

Guaiacol Hydrodeoxygenation and Hydrogenation over Bimetallic Pt-M (Nb, W, Zr)/KIT-6 Catalysts with Tunable Acidity

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Cite This: <https://doi.org/10.1021/acssuschemeng.1c07071>

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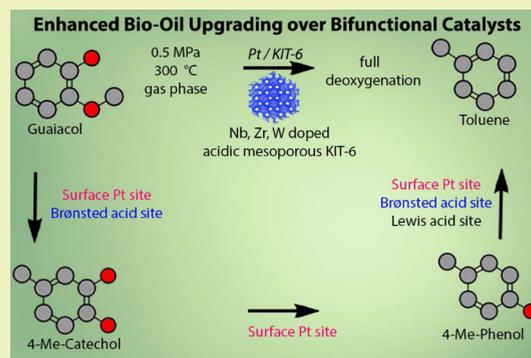
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Supporting Information

ABSTRACT: Owing to a high oxygen content, bio-oils from the fast pyrolysis of biomass require upgrading to meet fuel specification standards. Catalytic hydrodeoxygenation (HDO) of bio-oils faces several challenges such as low hydrocarbon yields, the requirement of high H₂ partial pressure for complete deoxygenation, and catalyst deactivation caused by coking/carbon deposition. In the present work, Pt supported on Nb, W, and Zr-incorporated KIT-6 materials were prepared, characterized, and tested for the gas-phase HDO of guaiacol, a widely used model compound of bio-oil. Facile HDO of guaiacol was observed over a 1 wt % Pt/Nb-KIT-6 catalyst, with ~90% conversion and ~75% hydrocarbon selectivity under relatively mild hydrogen partial pressure (0.5 MPa) at 400 °C and 33 h⁻¹ weight hourly space velocity (WHSV). No significant catalyst deactivation was observed during a 24-h continuous run indicating that the mesoporous support provides enhanced coking resistance. Mechanistic investigations indicate that the tunable acidity of the supports promotes transalkylation reactions, which favor increased aromatic hydrocarbon yields. A plausible reaction mechanism is postulated based on correlating the number of metal and acid sites with the measured rates for the individual reaction steps.

KEYWORDS: Full hydrodeoxygenation, Guaiacol, Bimetallic PtNb PtW PtZr catalysts, Mesoporous KIT-6 support, Tunable acidity, Biofuels, Bio-oil



INTRODUCTION

Pyrolysis-derived bio-oils from biomass sources cannot be used directly as fuels because they typically contain a high oxygen content, in contrast to petroleum-based fuels. Catalytic hydrodeoxygenation (HDO) offers a plausible route to upgrade bio-oils and meet fuel specification standards.^{1–4} Owing to the complex composition (hundreds of species) of bio-oils, model compounds are often selected to investigate bio-oil upgrading for catalyst development purposes. In this context, guaiacol, containing both hydroxy (–OH) and methoxy (–OCH₃) groups, has been studied as a representative model compound.^{5,6} Various catalytic materials have been reported for guaiacol HDO. In general, supported transition metals such as Pt,^{7,8} Ru,⁹ Co,^{10,11} and Ni¹² are active for gas-phase guaiacol HDO. However, these catalysts typically form partially deoxygenated species such as phenol and anisole (methoxybenzene) at 0.1 MPa H₂ pressure and temperatures ranging from 250 to 500 °C. Fully deoxygenated species such as benzene, toluene, and cyclohexane are only reported at elevated H₂ partial pressures (e.g., 3–5 MPa)^{13–16} or liquid-phase HDO at relatively low conversions^{17,18} or high H₂/guaiacol molar ratios (e.g., ~3300; see Table S1).¹⁹

Catalyst supports play a crucial role in guaiacol HDO activity, product selectivity, and catalyst stability.^{20–23} As compared to conventional microporous catalyst supports,

mesoporous materials show better performance because of easier accessibility to substrates and enhanced coke resistance.²⁴ Microporous acidic supports such as H-Beta²⁵ and H-ZSM-5²⁶ zeolites are known to promote guaiacol HDO while favoring transalkylation reactions.²⁷ Bifunctional catalysts containing both metal and acid sites have shown excellent guaiacol HDO activity to deoxygenated species. Such studies have employed either noble metals or a combination of noble and non-noble metals supported over microporous zeolites. They require elevated H₂ partial pressures (3–5 MPa) for full deoxygenation. For example, Pd supported on ZSM-5 zeolite produced alkylated aromatics at 250 °C and ring-saturated hydrocarbons at 200 °C during guaiacol HDO at 4 MPa H₂.²⁸ Remarkably, guaiacol HDO over Pt/H-Beta at 0.1 MPa H₂ partial pressure yielded 42% benzene, 29% toluene, and 12% xylenes when the H₂/guaiacol molar ratio was 50. The Pt/H-Beta catalyst, however, deactivated within 5 h time on stream.²⁵ Full deoxygenation of guaiacol over acidic Pt/

Received: October 17, 2021

Revised: March 18, 2022

Mo_2C ²⁹ and Ni/Rh_2 ²¹ catalysts using 0.44 MPa H_2 has been reported to yield >75% benzene. However, the catalyst stability was not reported.

The introduction of a second metal has been reported to improve guaiacol HDO. Bimetallic $\text{Ni-Re}/\text{SiO}_2$ catalyst showed a higher guaiacol HDO activity compared to monometallic (Ni , Re , Cu , Co) and other bimetallic (Cu-Re and Co-Re) catalysts, yielding cyclohexane as the major product at 250 °C and at 3 MPa H_2 pressure.³⁰ Pd-Co and Pd-Fe supported on Al-MCM-41 were also reported for atmospheric guaiacol HDO at ~400 °C, with the yield of fully deoxygenated products being <20%.³¹ Pd-Fe was superior in activity, stability, and regeneration ability compared to Pd-Co . $\text{Ni}/\text{H-USY}$ catalysts doped with Fe , Ga , Ce , La , or Sm were investigated for gas-phase HDO of guaiacol at 350 °C and atmospheric H_2 pressure, yielding <10% of fully deoxygenated products.²⁸ Bimetallic Ni-V supported on biochar-modified H-Beta yielded <40% aromatics during atmospheric pressure HDO with a $\text{H}_2/\text{guaiacol}$ ratio = 40. The catalyst required regeneration after 2 h.³² Bimetallic Ni-Co catalyst supported on HZSM-5 was reported to be more effective than monometallic $\text{Ni}/\text{HZSM-5}$ for bio-oil deoxygenation.³³ The foregoing studies suggest that a catalyst that shows enhanced HDO activity and stability at mild H_2 partial pressures (<1 MPa) continues to be elusive. Furthermore, the reaction mechanism/pathways and the roles of the active sites (e.g., metal vs acid) for guaiacol HDO over bifunctional catalysts are not well understood.³⁴

To address the foregoing issues, we investigated gas-phase HDO of guaiacol over metal (Nb , W , Zr)-exchanged mesoporous materials (primarily of the KIT-6 type) as supports for impregnating Pt . We had previously shown that such metal-exchanged KIT-6 materials exhibit tunable Lewis and Brønsted acidities, depending on the type of metal and extent of metal loading.^{35–40} The rationale for investigating these materials as supports is that tunable acid sites can be located in mesoporous supports to not only influence selectivity but also provide enhanced coking resistance. The Pt -based bimetallic catalysts synthesized in this manner were systematically investigated in the present work for gas-phase HDO of guaiacol. It is found that the aromatic hydrocarbon selectivity is generally enhanced on these catalysts via transalkylation reactions. A reaction pathway comprised of several steps and associated metal/acidic active sites is proposed, demonstrating the bifunctional nature of these catalysts. Among the tested catalysts, 1% $\text{Pt}/\text{Nb-KIT-6}$ provides enhanced and stable HDO performance with ~90% guaiacol conversion and ~75% selectivity to deoxygenated aromatic species in a 24-h test at 400 °C, 1.0 MPa total pressure (0.5 MPa H_2), and a WHSV of 33 h^{-1} . Clearly, the mesoporous nature of the support provides enhanced coking resistance.

EXPERIMENTAL SECTION

Hexachloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$, >99.9% metal basis from Sigma-Aldrich) was used as a Pt precursor. The 60–80 mesh activated carbon (AC) support was purchased from Norit Americas Inc. Guaiacol (>98.0%) and all other calibration compounds, including catechol, phenol, cyclopentanone, 4-methylcatechol, 4-methylphenol (*p*-cresol), and toluene, were purchased from Sigma-Aldrich. GUA, CAT, and PHE are used as abbreviations for guaiacol, catechol, and phenol, respectively, while 4-Me-CAT and 4-Me-PHE are used as abbreviations for 4-methylcatechol and 4-methylphenol, respectively. The Pt -based catalysts were prepared by

an incipient wetness impregnation procedure as described in our prior works.^{41–43}

The BET N_2 adsorption and desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020 apparatus. For Pt -loaded catalysts supported on various mesoporous materials, $\text{H}_2\text{-O}_2$ titration was carried out at room temperature to determine Pt metal dispersion. The TEM scans were obtained at 200 kV with a LaB_6 source (FEI-Tecnai). Elemental analysis of catalysts was carried out by the ICP-AES method (SPECTRO Instrument). For temperature-programmed surface reaction (TPSR) experiments, the catalyst was reduced using 5 vol % H_2 at 400 °C for 2 h before the measurement. Upon cooling to room temperature, a 1% reactant in 10% H_2 gas mixture was fed at 20 std mL/min, and the temperature was increased from room temperature to 550 °C at a heating rate of 5 °C/min. A TCD was used to detect products. In the temperature-programmed oxidation (TPO) procedure, 5% O_2 in a N_2 gas mixture was used as the oxidizing gas. The used catalysts were packed in a reactor for TPO measurements without any pretreatment, while the heating rate was 5 °C/min as well.

To investigate acidic properties of the bifunctional catalysts, we first determined the total number of acid sites (Lewis and Brønsted) by both TPD-pyridine (temperature-programmed desorption of pyridine) and TPD- NH_3 (temperature-programmed desorption of ammonia). The individual numbers of Lewis and Brønsted acid sites by DRIFT spectroscopy of adsorbed pyridine were determined using a Tensor-27 instrument with a Pike diffuse reflectance accessory. In a typical TPD-pyridine measurement, 25 mg catalysts were pretreated at 300 °C for 4 h in air. Then, the catalyst was exposed to pyridine, which is desorbed from the catalyst by heating the sample room temperature to 600 °C at 10 °C/min. NH_3 -TPD experiments were performed using a Micromeritics Autochem II 2920 Chemisorption analyzer equipped with an Agilent 5975C mass selective detector (MSD) to identify the gaseous species evolved from the catalyst samples. The samples were placed between two quartz wool plugs inside a U-shaped quartz cell held within a clamshell furnace. UHP helium was flowed at 50 std mL/min at ambient temperature for 1 h, followed by heating to 600 °C. Results showed that the total numbers of acidic sites calculated by TPD-pyridine and TPD- NH_3 were essentially the same. To differentiate the numbers of Lewis and Brønsted acids, DRIFT spectroscopy of adsorbed pyridine was conducted. Prior to measurements, samples were heated to 450 °C for 2 h in a flow of He gas, followed by cooling down to room temperature. Then the samples were wetted with pyridine followed by evacuation of physisorbed pyridine at 120 °C. The FTIR spectra were measured at three different temperatures (120, 250, and 400 °C), each yielding essentially the same acid site numbers. Since the guaiacol HDO reaction was typically tested at 300 °C, measurements of acid site numbers were made at the working temperature. The results clearly indicate the presence of both the Lewis acid sites (1455 cm^{-1}) and Brønsted acid sites (1550 cm^{-1}). The spectra with pyridine desorption were subtracted from those measured prior to pyridine adsorption to determine the numbers of Lewis and Brønsted acidic sites.

The catalytic performance tests were conducted in a fixed-bed reactor, as described in our prior work.^{42,44} Prior to the test, activation of the packed catalyst was performed at 450 °C for 4 h with a flowing H_2/N_2 mixture ($\text{H}_2/\text{N}_2 = 1:2$, 100 std mL/min). The reactor was then purged with flowing nitrogen at 50 std mL/min for 15 min. The following standard operating conditions were used for catalyst testing: 50 mg catalyst, 50 std mL/min hydrogen, 50 std mL/min nitrogen, 0.025 mL/min guaiacol (liquid, room temperature) at 300 °C. All experiments have carbon mass balances, including both liquid and gas phases, of 93 ± 3%, similar to those reported in the literature.^{45–47} Unless stated otherwise, all data were taken at 10 min time on stream (TOS). As in our prior work, a GC (Agilent GC6890) instrument with a flame ionization detector (FID) equipped with a DB-1701 column (30 m × 0.25 mm) was used for quantitative analysis of the liquid products. The gaseous effluent was analyzed using a Micro GC (Agilent 3000A Micro GC) instrument equipped with two columns (Column A, MolSieve 5 Å, 10 m × 0.32 mm; Column B: Plot U, 8 m

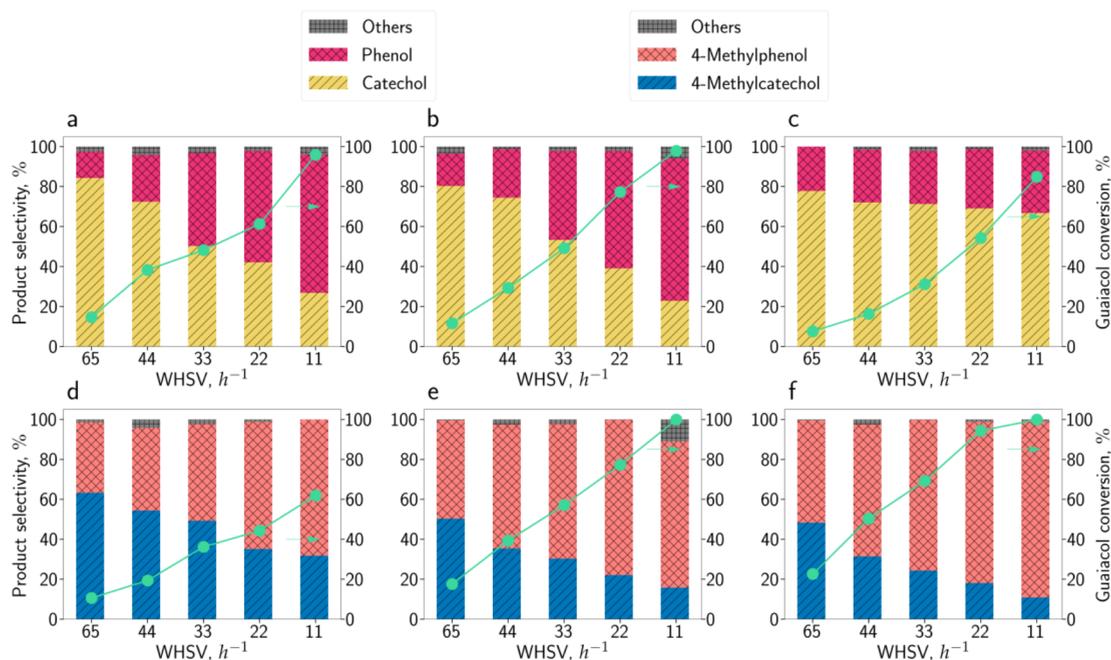


Figure 1. Initial performance of guaiacol hydrodeoxygenation at 300 °C and atmosphere pressure (0.1 MPa), H_2 /guaiacol molar ratio = 10 over (a) 1% Pt/SBA-15 (carbon-based), (b) 1% Pt/Si-KIT-6, (c) 1% Pt/Si-ZSM-5, (d) 1% Pt/Zr-KIT-6, (e) 1% Pt/Nb-KIT-6, and (f) 1% Pt/W-KIT-6 catalysts with 50 std mL/min hydrogen and 50 std mL/min nitrogen. The green dots refer to guaiacol conversion as indicated on the right y-axis.

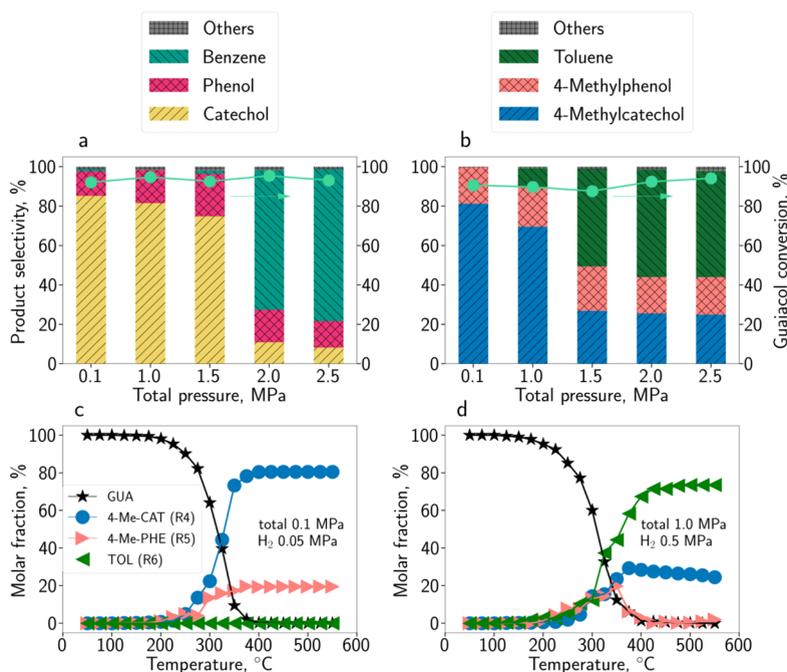


Figure 2. Effects of total pressure ($H_2/N_2 = 1:1$) and temperature on guaiacol conversion and product distribution with 50 mg of catalyst, 50 std mL/min hydrogen, 50 std mL/min nitrogen, $WHSV = 33.3 h^{-1}$, 0.025 mL/min guaiacol (liquid, room temperature) for (a) 1% Pt/AC (activated carbon) catalyst at 300 °C, (b) 1% Pt/Nb-KIT-6 catalyst at 300 °C. The green dots refer to guaiacol conversion as indicated on the right y axis. (c) Temperature-programmed surface reaction (TPSR) profiles under 0.1 MPa pressure ($H_2/N_2 = 1:1$), and (d) TPSR under total 1.0 MPa pressure ($H_2/N_2 = 1:1$).

× 0.32 mm) and two thermal conductivity detectors (TCD). For the reaction experiments, good repeatability, generally within less than 2% deviation, was achieved for all quantitative analyses. The spent catalyst (Pt/Nb-KIT-6) from the extended run was extracted using dichloromethane, and the resulting extract was analyzed using a GC-MS (LECO Pegasus 4D GCxGC-TOF) instrument equipped with a DB-WAX column (30 m × 0.32 mm). The GC-MS spectra were used to

qualitatively assess the nature of the carbon species over the spent catalysts.

RESULTS AND DISCUSSION

Various mesoporous catalysts, including 1 wt % Pt loaded over carbon-SBA-15 (abbreviated as Pt/C-SBA-15), Si-KIT-6, Nb-

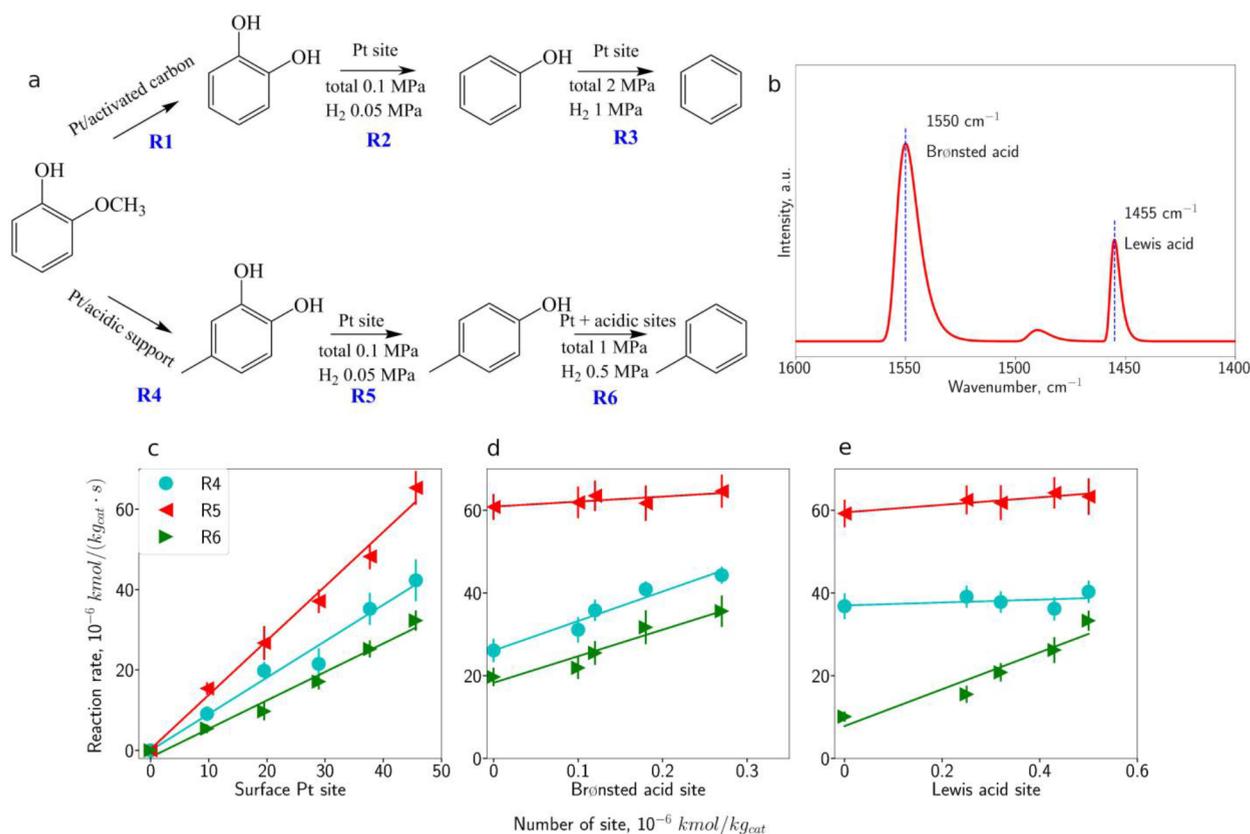


Figure 3. Reaction pathway of guaiacol hydrodeoxygenation for (a) reaction network over nonacidic and acidic catalysts; the pressure refers to the total pressure ($H_2/N_2 = 1:1$); (b) pyridine-IR results from 1% Pt/Nb-KIT-6 catalyst, (c) reaction rates of R4–R6 vs the number of Pt sites (C06, and C11–C15 in Table S3), (d) reaction rates of R4–R6 vs the number of Brønsted acid sites (C15, and C21–C24 in Table S3), and (e) reaction rates of R4–R6 vs the number of Lewis acid sites (C16–C20 in Table S3). Total pressure ($H_2/N_2 = 1:1$) = 0.5 MPa, temperature = 300 °C, 50 mg catalyst, 50 std mL/min hydrogen, 50 std mL/min nitrogen, WHSV = 33.3 h⁻¹, 0.025 mL/min guaiacol (liquid, room temperature).

KIT-6 (Si/Nb = 20),³⁵ W-KIT-6 (Si/W = 20),³⁶ and Zr-KIT-6 (Si/Zr = 20),³⁷ were tested under the standard operating conditions (300 °C, atmosphere pressure, H_2 /guaiacol molar ratio = 10) as described in the Experimental section. As a comparison, 1 wt % Pt over microporous Si-ZSM-5 (no Al in the MFI framework) was also tested. Under standard operating conditions, the catalytic performances [based on data taken at a time on stream (TOS) = 10 min] of these catalysts are compared in Figure 1. Pt/C-SBA-15 and Pt/Si-KIT-6 catalysts essentially exhibited the same distribution of product species, including catechol as a undeoxygenated species and phenol as a partially deoxygenated species. Note that fully deoxygenated species (such as benzene or toluene) were not observed on these nonacidic catalysts. As expected, the guaiacol conversion as well as partial deoxygenation performance (i.e., phenol selectivity) improved at decreased WHSV for both 1% Pt/C-SBA-15 (Figure 1a) and 1% Pt/Si-KIT-6 (Figure 1b). For Pt/Si-ZSM-5 (Figure 1c), although guaiacol conversion values increased up to 90%, the selectivity to phenol (~20–30%) and catechol (~70–80%) changed less compared to the other catalysts. The observations from Figure 1a,b are consistent with our prior work over Pt/AC (activated carbon) catalysts.^{42,44,48} The C-SBA-15, Si-KIT-6, and AC are all mesoporous materials, while Si-ZSM-5 is microporous. This suggests that mesoporous supports perform better, likely owing to the easier accessibility of substrates as compared to microporous materials. Interestingly, as seen in Figure 1d–f, 4-methylcatechol (4-Me-CAT) and 4-methylphenol (4-Me-

PHE) were observed as major products over Pt-loaded acidic mesoporous supports (1% Pt/Zr-KIT-6, 1% Pt/Nb-KIT-6, and 1% Pt/W-KIT-6). On these three catalysts (Figures 1d–f), the selectivity toward deoxygenated species was generally favored at lower space velocities. The lower guaiacol conversion over the 1% Pt/Zr-KIT-6 catalyst (Figure 1d) is attributed to a lack of Brønsted acid sites, as discussed later. Both 4-Me-CAT and 4-Me-PHE are derived from the transalkylation of guaiacol, which is likely promoted by acidic sites on these bifunctional catalysts.²⁷ In fact, transalkylation of guaiacol increased the yield of aromatics, which is desirable for enhancing fuel quality. As compared with nonacidic supports, the Pt-loaded acidic mesoporous materials generate different species.

Although Pt-based acidic mesoporous catalysts exhibit promising HDO performance of guaiacol (Figure 1), the products are still partially deoxygenated. As reported in the literature, full HDO of guaiacol requires relatively high H_2 partial pressure (several MPa). In our experiments, at 0.1 MPa total pressure (0.05 MPa H_2 pressure), only 4-methylcatechol (4-Me-CAT) and 4-methylphenol (4-Me-PHE) were generated (Figure 2). However, when the total pressure was increased to 1 MPa (0.5 MPa H_2), a small amount of toluene (selectivity ~10%) was observed. At higher total pressures of 1.5–2.5 MPa (0.75–1.25 MPa H_2), the major product is toluene (selectivity ~55%) followed by the undeoxygenated species (4-Me-CAT) with a selectivity ~25% and the partially deoxygenated species (4-Me-PHE) with a selectivity ~20%. In the entire total pressure range (0.1–2.5 MPa), the guaiacol

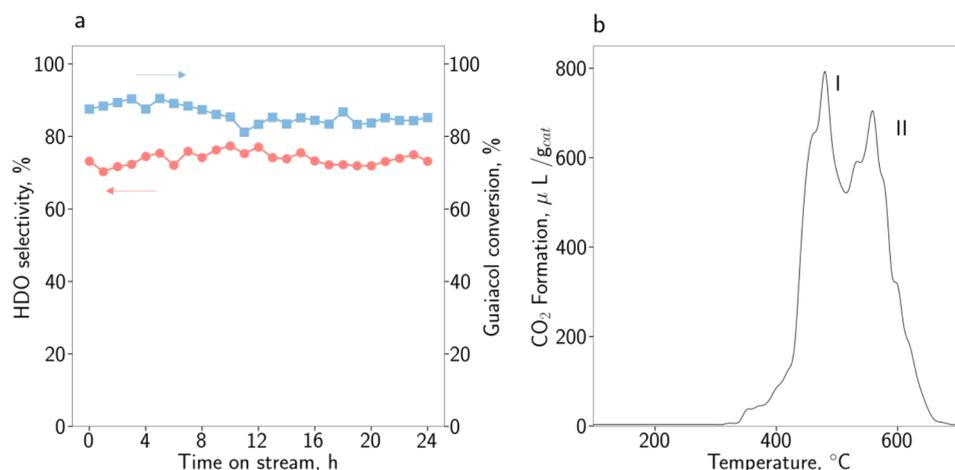


Figure 4. Catalyst stability of 1% Pt/Nb-KIT-6 for guaiacol hydrodeoxygenation (HDO) with 50 mg of catalyst, 50 std mL/min hydrogen, 50 std mL/min nitrogen, WHSV = 33.3 h⁻¹, 0.025 mL/min guaiacol (liquid, room temperature), total pressure 0.5 MPa (H₂/N₂ = 1:1) for (a) TOS vs HDO selectivity and guaiacol conversion, and (b) temperature-programmed oxidation (TPO) profile of 1% Pt/Nb-KIT-6 after a 24-h test under standard operating conditions as follows, 50 mg of catalyst, 50 std mL/min hydrogen, 50 std mL/min nitrogen, 0.025 mL/min guaiacol (liquid, room temperature) at 400 °C.

conversion was essentially constant. These observations indicate that the H₂ partial pressure plays an important role in guaiacol HDO, specifically by converting 4-methylcatechol to 4-methylphenol, followed by converting 4-methylphenol to toluene. In contrast, only a trace amount of fully deoxygenated species (benzene) was produced when the reaction was operated with total pressures 0.1–1.5 MPa (0.05–0.75 MPa H₂) over the nonacidic AC support (Figure 2b). At higher total pressures 2.0–2.5 MPa (1.0–1.25 MPa H₂), however, benzene was the dominant product with a selectivity between 70 and 80%.

To further investigate the effects of operating temperature and pressure on guaiacol HDO performance, temperature-programmed surface reactions (TPSRs) at 0.1 and 1.0 MPa total pressure (0.05 and 0.5 H₂ pressure) were carried out in the temperature range of 50–550 °C. At both operating pressures, guaiacol was activated at about 250 °C, reaching full conversion at about 400 °C (Figure 2c,d). When the total pressure was 0.1 MPa, only 4-methylphenol and 4-methylcatechol, with selectivity values of 20% and 80% respectively, were generated over the entire temperature range. Only traces of toluene (<0.1%) were observed as a byproduct. This implies that temperature does not influence the hydrodeoxygenation activity at lower pressure. When the total pressure was increased to 1.0 MPa (0.5 MPa H₂ pressure), a significant amount of toluene was produced even at a relatively low temperature (300 °C). Remarkably, the selectivity to 4-Me-PHE dropped beyond 350 °C, indicating that at relatively high temperatures, 4-Me-PHE was converted to toluene. On the basis of these experimental observations, a reaction pathway is proposed in Figure 3a, in which steps R1–R3 demonstrate guaiacol HDO over monometallic Pt catalyst on nonacidic supports, while steps R4–R6 refer to guaiacol HDO over bifunctional catalysts with acidic supports. As shown in Figure 4a, no significant catalyst deactivation, in terms of both guaiacol conversion and selectivity to deoxygenated species, was observed during the 24-h run. Furthermore, temperature-programmed oxidation (TPO) studies reveal that only a small amount of coke (~52 mg/g_{cat}) formed during the 24 h run (Figure 4b), indicating the excellent coke-resistant property of

the 1% Pt/Nb-KIT-6 catalyst. Note that for a non-coke-resistant catalyst, the amount of coke reaches ~500 mg/g cat within several hours.⁴⁹ The spent Pt/Nb-KIT-6 catalyst was extracted using dichloromethane, and the resulting solution was analyzed using GC–MS analysis. Dichloromethane is not considered to be an environmentally benign solvent but had to be used in relatively small amounts here just for the purpose of effectively extracting the heavy hydrocarbons from the catalyst for characterization purposes. The GC–MS spectra revealed the presence of C₆–C₁₁ species (Figure S2), lighter than the C₂₀–C₄₀ species as reported in the literature on Pt/MXene catalysts.⁵⁰ This confirms the coke-resistant nature of the mesoporous catalyst. In addition, ICP–AES measurements, performed on the Pt/Nb-KIT-6 catalyst before and after a 24-h test run, reveal no detectable loss of elements. This is consistent with the nearly steady activity observed during a 24-h test run (Figure 4). In addition to these desirable performance attributes, the catalyst is made up of abundantly available and benign SiO₂ as the major component. Given that the usage amounts of the metals (typically tens of kg) are considerably small and that most of the metals are recycled, the environmental impacts associated with the mining of the metals are also commensurately very small compared to those associated with the extraction of other raw materials (thousands of tons) used for making fuels and chemicals with these catalysts.

The active sites on the bifunctional catalysts were systematically probed for each of the reaction steps (R4–R6) shown in Figure 3. The pyridine-IR result in Figure 3b shows both Lewis acid sites (1455 cm⁻¹) and Brønsted acid sites (1550 cm⁻¹). Here, three possible active sites were considered as follows: surface Pt sites measured by H₂–O₂ titration and Brønsted acid and Lewis acid sites measured by pyridine-IR at 1550 and 1455 cm⁻¹, respectively. As shown in Table S2, the calcination temperature affects the acidity of supports. Using W-KIT-6 support with constant acidity, various amounts (0–1%) of Pt were loaded (C06, C11–C15 in Table S3) at essentially constant metal dispersion (89–95%) and a nearly identical Pt particle size (1 nm). The constant acidity values indicate that the Pt loading does not alter the acidic sites.¹⁹

TEM micrographs (Figure 5) confirm that the particle size of Pt is relatively uniform at various metal loadings (0.2–1 wt %).

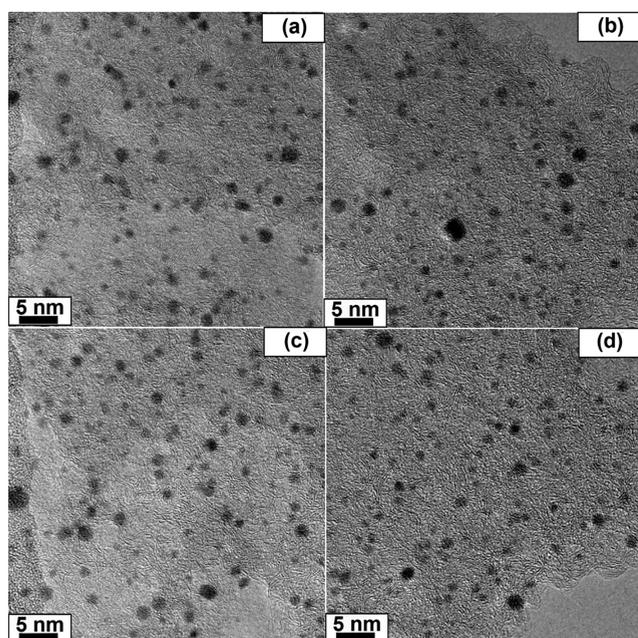


Figure 5. TEM scans of catalysts for (a) 0.2% Pt/W-KIT-6, (b) 0.4% Pt/W-KIT-6, (c) 0.8% Pt/W-KIT-6, and (d) 1.0% Pt/W-KIT-6.

The various catalysts exhibit similar surface areas (700–800 m²/g), pore sizes (8.5–10 nm), and pore volumes (0.7–1.0 cm³/g) at the targeted Pt loading (Table S4). Further, both the number of Brønsted acids (0.26–0.27 × 10⁻⁶ kmol/kg cat) and Lewis acids (0.05–0.06 × 10⁻⁶ kmol/kg cat) sites are nearly identical on these catalysts (Table S3). Thus, only one parameter, the number of surface Pt sites, was varied. Similarly, only the number of Lewis acid sites is varied in Pt/Zr-KIT-6 (C16–C19 in Table S3) and Pt/Si-KIT-6 (C20 in Table S3), and the number of Brønsted acid sites is varied in the Pt/W-KIT-6, Pt/Nb-KIT-6 and Pt/Zr-KIT-6 samples (C15, C21–C24 in Table S3). To individually investigate the reaction steps R4–R6 (Figure 3 and Figure S1), the intrinsic rate of each step on the various bifunctional catalysts was measured under differential operating conditions (reactant conversion <10%) by separately cofeeding guaiacol (R4), 4-methylcatechol (R5), or 4-methylphenol (R6) with hydrogen. As shown in Figure 3b, the reaction rates of steps R4–R6 correlate linearly with the number of surface Pt sites. Remarkably, all these three reaction rates are negligible without surface Pt, even though acidic sites (both Brønsted and Lewis) are present. Furthermore, the rate of step R5 (red triangles) is essentially independent of the number of either Brønsted or Lewis acid sites (Figure 3c,d). These observations indicate that the active site for step R5, a hydrodeoxygenation reaction, is solely the surface Pt site, but not any acidic sites. For step R4, while the reaction rate correlates well with the number of Brønsted acid sites, it was relatively independent of the Lewis acid sites. Note from Figure 3c that when the number of Brønsted acid sites was close to zero, significant reaction rates were still observed. This implies that in addition to Brønsted acid sites, the Pt sites also promote step R4. Interestingly, all three curves for step R6 (green triangles) correlate linearly with Pt, Brønsted, and Lewis acid sites. In addition, as seen from Figure 3c,d, both

Brønsted and Lewis acid sites accelerate the rate when the required number of Pt sites is present.

CONCLUDING REMARKS

Various Pt-based bifunctional catalysts supported over mesoporous metal-exchanged silicates (Zr-KIT-6, W-KIT-6, and Nb-KIT-6) with varying Pt, Lewis, and Brønsted acid sites were prepared, characterized, and tested for HDO of guaiacol, a widely used model compound of bio-oil. It was found that the acidic supports promote transalkylation reactions, which enhance aromatic hydrocarbon yields. Full HDO with a yield of aromatic hydrocarbons at ~70% was observed on these catalysts at total pressures ranging from 1.0 to 2 MPa (0.5–1 MPa H₂). A HDO reaction pathway consisting of several reaction steps along with correlations between the rates of the individual reaction steps and either the metal and/or acid function is delineated. It is demonstrated that 1 wt % Pt/Nb-KIT-6 provides an enhanced and stable guaiacol HDO performance with ~90% guaiacol conversion and 75% selectivity to deoxygenated species during the entirety of a 24-h test. The present contribution provides a new class of promising catalysts and insights into active site requirements for various reactions involved in bio-oil upgrading.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c07071>.

Figure S1: Proposed individual reactions of guaiacol hydrodeoxygenation over bifunctional catalysts; Figure S2: Coke precursor compounds detected by GC-MS; Table S1: Literature summary of guaiacol full HDO; Table S2: Properties of various unsupported catalyst samples; Table S3: Properties of various supported catalyst samples; Table S4: ICP-AES elemental analysis and BET surface area of various catalyst samples; and additional references (PDF)

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Notes

The authors declare no competing financial interest.

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ACKNOWLEDGMENTS

This work was supported by the R. Games Slayter fund and the Varma Reaction Engineering fund (both from Purdue University) and the Dan F. Servey Professorship funds (from the University of Kansas). Y.X. appreciates the financial support from the Davidson School of Chemical Engineering at Purdue University. It is a pleasure to be invited to contribute to this Festschrift honoring Professor James Dumesic, whose impactful contributions to the fields of catalysis and biomass processing we greatly admire.

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