn.

In our work, DRIFTS experiments of adsorbed cyclohexanone followed by desorption at different temperatures were carried out. The spectra obtained after desorption at 323 K in the region between $1600 - 1750 \text{ cm}^{-1}$ are shown in Fig. 8. The band associated with the v(C=O) of cyclohexanone is observed for all samples. For instance, Pd/SiO₂ exhibited a band at 1709 cm⁻¹ and a shoulder with weak intensity at 1683 cm⁻¹. Pd/Al₂O₃, Pd/CeO₂ and Pd/CeZrO₂ catalysts displayed similar spectra to that of Pd/SiO₂. However, Pd/TiO₂ and Pd/ZrO₂ catalysts exhibited an intense band at around 1683 cm⁻¹, with a

shoulder at 1709 cm⁻¹. Therefore, cyclohexanone spectra can be decomposed into three regions: high (> 1695 cm⁻¹), medium (1660 - 1695 cm⁻¹) and low (<1660 cm⁻¹) wavenumbers (Table 5). Considering the distribution of these regions, Pd/SiO₂ catalyst showed 67.1% of this band located in the high wavenumber region, whereas the Pd/TiO₂ catalyst revealed higher proportion in the medium/low wavenumber region (63.1%).

Recently, we demonstrated that the v(C=O) of carbonyl groups shifted to lower wavenumber corresponding to 2-cyclohexen-1-one species³¹. This shift is caused by the conjugation of the carbonyl group with the unsaturated ring. DRIFT spectra also revealed the formation of 2,4-cyclohexadien-1-one. Therefore, the stronger interaction between the oxygen from the carbonyl group and Ti^{4+}/Ti^{3+} and Zr^{4+}/Zr^{3+} cations promotes the conversion of cyclohexanone to 2-cyclohexen-1-one and 2,4-cyclohexadien-1-one. The shift in the cyclohexanone band to lower wavenumbers, as suggested by Corma et al..^{53,54} may be used to measure the strength of the interaction between the oxygen of phenolic compounds and the oxophilic sites. Fig. 9 shows a correlation between deoxygenated product selectivity and the strength of the interaction between oxygen from the carbonyl group and oxophilic cations represented by the fraction of medium and low wavenumber cyclohexanone bands. The more oxophilic cation promotes the deoxygenation of phenol.



Figure 8. Cyclohexanone spectra after desorption at 323 K over (a) Pd/SiO₂, (b) Pd/Al₂O₃, (c) Pd/CeO₂, (d) Pd/CeZrO₂, (e) Pd/ZrO₂, (f) Pd/TiO₂.

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cyclonexanone.							
	% Wavenumber Bands						
Catalyst	High	Medium	Low				
	$\geq 1695 \text{ cm}^{-1}$	1660 - 1695 cm ⁻¹	1620 - 1660 cm ⁻¹				
Pd/SiO ₂	67.1	17.3	15.6				
Pd/Al_2O_3	70.4	17.9	11.7				
Pd/CeO ₂	76.6	26.4					
Pd/CeZrO ₂	80.7	19.3					
Pd/ZrO ₂	52.2	31.8	16.0				
Pd/TiO ₂	36.8	44.4	18.7				

Table 5.	Distribution	of the	different	regions	in	the	band	associated	with	v(C=O)	of
cyclohexa	anone.										



Figure 9. Selectivity to deoxygenated products versus the strength of the interaction between oxygen from the carbonyl group and oxophilic cations represented by the fraction of medium and low wavenumber of cyclohexanone bands.

Therefore, the reaction pathways for HDO of phenol over Pd-supported catalysts could be described by Scheme 1. The same reaction mechanism was demonstrated for m-cresol HDO.⁵⁵ In all the cases, the phenolic compound adsorbs on the Lewis acid sites via the oxygen atom and the oxophilic sites play a key role in the reaction pathway.^{13,55}

Scheme 1. Reaction routes for HDO of phenol over supported Pd catalysts.

3.6- Stability of Pd catalysts on HDO of phenol

The stability of the catalysts was compared at similar initial phenol conversion (around 60 %) during 20 h of reaction. Figure 10 shows the conversion of the phenol and product distribution as a function of time on stream (TOS) for all catalysts.

Figure 10. Conversion of phenol and selectivity to products as a function of TOS for: (A) Pd/SiO_2 (W/F = 0.642 h); (B) Pd/Al_2O_3 (W/F = 0.824 h); (C) Pd/TiO_2 (W/F = 0.134 h); (D) Pd/ZrO_2 (W/F = 0.134 h); (E) Pd/CeO_2 (W/F = 0.824 h); (F) $Pd/CeZrO_2$ (W/F = 0.824 h).

All catalysts deactivated during 20 h of TOS but the deactivation degree depended on the support. Pd/SiO₂, Pd/Al₂O₃, Pd/TiO₂ and Pd/ZrO₂ catalysts significantly deactivated with TOS. However, Pd/CeO₂ and Pd/CeZrO₂ were more stable and only slight losses in activity were observed. Changes in the distribution of products occurred with TOS. benzene selectivity decreased and the formation of cyclohexanone increased as the phenol conversion decreased for all catalysts, except for Pd/TiO₂. These changes were more significant for Pd/SiO₂ and Pd/Al₂O₃ catalysts. In this case, the selectivity to cyclohexanone was much higher than that of benzene after 20 h TOS. For Pd/CeO₂ and Pd/CeZrO₂ catalysts, the selectivity to benzene and cyclohexanone were approximately the same, whereas Pd/TiO₂ and Pd/ZrO₂ catalysts exhibited a higher selectivity to benzene after 20 h TOS. In addition, the selectivity to cyclohexanol slightly increased at the beginning of the reaction, remaining constant with TOS. The selectivity to C₁₂ hydrocarbons decreased with TOS and then was no longer observed over Pd/ZrO₂, Pd/CeO₂ and Pd/CeZrO₂ catalysts. However, the selectivity to C₁₂ hydrocarbons remained constant and high (around 20%) for the Pd/Al₂O₃ catalyst.

To shed light on the surface species formed and follow their evolution during the reaction on supported Pd catalysts, DRIFTS spectra were recorded during 6 h under a steady flow of the phenol/H₂ mixture at 573 K. The results obtained for Pd/Al₂O₃ catalyst are shown in Fig. 11.

Figure 11. DRIFTS spectra under HDO of phenol over Pd/Al₂O₃ at 573 K with time, including: (a) 34; (b) 60; (c) 87; (d) 112; (e) 151; (f) 198; (g) 231; (h) 268; (i) 309; (j) 349; (k) 358 min.

The DRIFTS spectra obtained at the beginning of the reaction were similar to those observed at 573K. The spectrum exhibits bands at 1291, 1492, 1589, 3029 and 3065 cm⁻¹. These bands are due to the various modes of vibration of phenoxy species. Phenol adsorbs dissociatively on metal oxide cation sites in unidentate or bidentate mode. The band positioned at 1291 cm⁻¹ is likely due to the mono stretching mode of v(CO) of phenoxy species. The bands located at 1492 and 1589 cm⁻¹ are likely assigned to aromatic ring

vibrations v(C=C_{ring}), while those at 3029 and 3065 cm⁻¹ are assigned to v(CH) stretching of the phenol aromatic ring. Significant changes were observed in DRIFTS spectra during the reaction. The intensity of bands attributed to phenoxy species significantly increased, leveling off at 268 min TOS, which indicates that the surface population of phenoxy species increased. Furthermore, new bands appeared during the reaction. After 231 min of TOS, it is noticed the appearance of bands at 2931, 2856 and a shoulder at 1677 cm⁻¹. These bands have been assigned to 2-cyclohexen-1-one.¹² The IR spectrum of adsorbed 2cyclohexen-1-one on Pd/Al₂O₃ displayed bands at 2950, 2870, and 1686 cm⁻¹, very similar to the bands observed herein.

For Pd/ZrO₂ catalyst, the DRIFTS spectrum revealed bands at 1279, 1441, 1486, 1587, 2852, 2930, 3021 and 3064 cm⁻¹ after 30 min with TOS (Figure 12). These bands are ascribed to the various vibrational modes of adsorbed phenoxy species and cyclohexanol. With increasing reaction time, the band intensities of these species increased.

Figure 12. DRIFTS spectra under HDO of phenol over Pd/ZrO₂ at 573 K with time, including: (a) 34; (b) 60; (c) 87; (d) 112; (e) 151; (f) 198; (g) 231; (h) 268; (i) 309; (j) 349; (k) 358 min.

The DRIFTS spectrum under reaction conditions over Pd/CeO_2 catalyst after 30 min TOS exhibited bands at 1275, 1367, 1485, 1515, 1583 cm⁻¹, which are due to the presence of phenoxy and cyclohexanol species (Figure 13). The intensity of these bands increased up to 120 min and then remained constant.

Figure 13. DRIFTS spectra under HDO of phenol over Pd/CeO₂ at 573 K with time, including: (a) 29; (b) 55; (c) 81; (d) 120; (e) 146; (f) 172; (g) 198; (h) 268; (i) 224.

Figure 14 displays the DRIFTS spectra recorded during HDO of phenol for 6 h over Pd/CeZrO₂ catalyst. Basically, they exhibit the same bands attributed to phenoxy and cyclohexanol species as observed in the DRIFTS spectra of the Pd/ZrO₂ catalyst. However, the spectra of both catalysts reveals a remarkable difference. The intensity of all the bands observed in the spectra of Pd/ZrO₂ catalyst significantly increased during 6 h TOS, consistent with the significant decrease in conversion (Figure 10 (D)). On the other hand, the bands only slightly increased from 26 to 63 min and then remained constant up to the

end of reaction for the Pd/CeZrO₂ catalyst. This result is also in agreement with the catalytic test (Figure 10 (F)), where only a small loss in phenol conversion occurred. These changes in the intensities of the bands as a function of TOS are more clearly observed in Figure 15, which shows the curves corresponding to the integration of the areas of the absorbance bands between 2750 and 3200 cm⁻¹. In general, the trends in increasing inventory of the adsorbed species mirror the decreases in conversion observed as a function of time (i.e., deactivation) from Figure 10. The Pd/Al₂O₃ and Pd/ZrO₂ catalysts show steadily increasing coverages suggesting that the intermediates become more difficult to turn over as a function of time on stream. In agreement with this, the conversions tend to steadily decrease with time. With Pd/CeO₂ and Pd/CeZrO₂ catalysts, although the absolute areas are generally higher, the inventory established initially does not significantly increase as a function of time. The catalysts have greater stability, in agreement with the flat conversion trend curves in Figure 10.

Figure 14. DRIFTS spectra under HDO of phenol over Pd/CeZrO₂ at 573 K with time, including: (a) 26; (b) 63; (c) 96; (d) 126; (e) 160; (f) 188; (g) 217; (h) 268; (i) 295; (j) 329; (k) 358 min.

Figure 15. Sum of band areas from 2750 to 3200 cm⁻¹ in DRIFTS spectra obtained over Pd/Al₂O₃, Pd/ZrO₂, Pd/CeO₂, and Pd/CeZrO₂ catalysts at 573 K and under the reaction mixture containing phenol and hydrogen as a function of TOS.

According to the reaction mechanism proposed for HDO of phenol,¹³ phenol adsorbs as phenoxy species on the support Lewis acid sites, followed by the tautomerization and formation of a cyclohexadienone as an intermediate. This highly unstable intermediate may react by different pathways, as shown in Scheme 1. (i) The first is hydrogenation of the ring, resulting in the formation of 2-cyclohexen-1-one, which hydrogenates to cyclohexanone (and then cyclohexanol); the latter is dehydrated to cyclohexene and dehydrogenated to benzene. This reaction route occurs over Pd/Al₂O₃ catalyst (with the exception of the 2-cyclohexen-1-one as an intermediate). The second involves the hydrogenation of the carbonyl group to 2,4-cyclohexadienol, which

dehydrates to benzene. This is suggested to occur with Pd/ZrO₂ and Pd/TiO₂ catalysts. In the present work, the DRIFTS experiments under steady state conditions revealed an accumulation of phenoxy, 2-cyclohexen-1-one and cyclohexanol species on the surface of Pd/TiO₂, Pd/ZrO₂, Pd/Al₂O₃ and Pd/SiO₂ catalysts. These results are consistent with the long-term catalytic tests that showed decreases in phenol conversion and benzene selectivity with corresponding increases in the formation of cyclohexanone and cyclohexanol.

As it was discussed previously, the HDO reaction requires a metallic site for hydrogenation/dehydrogenation as well as an acid site that adsorbs the oxy compound and promotes dehydration, alkylation and polymerization reactions. Therefore, the buildup of intermediate species on the surface could be caused by the loss of the Pd-support interaction. This, is turn, could be associated with: (i) carbon deposition resulting in site blocking at the interface; (ii) metal sintering, which decreases the interface between metal particles and support; or (iii) changes in the acid sites of the support (e.g., decreases in Lewis acid sites due to site blocking by strong adsorbates).

Catalyst deactivation during HDO is one of the main issues associated with this process. Therefore, fundamental understanding of the catalyst deactivation mechanisms for model molecules representative of bio-oil should contribute to the development of more efficient catalysts.

In the present work, the used catalysts were characterized by Raman spectroscopy, cyclohexane dehydrogenation and cyclohexanol dehydration to shed light on the mechanism of catalyst deactivation. Raman spectroscopy was used to investigate the formation of carbon on spent catalysts after 20 h of TOS. Carbon may be produced by polymerization and polycondensation reactions on the acid sites of the support, leading to the formation of polyaromatic compounds strongly bonded to the surface. The deposition

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of carbonaceous species may also occur by the hydrogenolysis of the oxygenated compounds on the metal particles. The Raman spectra of the used catalysts did not reveal bands characteristic of carbon materials in the range of 1200 - 1800 cm⁻¹. Thus, the deactivation of Pd catalysts was likely not caused by the coverage of Pd particles or acid sites by carbonaceous deposits.

The dehydrogenation of cyclohexane reaction was carried out after the HDO of phenol reaction without exposure of the catalyst to air to determine the changes in Pd dispersion during reaction. Table 6 lists the ratio between the reaction rates of dehydrogenation of cyclohexane at 543 K over fresh and used (after 20 h of HDO of phenol reaction) catalysts. The reaction rate significantly decreased, indicating that the sintering of Pd particles is one of the causes of catalyst deactivation. However, the degree of sintering varied depending on the support. For Pd/SiO₂ catalyst, the decrease in the reaction rate was approximately the same as that of phenol conversion, suggesting that Pd sintering is likely the main cause for catalyst deactivation. For Pd/TiO₂ and Pd/ZrO₂ catalysts, losses in activity were higher than expected if deactivation was solely attributed to an increase in Pd particle size, suggesting a possible loss in activity of the Lewis acid sites of the supports (e.g., site blocking). The largest decrease in the reaction rate of dehydrogenation of cyclohexane was observed for the Pd/CeO₂ and Pd/CeZrO₂ catalysts.

Table 6. The ratio between the reaction rates of dehydrogenation of cyclohexane at 543 K over fresh and used (after 20 h of HDO of phenol reaction) catalysts and the reaction rates of dehydration of cyclohexanol at 543 K over fresh and used (after 20 h of HDO of phenol reaction) catalysts.

Catalyst	Dehydrogenation of cyclohexane ratio	Dehydration of cyclohexanol ratio
Pd/SiO ₂	1.22	1.14
Pd/Al ₂ O ₃	6.25	1.04
Pd/TiO ₂	2.84	1.37
Pd/ZrO ₂	1.90	15.00
Pd/CeO ₂	10.33	1.00
Pd/CeZrO ₂	6.11	2.77

The changes in the density of acid sites was studied by the dehydration of cyclohexanol reaction. The ratio between the reaction rates for dehydration of cyclohexanol before and after HDO reaction is listed in Table 6. A significant decrease in the rate of cyclohexanol dehydration is observed for Pd/ZrO₂ catalyst. In the case of Pd/CeZrO₂ and Pd/TiO₂ catalysts, the reaction rate only slightly decreased after 20 h of TOS. Pd/SiO₂, Pd/Al₂O₃ and Pd/CeO₂ catalysts did not exhibit a decrease in the reaction rate of cyclohexanol dehydration. Therefore, the changes in the density of Lewis acid sites during the phenol reaction depended on the type of the support. Comparing the variation of Pd dispersion and the density of acid sites during HDO of phenol over all catalysts, it is clear that Pd sintering is the primary mode of catalyst deactivation. The growth of Pd particle size decreases the metal particle-support interface that affects the ability of the

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adsorbed species to turnover, leading to an accumulation of phenoxy species during reaction, as revealed by DRIFTS experiments. However, the decrease in the density of acid sites is significant in the case of the Pd/ZrO₂ catalyst.

Considering that the HDO of phenol is a bifunctional mechanism, the decrease of both the metal particle-support interface (Pd sintering) and the number of Lewis acid sites (site blocking) might contribute to the deactivation observed of Pd supported catalysts during the reaction. Curiously, Pd/CeO₂ and Pd/CeZrO₂ catalysts exhibited a low degree of deactivation in spite of the significant increase in the Pd particle size. The DRIFTS experiments revealed that there was no significant buildup of intermediate species on the surface during the reaction. This suggests that the loss of the metal particle-support interface does not produce an accumulation of intermediate species over the ceria and ceria-zirconia supports. The CO adsorption experiments showed that these catalysts have high densities of defect-associated hydroxyl groups. Therefore, increasing the amount of oxygen vacancies could improve catalyst stability. In order to demonstrate the role of oxygen vacancies on catalyst stability, the HDO of phenol was performed after reduction of Pd/CeZrO₂ catalyst at 773 K (Figure S3). As expected, catalyst did not lose activity during 20 h TOS. Unfortunately, the gain in catalyst stability was followed by a loss of selectivity to deoxygenated products, regardless of the reduction temperature. These catalysts exhibited a high formation of cyclohexanone and cyclohexanol because they do not have enough oxophilicity to promote the hydrogenation of the tautomer intermediate carbonyl group.

However, the adsorption strength could also play an important role on catalyst deactivation. The adsorption of cyclohexanone in DRIFTS experiments revealed stronger adsorption between the carbonyl function with oxides such as TiO₂, ZrO₂, SiO₂, and Al₂O₃. This higher oxophilicity could contribute to the greater deactivation rate of these catalysts,

resulting from an accumulation of O-containing byproducts that are difficult to desorb. Furthermore, the CeO₂ and CeZrO₂ supported catalysts have a high concentration of defects such as O-vacancies and related bridging OH groups. Thus, there appears to be a link between the stability of Pd/CeO₂ and Pd/CeZrO₂ catalysts and their reduced defect centers. Assuming that adsorbed oxygenates are bound at defect centers by their O-atoms, possible explanations for improved stability are: (1) the formation of oxygen vacancies expose additional cationic sites that turn over oyxgenate intermediates and/or allow facile desorption of oxygenate products; or (2) water from dehydration reactions may be activated at these defects to assist in turning over oxygenate intermediates and/or enable facile desorption of oxygenate products. Although Pd/TiO₂ and Pd/ZrO₂ also possess reduced defect centers, their surface concentrations are deemed to be more limited than ceria-based materials. Moreover, the greater oxophilicity of Pd/TiO₂ and Pd/ZrO₂ catalysts that results in an accumulation of O-containing byproducts likely outweighs any advantage that may be provided by the limited surface concentration of reduced defects.

4- Conclusion

The deoxygenation activity and product distribution for HDO of phenol is significantly affected by the type of the support. Pd/TiO₂ and Pd/ZrO₂ catalysts exhibited the highest activity for HDO and selectivity to benzene. The other catalysts showed a higher formation of cyclohexanone. The dehydration of cyclohexanol reaction revealed that the density of acid sites of Pd supported catalysts varied significantly and drove the reaction pathway. For Pd/Al₂O₃ catalyst, the relatively high density of acid sites favors the dehydration of cyclohexanol formed to cyclohexene, followed by the formation of benzene. However, there was no correlation between the density of acid sites and the

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deoxygenation activity. The density of acid sites of the other catalysts was too low such that this reaction pathway does not occur. In this case, the formation of benzene takes place by an alternative route that involves the tautomerization of phenol to a cyclohexadienone intermediate. For Pd/SiO₂, Pd/CeO₂ and Pd/CeZrO₂ catalysts, ring hydrogenation of 2,4cyclohexadien-1-one occurs, with significant formation of cyclohexanone and cyclohexanol. For Pd/TiO₂ and Pd/ZrO₂, the oxophilic sites (incompletely coordinated Ti and Zr cations) promote an interaction with the oxygen atom in the keto-tautomer of phenol. Then, hydrogenation of the carbonyl function preferentially takes place, producing 2,4-cyclohexadienol, which is followed by its dehydration to benzene. DRIFTS experiments of adsorbed cyclohexanone revealed the existence of a correlation between the deoxygenation activity and strength of interaction of oxygen of phenolic compounds with oxophilic sites

Pd/SiO₂, Pd/Al₂O₃, Pd/TiO₂ and Pd/ZrO₂ catalysts significantly deactivated with TOS. However, Pd/CeO₂ and Pd/CeZrO₂ were more stable and only slight losses in activity were observed. Raman spectroscopy ruled out the presence of carbon deposits. However, the dehydrogenation of cyclohexane and dehydration of cyclohexanol revealed sintering of Pd and a reduction in the density of acid sites during the HDO of phenol reaction. The DRIFTS spectra under steady state conditions showed an accumulation of phenoxy and intermediate species during reaction. These species remained adsorbed on the Lewis acid sites, blocking those sites and inhibiting further reactant adsorption. Considering that the HDO of phenol takes place at the metal-support interface, Pd sintering and blocking of Lewis acid sites will lead to catalyst deactivation. The lower degree of deactivation of Pd/CeO₂ and Pd/CeZrO₂ catalysts is likely due to the higher density of oxygen vacancies of these supports. The formation of oxygen vacancies expose additional cationic sites that turn over oyxgenate intermediates and/or allow facile desorption of

oxygenate products. In addition, water from dehydration reactions may be activated at these defects to assist in turning over oxygenate intermediates and/or enable facile desorption of oxygenate products. However, the adsorption strength also contributed to catalyst deactivation. The stronger adsorption between the carbonyl function with oxides such as TiO₂, ZrO₂, SiO₂, and Al₂O₃ resulted in an accumulation of O-containing byproducts and led to catalyst deactivation.

Supporting information

XRD patterns of: (A) Pd/SiO₂; (B) Pd/Al₂O₃; (C) Pd/TiO₂; (D) Pd/ZrO₂; (E) Pd/CeO₂; (F) Pd/CeZrO₂.

Phenol conversion and products yield as a function of W/F over (A) Pd/SiO₂; (B) Pd/Al₂O₃; (C) Pd/TiO₂; (D) Pd/ZrO₂; (E) Pd/CeO₂; (F) Pd/CeZrO₂.

Conversion of phenol and selectivity to products as a function of TOS for $Pd/CeZrO_2$ (W/F = 0.824 h) reduced at 500 °C.

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