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Hydrodeoxygenation of Guaiacol over Pd–Co and Pd–Fe Catalysts: Deactivation and Regeneration

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Abstract: In bio-oil upgrading, the activity and stability of the catalyst are of great importance for the catalytic hydrodeoxygenation (HDO) process. The vapor-phase HDO of guaiacol was investigated to clarify the activity, stability, and regeneration ability of Al-MCM-41 supported Pd, Co, and Fe catalysts in a fixed-bed reactor. The HDO experiment was conducted at 400 °C and 1 atm, while the regeneration of the catalyst was performed with an air flow at 500 °C for 240 min. TGA and XPS techniques were applied to study the coke deposit and metal oxide bond energy of the catalysts before and after HDO reaction. The Co and Pd–Co simultaneously catalyzed the C_{Ar}O–CH₃, C_{Ar}–OH, and multiple C–C hydrogenolyses, while the Fe and Pd–Fe principally catalyzed the C_{Ar}–OCH₃ hydrogenolysis. The bimetallic Pd–Co and Pd–Fe showed a higher HDO yield and stability than monometallic Co and Fe, since the coke formation was reduced. The Pd–Fe catalyst presented a higher stability and regeneration ability than the Pd–Co catalyst, with consistent activity during three HDO cycles.

Keywords: hydrodeoxygenation; guaiacol; regeneration; catalyst deactivation

1. Introduction

The lignocellulose biomass resource can be used not only as direct energy in combustion, but also as a more valuable fuel after the conversion and upgrading process [1]. Pyrolysis is a thermal conversion of biomass to produce bio-oil, which has significant advantages in storage, transportation, and the ability to be utilized as useful petrochemicals and fuel [2]. However, the presence of oxygenated compounds (e.g., acids, esters, alcohols, ketones, furans, and phenols) gives the bio-oil a low heating value, low chemical and thermal stability, high viscosity, and high corrosiveness [3–7]. These disadvantages can be mitigated or solved if oxygen is removed partially or entirely, respectively [8]. Catalytic hydrodeoxygenation (HDO) is a prominent process for bio-oil upgrading, since it can eliminate the oxygen significantly and preserve the carbon of the bio-oil [9,10].

The stability and regeneration abilities of catalysts are very important in the catalytic HDO process. In the HDO process, the deactivation of catalysts is mainly from coke deposits, sintering, poisoning, and metal deposition [8,11,12]. Coke deposits are formed through polymerization and polycondensation reactions on the catalytic surface, resulting in pore blockages and active site coverage [8]. Water and S- or N-containing compounds in the feed can cause poisoning on the catalytic surface [13]. Sintering is the agglomeration of nanoparticles into larger particles, resulting in a decrease in the active sites [14]. In the hydrotreating of different bio-oil sources over different catalyst types (e.g., guaiacol



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). over noble metal catalysts [15], grass bio-oil over noble metal Ru and Pt [16], rice husk bio-oil over Ni–Cu catalyst [17], or pine bio-oil over NiAl₂O₄ [18]), the coke deposit is the main cause of the catalyst deactivation. The coke deposit is dependent on the catalyst type, feedstock, and operating conditions [17]. The deactivated catalysts can be regenerated via coke combustion at medium to high temperatures, depending on the HDO reaction conditions [16]. In a catalyst HDO, the mesoporous supports exhibited much higher stability than the microporous supports [18,19]. There are numerous research studies on catalyst deactivation effects, e.g., the type of carbon deposit, metal sintering, deactivation mechanism, and bio-oil impurities (H₂O, H₂S, etc.) [14,16,20–22]. However, the regeneration abilities of catalysts during catalytic HDO are not well understood and have only been examined in a few studies [9,23,24].

In this study, the HDO of guaiacol on Al-MCM-41 supported Pd–Co and Pd–Fe catalysts were investigated in a fixed-bed, continuous-flow reactor at ambient pressure. The Al-MCM-41 is an acidic and mesoporous support, which can enhance the transalkylation activity and stability of the catalyst in the HDO process [18,25,26]. Guaiacol was chosen as a model compound because it contains both major functional groups of lignin-derived phenolic, such as hydroxyl (–OH) and methoxy (–OCH₃) groups. The HDO of guaiacol was conducted to screen the HDO activity, stability, and regeneration ability of the catalysts. TGA and XPS were applied to characterize the deactivation that occurred during catalytic HDO.

2. Materials and Methods

2.1. Materials

Mesoporous aluminosilicate Al-MCM-41 support (3–4% Al_2O_3) was supplied by ACS Material (Pasadena, CA, US). Guaiacol (2-methoxyphenol) purchased from Merk (Kenilworth, NJ, US) was used as the model compound for the HDO study. Metal precursors (palladium(II) nitrate, cobalt(II) nitrate (99.999%), and iron(III) nitrate (99.95%)) were purchased from Aldrich (St. Louis, MO, US).

2.2. Catalyst Preparation and Characterization

The catalysts were prepared via an incipient wetness co-impregnation method. The detailed characterization of the catalyst has been previously described [27]. The Al-MCM-41 supported catalysts had a mesoporosity structure, with a pore size of around 3 nm. The total acidity of the Al-MCM-41 support measured by temperature programmed desorption (TPD) of ammonia was 1.06 mmol/g. The transmission electron microscopy (TEM), temperature programmed reduction (TPR) in hydrogen, and powder X-ray diffraction (XRD) results implied that the addition of Pd could improve the dispersion and reducibility of Co and Fe oxides with the formation of Pd–Co and Pd–Fe alloys.

Thermogravimetric analysis (TGA) under the flow of air was conducted in a TA Instrument model QA50. During the TGA analysis, temperature was increased from room temperature to 900 °C, at a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific K-Alpha system equipped with an Al K α radiation source. The spectrometer was operated with the constant analyzer energy (CAE) mode at a pass energy of 50 eV and a step of 0.1 eV. Quantification and deconvolution were performed using the Gaussian functions of the OriginPro 2015 software (OriginLab, Northampton, MA, US).

2.3. HDO of Guaiacol

A Catalytic HDO reaction was conducted in a fixed-bed reactor at 400 °C and ambient pressure. The details of the experimental set-up of the HDO of guaiacol were mentioned in a previous report [27]. Before the HDO reaction, all the catalysts were reduced to 450 °C using a hydrogen flow of 90 mL/min for 2 h. Pure guaiacol was fed at a flow rate of 1.08 mL/h using a syringe pump and vaporized at 350 °C in the top glass wool bed. Catalyst regeneration was carried out after 210 min of guaiacol HDO reaction. The used

catalyst was first treated with an air flow at 500 °C for 240 min. Afterwards, the catalyst was reactivated in hydrogen flow at 450 °C for 120 min and catalyzed a new HDO reaction cycle. The liquid products were quantified by a Shimadzu GC-2014 gas chromatography (GC), with a SGE BPX–5 capillary column (30 m, ID 0.25 mm, and 0.25 μ m) and a flame ionized detector (FID). The gas products were analyzed by a Shimadzu GC–8A system equipped with a thermal conductivity detector (TCD). The carbon balance of the HDO experiments was between 93% and 98%. The HDO of guaiacol over the Pd–Fe catalyst at W/F of 1.67 h and temperature of 400 °C were repeated twice, and the standard deviation of all product yields was less than 1.0 Mol_C%. Meanwhile, the other HDO experiments were conducted once. Carbon-based guaiacol conversion (X_{Gua}), product yields (Y_i), and HDO yields were calculated in Mol_{Carbon}% by the following equations.

$$X_{Gua}(\%) = \frac{Mol(gua)_{in} - Mol(gua)_{out}}{Mol(gua)_{in}} \times 100$$
(1)

$$Y_i(\%) = \frac{Mol_i \times \alpha_i}{Mol(gua)_{in} \times \alpha_{gua}} \times 100$$
(2)

$$HDO yield (\%) = \sum_{i=1}^{25} \frac{Y_i \times (\beta_{gua} - \beta_i)}{\beta_{gua}}$$
(3)

where α_i and β_i are the carbon and oxygen numbers in the product *i*; $\alpha_{gua} = 7$ and $\beta_{gua} = 2$.

3. Results

3.1. Catalytic Stability of Mono- and Bimetallic

Figure 1 compares the conversion of guaiacol and product yields over the supported mono- and bimetallic catalysts with time on stream (TOS). The monometallic Fe catalyst had higher mono-oxygenated products and lower gas phase (which mainly contained methane) yields than monometallic Co, resulting in higher HDO yield. Addition of Pd to the Co catalyst increased the guaiacol conversion and deoxygenated product (aromatics and mono-oxygenated) yields. However, this addition to the Fe catalyst only showed the increment of guaiacol conversion and mono-oxygenated product yield, while the oxygen-free aromatic yield was decreased. These implied that the Fe active sites mainly catalyzed the C_{Ar}–OCH₃ cleavage reaction instead of the C_{Ar}–OH cleavage and produced mono-oxygenate as the main product. Meanwhile, the hydrogenolysis of CAr-OR and C-C groups occurred simultaneously in the HDO over the Pd–Co and Co catalysts, resulting in the formation of deoxygenated products and methane. The reaction routes of HDO of guaiacol over different catalysts can be found in Scheme 1. As shown in Figure 1, the monometallic Co and Fe catalysts showed a faster deactivation than the bimetallic Pd–Co and Pd–Fe. The addition of Pd significantly enhanced the stability of both Co and Fe catalysts. Among these catalysts, Pd-Fe presented as the most promising catalyst due to its higher stability and HDO yield. In summary, the addition of Pd enhanced the guaiacol conversion, HDO yield, and stability of the Co and Fe catalysts. Previous studies mentioned the enhancement in conversion and HDO yields when novel metals (Pd and Pt) were added [9,28,29]. However, there was no report on the stability enhancement like in our findings (Supplementary materials).



Figure 1. Catalytic hydrodeoxygenation (HDO) of guaiacol over mono- and bimetallic catalysts (**A**) Co, (**B**) Pd-Co, (**C**) Fe and (**D**) Pd-Fe. Reaction conditions: $T = 400 \degree C$, P = 1 bar, $H_2/Gua = 25$, W/F = 0.83 h.



Scheme 1. Simple reaction pathways of HDO of guaiacol. More details can be found elsewhere [27].

To understand the contribution of Pd to the stability of Co and Fe catalysts, the TGA of the used catalysts was applied to understand the coke formation in catalysts, as shown in Figure 2. There was a negative peak, which appeared at around 200 $^{\circ}$ C in the derivative thermogravimetric (DTG) curves (in Figure 2A). This peak could be attributed to the oxidation of the remaining metallic Fe or Co, which were reduced during the HDO reaction. The main peaks in the DTG curves were observed from 200 to 650 °C, which was associated with coke removal by oxidation. These mass loss data of used mono- and bimetallic catalysts are compared in Figure 2B. The bimetallic Pd–Co and Pd–Fe catalysts had a lower coke formation than the corresponding monometallic catalysts. In summary, the addition of Pd prevented coke formation during HDO reactions and made the catalyst more stable. As shown in Figure 2B, the used Fe and Pd–Fe catalysts had a higher coke formation than the used Co and Pd–Co catalysts. Nevertheless, the stability of Fe and Pd– Fe catalysts was higher than that of Co and Pd–Co catalysts (Figure 1). This contradiction could be explained by the DTG results, in which the used Fe and Pd–Fe catalysts had lower temperature degradation peaks (i.e., 350 °C) than Co and Pd–Co ones (i.e., 500 °C). Hence, the coke formation during HDO over Fe and Pd–Fe was more easily degraded than the one over Co and Pd-Co.



Figure 2. TG results of mono- and bimetallic catalysts. (**A**) DTG curves of used catalysts in air atmosphere, (**B**) Mass loss of used and fresh catalysts.

3.2. Regeneration of Bimetallic Catalysts

During HDO reactions, catalysts are deactivated due to carbon deposition, sintering, or poisoning; hence, regeneration ability becomes an important issue in practical applications [14,22]. In our previous study [30], with the regeneration of air at 450 °C for 2 h, the coke deposit remained on the catalyst surface. Hence, the treatment temperature was increased to 500 °C, and the time was prolonged to 4 h in order to improve the regenerated catalyst in this current work. Figure 3 illustrates the details of the regeneration ability of the Pd-Co and Pd-Fe catalysts. During the first HDO reaction, Pd-Fe and Pd-Co had the same guaiacol conversion. However, Pd-Fe presented a higher HDO yield than Pd-Co, due to its lower gasification activity. The regenerated Pd–Co catalyst showed a decrease in guaiacol conversion and HDO yield compared with the fresh one. In addition, this regenerated catalyst gave a faster deactivation than the fresh one, and the deactivation rate increased with the increase in recycle time. In contrast to Pd–Co, Pd–Fe had considerably higher stability and regeneration ability. The regenerated Pd–Fe catalyst had a higher HDO yield than the fresh one. Even at the 3rd cycle, the Pd–Fe catalyst gave no significant deactivation after a 210 min reaction. In summary, the Pd–Fe catalyst could be regenerated due to there being no significant change in the guaiacol conversion and HDO yield during the three reaction cycles.



Figure 3. Recycling of HDO of guaiacol over Pd–Co and Pd–Fe catalysts (Reduction–Regeneration). Reaction condition: $T = 400 \degree C$, P = 1 bar, $H_2/\text{Gua} = 25$, W/F = 1.67 h.

The regenerations of catalysts in previous studies were conducted in air at 350 °C [23] or 500 °C [24,26]. There were slight changes in the conversion and product selectivity of the used catalyst. When the catalyst was treated in air at 350 °C, the coke deposits on the Pt catalysts remained during the regeneration, which resulted in a slight decrease in m-cresol conversion and higher selectivity to toluene in the second cycle [23]. In our current report, the treatment with air at 500 °C could even increase the HDO yield of Pd–Fe catalyst.

The addition of Pd can improve the stability of the Fe and Co catalyst. Moreover, the Pd–Fe catalyst showed considerably higher stability and regeneration ability than the Pd–Co catalyst. TGA and XPS analysis were applied to study the catalyst deactivation and regeneration during HDO reactions. After three cycles of HDO reaction, the used Pd–Co and Pd–Co catalysts were taken out and regenerated with air at 500 °C for 4 h in the muffle furnace. These fresh, used, and regenerated catalysts were analyzed with XPS and TGA to clarify the deactivation of the catalyst. According to the DTG results in Figure 2A, the coke deposits on Pd–Fe degraded at a lower temperature than Pd–Co, resulting in a higher regeneration ability of Pd–Fe catalysts.

Using the XPS spectra of Al-MCM-41 support, fresh (calcined), reduced, used, and regenerated catalysts were plotted and compared to reveal the change of elemental components and chemical state of the catalyst. Figures 4 and 5 illustrate the deconvoluted XPS spectra of Pd–Co and Pd–Fe catalysts, respectively. The XPS spectra of other elements (Si 2p, Al 2p, and Pd 3d) can be found in Figures S1 and S2. All spectra were calibrated by referring to the maximum of the O 1s peak at 533.0 eV, which corresponded to Si–O–Si binding in SiO₄ species [31–34].

Figures 4A and 5A show the C 1s XPS spectra of reduced, used, and regenerated Pd–Co and Pd–Fe, respectively. The used catalyst surface was covered with a carbon deposit, which formed during HDO reaction; hence, the carbon signal of the used catalyst was higher than the other catalysts, while the metal signals (Co 2p and Fe 2p) of the used catalyst were lower than others. C 1s spectra of used Pd–Co had two distinct peaks at 284.7 and 282.1 eV, whereas the used Pd–Fe had one additional peak at 280.0 eV. The peak at 284.7 eV was attributed to contaminated carbon, which appeared on all reduced, used, and regenerated catalysts [35,36]. The peak at 282.3 eV in used catalysts could be assigned to graphite-like carbon [35–39]. According to previous papers on coke deposits in used catalysts [35,37–39], the peaks of oxidized carbon should appear at a higher binding energy position than the contaminated carbon peak. These oxidized carbon peaks were absent in our used Pd–Co and Pd–Fe catalysts. The additional peaks at 280.0 eV in the used Pd–Fe catalyst could be attributed to dehydrogenated carbon species [38,39]. In general, the regeneration process can remove the carbon deposit on the catalyst surface significantly.



Figure 4. The deconvoluted core level XPS scans of C1s (**A**), O1s (**B**), and Co2p (**C**) of fresh, reduced, used, and regenerated Pd–Co/Al-MCM-41 catalysts.



Figure 5. The deconvoluted core level XPS scans of C1s (**A**), O1s (**B**), and Fe2p (**C**) of fresh, reduced, used, and regenerated Pd–Fe/Al-MCM-41 catalysts.

In Figures 4B and 5B, the O 1s spectra of support and reduced catalysts had only one peak at 533.0 eV, while other catalysts had additional peaks at lower binding energy. The profile of the O 1s spectra (Figures 4B and 5B) was extremely similar to the profile of Si 2p and Al 2p spectra (see Figures S1 and S2) for all catalysts; this implies that the oxygen would bond with at least one silicon or aluminum atom (small amount) [33,34]. The first peak at 533.0 eV might correspond to Si–O–Si binding in SiO₄ species [31–34], while the second peak at 531 to 529 eV could be ascribed to the Si–O–Me bindings (Me = Co or Fe). The second peak in fresh catalyst corresponds to Si–O–Me bindings, since it disappeared after the catalysts were reduced. The second peak of fresh Pd–Co appeared at 529 eV, whereas the fresh Pd–Fe appeared at a higher energy binding of 531 eV. The second peak of the Pd–Co catalyst was shifted to higher binding energy after the catalyst was used and regenerated; this might explain the drop in HDO activity of this catalyst. The O 1s oxidation state of Pd–Co did not change as much as Pd–Fe between fresh, used, and regenerated catalysts. The fresh Pd-Fe had two peaks at 533 and 531 eV; however, the used and regenerated Pd-Fe formed a new peak at a lower binding energy (528 or 527 eV). This formation of a lower binding energy peak of Pd–Fe might be related to the enhancement in HDO activity in the regenerated catalyst, as discussed above.

As can be seen in Figure 4C, the binding energies of Co $2p_{3/2}$ and Co $2p_{1/2}$ appeared as two distinct peaks, at around 781.0 and 796.5 eV. The spin–orbit splitting energy ($\Delta E_{Co2p1/2-Co2p3/2}$) of the fresh, used, and regenerated catalysts was about 15.1 eV, combining with the very weak satellites. This observation indicated the coexistence of Co²⁺ and Co³⁺ in this Pd–Co catalyst [40,41]. The reduced catalyst had higher spin–orbit splitting energy (15.5 eV) and shake-up satellite than others. The surface of the used catalyst was covered by a carbon deposit; hence, the signal of the metal active site was smaller than that of the fresh, reduced, and regenerated catalysts. The regeneration process can remove the carbon deposit; however, the intensity of Co 2p peaks was not as high as that of fresh and reduced catalysts.

The XPS spectra of Fe 2p (Figure 5C) had two main peaks, which can be assigned as Fe $2p_{3/2}$ at 711.2 eV and Fe $2p_{1/2}$ at 725.0 eV [31]. The maximum Fe $2p_{3/2}$ peak was observed at around 711.0 eV with the satellites at higher binding energy, suggesting that Fe species were mainly in Fe³⁺ state [31,42,43]. Similar to the Pd–Co catalyst, the used and regenerated Pd–Fe catalyst had **a** lower signal intensity of Fe 2p compared to a fresh and reduced catalyst, due to the effect of coke deposit. However, the peak position of the Pd–Fe catalyst was not changed significantly, like the Pd–Co catalyst.

In summary, the XPS result reveals that the air treatment at 500 °C for 4 h could remove most of the coke deposit on the catalyst. Moreover, the Si–O–Co binding of used and regenerated Pd–Co catalyst shifted to higher binding energy, resulting in the drop of HDO activity in the second and third cycles. In addition, the used and regenerated Pd–Fe formed a new peak at lower binding energy, yielding the enhancement in HDO activity of the regenerated catalyst.

4. Conclusions

Hydrodeoxygenation of guaiacol over Al-MCM-41 supported Pd–Co and Pd–Fe catalysts were studied at 400 °C and ambient atmosphere. The Fe catalyst gave a higher HDO yield and lower gas-phase yield compared with the Co catalyst in HDO of guaiacol. The bimetallic Pd–Co and Pd–Fe achieved a higher conversion and HDO yield than the monometallic Co and Fe. Interestingly, the addition of Pd significantly improved the stability of the catalysts, since it could suppress the coke deposition on the catalysts. Furthermore, the Pd–Fe catalyst presented a higher stability and regeneration ability than the Pd–Co catalyst. The coke deposits were mostly removed by the treatment at 500 °C in air, which was confirmed by TGA and XPS results. The regenerated Pd–Co catalyst showed a decrease in HDO yield and stability, while the Pd–Fe catalyst presented consistent activity during three HDO cycles. This can be explained by the lower thermal stability coke deposit and the formation of lower binding energy Si–O–Fe bonds of the used Pd–Fe catalyst.

Supplementary Materials: The following are available online at https://www.mdpi.com/2227-9 717/9/3/430/s1, Figure S1: De-convoluted Si 2p, Al 2p and Pd 3d XPS spectra of fresh, used, and regenerated Pd–Co/Al-MCM-41catalysts; Figure S2: De-convoluted Si 2p, Al 2p and Pd 3d XPS spectra of fresh, used, and regenerated Pd–Fe/Al-MCM-41catalysts.

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