Anatase TiO₂ Activated by Gold Nanoparticles for Selective Hydrodeoxygenation of Guaiacol to Phenolics

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Supporting Information

ABSTRACT: Gold nanoparticles on a number of supporting materials, including anatase TiO₂ (TiO₂-A, in 40 nm and 45 μm), rutile TiO₂ (TiO₂-R), ZrO₂, Al₂O₃, SiO₂, and activated carbon, were evaluated for hydrodeoxygenation of guaiacol in 6.5 MPa initial H₂ pressure at 300 °C. The presence of gold nanoparticles on the supports did not show distinguishable performance compared to that of the supports alone in the conversion level and in the product distribution, except for that on a TiO₂-A-40 nm. The lack of marked catalytic activity on supports other than TiO₂-A-40 nm suggests that Au nanoparticles are not catalytically active on these supports. Most strikingly, the gold nanoparticles on the least-active TiO₂-A-40 nm support stood out as the best catalyst exhibiting high activity with excellent stability and remarkable selectivity to phenolics from guaiacol hydrodeoxygenation. The conversion of guaiacol (∼43.1%) over gold on the TiO₂-A-40 nm was about 33 times that (1.3%) over the TiO₂-A-40 nm alone. The selectivity of phenolics was 87.1%. The products are mainly phenolic compounds with no aromatics and saturated hydrocarbons such as cyclohexane. The gold particle size ranging from 2.7 to 41 nm and water content were found to significantly affect the Au/TiO₂-A-40 nm catalyst activity but not the product selectivity. The reaction rates of 0.26 and 0.91 (min⁻¹ g-cat⁻¹ cm³) were determined for guaiacol hydrogenation and catechol hydrogenation, respectively. Bimolecular methylation was established as the dominant mechanism for methyl group transfer among the phenolics. Two major pathways of guaiacol hydrogenation to phenolics over the 0.4Au-19 nm/TiO₂-A-40 nm are proposed: (1) direct hydrogenation of guaiacol to form phenol and methanol, (2) hydrodehydroxylation of catechol intermediate from the transmethylation between guaiacol and phenol.

KEYWORDS: guaiacol hydrogenation, phenol, gold catalyst, anatase, lignin

1. INTRODUCTION

Lignocellulosic biomass materials are abundant renewable feedstocks for the production of biofuels and biochemicals.¹,² Fast pyrolysis has been used to directly convert the biomass to oxygen-rich bio-oils.³,⁴ The liquid products contain a variety of lignin-derived phenolic compounds such as substituted phenols, guaiacols, and syringols. Because of the high oxygen content, the pyrolysis oils are typically unstable.⁵ Hydrodeoxygenation (HDO) catalysts and processes have been extensively studied to upgrade these compounds to stable compounds, such as hydrocarbons and aromatics.⁶,⁷ As an abundant component of lignin structure, guaiacol as a model compound has been widely studied in evaluating the effectiveness of hydrodeoxygenation catalysts.⁸,⁹

Supported metal HDO catalysts in the literature typically showed the following performance characteristics: (1) catalyst
deactivation either due to coking on the support or due to deactivation of the metal catalysts; (2) formation of saturated HDO products; and (3) formation of mixed aromatics and phenolic products, sometimes with saturated hydrocarbons.

Conventional Al2O3-supported hydrodesulphurization (HDS)/hydrodenitrogenation (HDN) catalysts exhibited promising activity in HDO of phenolic compounds such as phenols, anisole, and guaiacol. The products are mainly phenolics and aromatics. While Al2O3 has often been used as a support for metal catalysts and showed high activity, coke deposition due to high Lewis acidity of alumina support has been recognized to cause rapid catalyst deactivation.10,13

A CoMoS/ZrO2 catalyst in HDO of guaiacol showed over 60% selectivity to phenol at guaiacol conversion of 100%.14 Such catalysts suffer from deactivation due to loss of sulfur from the high water content in a typical biocrude. Continuous addition of sulfur is required in the process, but it caused serious problems for the downstream processes.15,16 Complete conversion of guaiacol in vapor phase was obtained on 10 wt % Co/Al-MCM-41 at 400 °C.17 With 30% C6 (CH4, CO, and CO2) as the major products, 19% benzene, 10% toluene, 15% phenol, and 7% cresol. Co and Mo catalysts on “neutral” support such as activated carbon10 showed improved selectivity to phenol but at lower activity than the alumina-support catalyst.

Zhao et al. reported the selectivity of ∼99% to catechol in the HDO of guaiacol over Co2P/SiO2.18 With a Fe/SiO2 catalyst, benzene and toluene were the major products (38% combined yield) under the best reaction conditions (400 °C).5 For bio-oil upgrading with precious metal catalysts,12,19,20 saturated hydrocarbons are typically the main products with the excess comsumption of H2. For example, guaiacol was converted in 100% at 180 °C over a 1%Pt/H-MFI catalyst, with 93% selectivity to cyclohexane. The hydrogenation of the aromatic ring occurred as the first step at mild temperature over the Pt-based catalysts. Dehydrogenation to aromatics took place in the presence of acidic sites mainly at higher temperatures. Alloying a noble-metal Pd with an early transition-metal Fe was shown to effectively alter the selectivity of Pd with retention of the high Pd hydrogenation activity. Over a FePd/C catalyst at 350 °C, the selectivities to benzene and phenol were 20% and 55%, respectively, at 100% guaiacol conversion. On this catalyst, the selectivity to phenol decreases and that to benzene increases at higher temperatures.

A recent study of guaiacol hydrogenation21 showed guaiacol conversions of 7% over TiO2 and 100% over a Ru/TiO2 at 400 °C. The products over the Ru/TiO2 catalyst were mainly aromatics (29%) and methylated phenols (67%). The enhanced activity of Ru/TiO2 was attributed to the reduction of the oxide support.

Supported gold catalysts in hydrogenation reactions have attracted increasing attention22−24 due to their unique selectivity. Studies of gold hydrogenation catalysts are exemplified by hydrodechlorination and hydrogenation of aromatic compounds;15,26 the aromatic structures were retained in the products. While gold alloyed with Ru showed large enhancement to the catalytic activity in the liquid-phase hydroenolysis of glycerol and levulinic acid, gold alone is a poor hydrogenation catalyst.27

In this work, our objective was to purely produce phenolics from guaiacol as a model compound. We studied the performance of supported gold catalysts for guaiacol hydrogenation. The results of this work identified a strikingly active Au/TiO2-A-40 nm catalyst with high selectivity to phenolics. In comparison, neither the Au nanoparticle nor the TiO2-A-40 nm support was active for the hydrogenation of guaiacol. Only the TiO2-A-40 nm exhibited such a pronounced effect after Au activation, in contrast to other supports such as TiO2 (rutile), activated carbon, silica, gamma alumina, and zirconia, which showed little catalytic effect by the supported Au nanoparticles. The pathways of guaiacol hydrogenation over Au/TiO2-A-40 nm were also studied.

2. EXPERIMENTAL SECTION

2.1. Materials. Gold(III) chloride trihydrate (HAuCl4·3H2O, 99%) and activated carbon (AC, 38−150 μm) were purchased from Aldrich. Potassium carbonate (>99.5%), trisodium citrate dihydrate, nitric acid (16 M), toluene, ethyl acetate, catechol, phenol, anisole, and methanol were obtained from Sinopharm Chemical Reagent Co., Ltd. TiO2 (anatase 40 nm, named as TiO2-A-40 nm), TiO2 (anatase 4.5 × 104 nm, named as TiO2-A-45 μm), TiO2 (rutile 40 nm, named as TiO2-R), ZrO2 (50 nm), γ-Al2O3 (20 nm), SiO2 (fumed silica 200 nm), guaiacol, tannic acid (>99.5%), cresol, xylenols, and trimethylphenols were obtained from Aladdin Industrial Inc. CH4 as calibration gas was obtained from DL-Gas Co., Ltd.

2.2. Synthesis of Gold Nanoparticles (Au NPs). Gold nanoparticles were synthesized using the Slot-Geuze method.28 For the preparation of Au NPs A, a 0.32 mM chloroauric acid (HAuCl4) solution (80 mL, solution I) was prepared. Solution II was prepared by mixing 4 mL of 1 wt % trisodium citrate dihydrate, 5 mL of 1 wt % tannic acid, 5 mL of 25 mM potassium carbonate (<0.070 g K2CO3 in 20 mL H2O), and 6 mL of H2O. Both solutions I and II were heated to 60 °C. At this temperature, the solution II was added to solution I under vigorous agitation. The resulting solution was left to boil for 2 min. The resulting sol was cooled to room temperature, and water was added so that the final sol volume reached 100 mL. Au NPs B and C were similarly prepared but no potassium carbonate was used, and the concentration of tannic acid in the solution II was changed. For Au NPs B, the solution II was prepared by using 0.5 mL of 1 wt % tannic acid solution, 4 mL of 1 wt % trisodium citrate dihydrate solution, and 15.5 mL of water. Au NPs C was made by using a solution II containing 0.1 mL of a 1 wt % tannic acid solution, 4 mL of a 1 wt % trisodium citrate dihydrate solution, and 15.9 mL of water.

2.3. Immobilization of Au Particles. A typical procedure was used in loading the Au NPs as prepared in 2.2 onto supports: 1 g of support, Au NPs sol (described in 2.2) in an appropriate amount to give a specific Au loading, and twice the volume of ultrapure water over that of the sol were mixed in an Erlenmeyer flask. The pH of the mixed solution was adjusted to specified values (pH = 2 for TiO2, Al2O3, and ZrO2, pH = 0.5 for SiO2, pH = 1.5 for active carbon) with an aqueous solution of HNO3 (1.0 M) under vigorous stirring. The suspension was stirred (1 h) under the specified pH before the separation of solid by filtration. Extensive washing of the solid with deionized water was then followed until it was free of chloride ions. The obtained residues were dried at 110 °C for 12 h. The powder materials were calcined at 350 °C for 2 h. The dried catalyst samples were then sealed and stored at room temperature (RT) in a desiccator.

2.4. Characterization. The BET surface area was measured by N2 adsorption on a Micromeritics ASAP 2020HD88
Table 1. Composition of Prepared Catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>Type of Au NPs</th>
<th>Support</th>
<th>BET (m²/g)</th>
<th>Loading of Au (wt %)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂-A-40 nm</td>
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<td>TiO₂-A-40 nm</td>
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<td>0.416</td>
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<td>TiO₂-A-40 nm</td>
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<td>0.427</td>
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<tr>
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<td>A</td>
<td>TiO₂-A-40 nm</td>
<td>88</td>
<td>0.427</td>
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<td>TiO₂-A-40 nm</td>
<td>88</td>
<td>0.427</td>
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<td>C</td>
<td>TiO₂-A-40 nm</td>
<td>88</td>
<td>0.427</td>
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<td>TiO₂-A-45 μm</td>
<td>26</td>
<td>0.077</td>
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<tr>
<td>0.1Au/TiO₂-A-45 μm</td>
<td>A</td>
<td>TiO₂-A-45 μm</td>
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<td>0.077</td>
</tr>
<tr>
<td>TiO₂-R</td>
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<td>TiO₂-R</td>
<td>13</td>
<td>0.367</td>
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<tr>
<td>0.4Au/TiO₂-R</td>
<td></td>
<td>TiO₂-R</td>
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<td>0.367</td>
</tr>
<tr>
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<td>SiO₂</td>
<td>198^a</td>
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<td>0.4Au/SiO₂</td>
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<td>AC</td>
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<td>AC</td>
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<td>0.389</td>
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<tr>
<td>0.4Au/AC</td>
<td></td>
<td>AC</td>
<td>554</td>
<td></td>
</tr>
</tbody>
</table>

^aThe loadings of gold on samples were determined by inductively coupled plasma (ICP). ^bThe details of the catalyst preparation are given in the Supporting Information. ^cThe data was provided by supplier.

instrument. Each sample was degassed for 2 h at 300 °C before measurement (Table 1).

Elemental analysis of samples was determined by PerkinElmer Optima 8000 inductively coupled plasma-optical emission spectrometer (ICP-OES). Gold loading and information about the support of the catalysts are shown in Table 1.

X-ray diffraction (XRD) measurements were conducted using PIXcel1D detector and PreFIX interface with an empyrean tube Cu LFF operated at 40 kV. The scanning range is in 10°−80° with a step of 0.013° (Figure S-1 in Supporting information).

Au particles were determined with TEM (JEM-2100). Samples were pretreated by first calcining the catalysts at 350 °C in flowing air for 2 h, cooling the samples to room temperature, and then preparing a suspension of the catalysts in ethanol. A few drops of the resulting suspension were then deposited on the TEM grid. The distributions of Au particles (about 20 particles) size were calculated by measuring all particles in the TEM image using a nano measure of 1.2.

The amount of guaiacol adsorbed on the catalyst was characterized by thermogravimetric analysis (TGA). In a typical operation, 1 g of guaiacol was introduced into 10 mL of ethyl acetate. Then the mixture was added to solid samples (supports or catalysts) with the ratio of 1 g of sample/1 mL of guaiacol/ethyl acetate solution. After it was sufficiently mixed, the suspension was treated with a flow of N₂ in 1L/min at room temperature to remove ethyl acetate until the mixture turned into dry powder (~4 h). TG experiments were performed on Netzsch STA 449 F3, employing air flame.

2.5. Catalyst Activity Measurements. A batch reactor containing 25 mL of toluene (as solvent, after initial verification in naphthalene as a suited solvent, details are discussed in section 3), 1.50 g of guaiacol, and 0.30 g of catalyst (for 0.4Au-19 nm/TiO₂-A-40 nm, Au/guaiacol ≈5.4 × 10⁻⁴ mol/mol). Decane was used as an internal standard reference. After being purged three times by pure N₂, the reactor was filled with high-purity H₂ to a pressure of 3.0 MPa. The reactor was then heated to 300 °C and kept at this temperature for several hours at 700 rpm. When the reaction was complete, the reactor was cooled to room temperature. Ethyl acetate (25 mL) was added into the solution to dissolve insoluble matters in toluene, such as catechol. The product was analyzed by gas chromatography (Agilent 7890A) equipped with a flame ionization detector (FID), and a DB-5 column (30m × 0.32 mm × 0.5 μm). The products were further identified by GC-MS (Agilent 7890A-5975C) calibrated by standard compounds. The gas phase was analyzed by an Agilent 7890A gas chromatography equipped with TCD.

The conversion of guaiacol was calculated on the basis of the molar ratio of consumed guaiacol (n_consumed_guaiacol) to the initial guaiacol in the feed (n_initial_guaiacol) (eq 1). The product yield was calculated based on the molar ratio of corresponding phenolic compounds in the product (n_phenolic_compound) to the initial guaiacol in the feed (n_initial_guaiacol) (eq 2). Methanol was also a major product, but because of its high volatility, its concentration is difficult to be accurately measured. In addition, the formation of methanol does not affect the quantification of products containing benzene rings, such as guaiacol in the feed, and phenolics and catechol in the products. We focus on the molar mass balance in aromatic products for the determination of the reaction pathways.

\[
\frac{\text{conversion}_\text{guaiacol}}{\text{yield}_\text{phenolic compound}} = \frac{n}_{\text{consumed guaiacol}} \times 100% \\
\frac{n}_{\text{phenolic compound}} \times 100% \\
\]

Catalyst reuse procedure for guaiacol hydrogenation was as follows: after the first/second run, the organic phase was extracted by ethyl acetate and analyzed by GC. The catalyst was separated from the solution by centrifugation. Then the catalyst was washed by acetone for three times and dried at 105 °C for 12 h.

The activity of a catalyst for the reaction, as characterized by the disappearance of the reactants, is expressed as pseudo-first-order reactions with the rate constant k. These are determined according to the equation by Gevert et al. 30

\[
-k = kWf(t/V)
\]
where \( f(t/V) \) is

\[
f(t/V) = \sum_{i=1}^{n} \frac{t_i - t_{i-1}}{V_{i-1}}
\]

where \( C_i \) and \( C_0 \) are the reactant concentrations of reactant \( i \) at time \( t \) and time zero, respectively; \( k \) is the rate constant expressed in \( \text{ml} \cdot \text{min}^{-1} \cdot \text{g-cat}^{-1} \); \( W \) is the catalyst weight (g); \( t \) is the time in minutes; \( n \) is the number of samples taken; and \( V \) is the solution volume (cm³). The rate constants reported in this work were determined using the concentration data that satisfied the linear relation. It has been verified that this expression of the catalytic activity gives identical results, but it is more reliable (with an improved fit) than activities determined on the basis of the initial reaction rates.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activities of Gold Particles Deposited on TiO₂, Al₂O₃, ZrO₂, SiO₂, and Active Carbon. In this work, the effect of different supporting materials on the supported gold catalysts for the hydrogenation of guaiacol was first studied. Presynthesized nanometer-sized gold colloidal particles were loaded on the supports in order to minimize possible differences due to gold particle size in the catalysis.

The BET surface areas of catalysts are given in Table 1. Activated carbon has the highest surface area (562 m²/g). The SiO₂, Al₂O₃, and TiO₂-A-40 nm supports have surface areas of 198, 140, and 89 m²/g, respectively. The BET surface areas of TiO₂-R (13 m²/g), TiO₂-A-45 μm (26 m²/g) and ZrO₂ (19 m²/g) are much lower. It should be noted that the BET surface areas of the supported gold catalysts did not substantially change from that of supports, except for SiO₂. After loading of Au and the treatment, some particles of SiO₂ (fumed silica) became visibly agglomerated with a certain degree of sintering, which caused the decrease of the BET surface area and better crystallinity (XRD from Figure S-1). To determine the oxidation state of gold over 0.4Au-19 nm/TiO₂-A-40 nm, X-ray photoelectron spectroscopy (XPS) characterization was conducted. For the 0.4Au-19 nm/TiO₂-A-40 nm, the binding energy of Au₄f₇/2 and Au₄f₅/2 were 82.6 and 86.4 eV, suggesting that Au species existed in their metallic state.31,32 The shift of Au 4f peaks of 0.4Au-19 nm/TiO₂-R (13 m²/g), TiO₂-A-45 μm (26 m²/g) and ZrO₂ (19 m²/g) are much lower. It should be noted that the BET surface areas of the supported gold catalysts did not substantially change from that of supports, except for SiO₂. After loading of Au and the treatment, some particles of SiO₂ (fumed silica) became visibly agglomerated with a certain degree of sintering, which caused the decrease of the BET surface area and better crystallinity (XRD from Figure S-1).

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The hydrogenation activity of the supports (activated carbon, SiO₂, ZrO₂, Al₂O₃, TiO₂-A-40 nm, and TiO₂-R, and that of Au nanoparticles on the corresponding supports) are compared for guaiacol hydrogenation reaction under the same reaction conditions (Figure 1). Hydrogenation of guaiacol over the Au containing catalysts (0.4Au-19 nm/TiO₂-A-40 nm, 0.4Au/TiO₂-R, 0.4Au/Al₂O₃, 0.4Au/ZrO₂, 0.4Au/SiO₂, 0.4Au/AC) was carried out initially with naphthene as solvent. It is important to point out that, in all experiments of this work, aromatic hydrocarbons such as benzene, toluene, cyclohexane, and cyclohexene were absent. Saturated oxygenated compounds, such as cyclohexanol and methoxy cyclohexanol, were also not detected. Even though methanol was the product in some reactions (to be discussed after Table 4), it could not be used to calculate the product yield due to inaccurate measurement of methanol concentrations associated with its high volatility. Therefore, the calculation of product yields was based on the quantitatively measured products containing aromatic rings. Because aromatic hydrocarbons were not detected in the product from the reaction using naphthene as solvent, we further verified that toluene alone was not hydrogenated over the 0.4Au-19 nm/TiO₂-A-40 nm catalyst. Therefore, toluene was used as a solvent for guaiacol hydrogenation in subsequent experimental evaluations for the 0.4Au-19 nm/TiO₂-A-40 nm catalyst. In addition, benzene and cyclohexane were not detected in the products of guaiacol hydrogenation over 0.4Au/Al₂O₃.

In experiments with Al₂O₃, 0.4Au/Al₂O₃, TiO₂-R and 0.4Au/TiO₂-R, xylene, xylenols, and dimethyldiphenylmethylenols were not detected. Methylguaiacol, methylcatechol, and dimethylcatechol were observed. "Others" represent undetected heavy products including cokes based on mass balance. The supports in general clearly played a decisive role in determining both the activity and the product distribution. The guaiacol conversions on 0.4Au/ZrO₂, 0.4Au/AC, and 0.4Au/SiO₂ are less than 8%.

The results in Figure 1 reveal two important messages: (1) except for the TiO₂-A-40 nm, gold nanoparticles do not play an apparent role in the catalysis, and (2) the coalition of the same gold nanoparticles with the least-active TiO₂-A-40 nm support produced a highly distinctive catalyst in both the catalytic activity and the product selectivity for guaiacol hydrogenation.

Guaiacol was hydrogenated dominantly to aromatics over Fe/SiO₂ and Ru/SiO₂.21 On 0.4Au/SiO₂, the conversion of guaiacol was less than 1% in this work. No product could be identified. The 0.4Au/AC does not exhibit meaningful activity in the conversion of guaiacol (<5%), even though the carbon support possesses high surface area. Therefore, the catalytic performance of other metals, such as Fe and Ru, on these supports reflects mainly the catalytic function of the metals. Lu et al.34 have studied the reaction mechanism of hydrodeoxygenation of guaiacol to aromatic products by density functional theory calculations and microkinetic modeling over a Ru(0001) model surface. Their model suggests the adsorption of aromatics on the Ru surface on which hydrodeoxygenation of guaiacol to major reaction product (phenol) can be carried out.
Bui et al.\textsuperscript{35} have studied guaiacol hydrogenation over zirconia and MoS\textsubscript{2}/ZrO\textsubscript{2}. Comparing with catechol as the main product over ZrO\textsubscript{2}, phenol and catechol were the main products over MoS\textsubscript{2}/ZrO\textsubscript{2}. In this work, catechol was the main product on ZrO\textsubscript{2} and 0.4Au/ZrO\textsubscript{2}. It can therefore be concluded that gold was not active alone in guaiacol hydrogenation.

Over γ-Al\textsubscript{2}O\textsubscript{3} and 0.4Au/Al\textsubscript{2}O\textsubscript{3}, catechol was the main product. There were some methylguaiacol and methylcatechol products. Higher selectivity to catechol than to phenol was reported over CoMoS on activated carbon and on Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{10} Nimmanwudipong et al.\textsuperscript{36} also reported high selectivity to catechol over Al\textsubscript{2}O\textsubscript{3}-supported metal catalysts. On the acidic support, demethylation of guaiacol, methyl-substitution of catechol, and methyl-substitution of catechol, forming the observed methylated products, were also found in this work.

Even though guaiacol conversion was very low on the TiO\textsubscript{2}-A-40 nm support alone, phenol was the main product. This observation is in sharp contrast to other supports and catalysts. This could be due to the adsorption of guaiacol from a prepared guaiacol solution.\textsuperscript{38} The selectivity of phenol over catechol was 56.1% (at 30 °C) while the selectivity of catechol over phenol was 11.4%. Catechol also appeared over the TiO\textsubscript{2}-A support indicating di-diethylenguaiacol as the major product was still catechol. Di-ethylenguaiacol conversion of 43.1%, the selectivity of phenol and other phenolic derivatives such as cresols, xylenols, and trimethylphenol reached 87.1%. Only a small amount of catechol (selectivity = 11.4%) was formed. Catechol also appeared over sulfided CoMo and NiMo catalysts supported on TiO\textsubscript{2} at the same temperature.\textsuperscript{34} Because neither the gold nanoparticle nor the TiO\textsubscript{2}-A-40 nm was active for the reaction, the active sites arising from coalescence of the two may be attributed to the metal-support interaction.\textsuperscript{35} As the support may contribute to the adsorption of guaiacol from a prepared guaiacol solution,\textsuperscript{38} the amount of adsorbed guaiacol was measured. Table 2 shows the results of guaiacol adsorption measurements over the supported Au catalysts. The boiling point of guaiacol is 205 °C; therefore, the sample of guaiacol was cooled to 205 °C.

The temperature of weight loss for pure guaiacol occurs at this temperature. After treating the samples with the guaiacol solution, weight loss in samples at higher temperatures is used to determine the amount of desorbed guaiacol. The 0.4Au-19 nm/TiO\textsubscript{2}-A-40 nm showed a slightly reduced guaiacol adsorption than that on the support alone (Table 2). Interestingly, 0.4Au/TiO\textsubscript{2}-R showed a rather high guaiacol adsorption on the basis of equal surface area, even though it showed poor activity in guaiacol hydrogenation. Other catalysts showed nearly the same amount of adsorbed guaiacol. Therefore, there is a poor relationship between activities in guaiacol hydrogenation and guaiacol adsorption among the catalysts.

Table 2. Absorption of Guaiacol on Samples As Measured by TGA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent of absorbed guaiacol on sample (wt %)</th>
<th>Adsorbed guaiacol (mol/m² cat. × 10⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}-A-40 nm</td>
<td>3.6</td>
<td>3.3</td>
</tr>
<tr>
<td>0.4Au/TiO\textsubscript{2}-A-40 nm</td>
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<td>3.0</td>
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<td>0.4Au/TiO\textsubscript{2}-R</td>
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<td>15.5</td>
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<td>1.7</td>
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<td>0.6</td>
<td>2.4</td>
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<tr>
<td>0.4Au/Al\textsubscript{2}O\textsubscript{3}</td>
<td>4.8</td>
<td>2.9</td>
</tr>
<tr>
<td>0.4Au/SiO\textsubscript{2}</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

"The adsorbed guaiacol on samples were counted with the weight loss above the boiling point of guaiacol from TGA. The molar of adsorbed guaiacol per square meter of the supports or catalysts.

The difference in the performances of Au/TiO\textsubscript{2} is evident when compared to Au/TiO\textsubscript{2}-A and Au/TiO\textsubscript{2}-R catalysts. The TiO\textsubscript{2}-A support has been observed to play an important role in the physical, chemical, and catalytic properties of supported Au particles.\textsuperscript{22} Strong metal-support interactions exist between Au particles and the SiO\textsubscript{2} surface.\textsuperscript{45} In the same study, Au/TiO\textsubscript{2} displayed a slightly improved performance in guaiacol hydrogenation compared to Au/TiO\textsubscript{2}-R. However, the TiO\textsubscript{2}-A catalyst showed a superior performance in the hydrogenation of guaiacol as compared to Au/TiO\textsubscript{2}-R (Figure 1). Even though the surface area of the TiO\textsubscript{2}-R was lower than that of the TiO\textsubscript{2}-A-40 nm, the performance of TiO\textsubscript{2}-R was lower than that of the TiO\textsubscript{2}-A-40 nm. The TiO\textsubscript{2}-R was predominantly catechol (selectivity ~76.9%). Small amounts of methylated products, such as methylguaiacol and methylcatechol, were also formed. Rutile TiO\textsubscript{2} contains Lewis acid sites,\textsuperscript{41} to which the formation of methylated products is attributed.\textsuperscript{14} The conversion of guaiacol and yield of phenol showed an insignificant change after loading Au. Compared with 0.4Au-19 nm/TiO\textsubscript{2}-A-40 nm, the conversion of guaiacol over 0.4Au/TiO\textsubscript{2}-R was lower, and the major product was still catechol. Different performances between 0.4Au-19 nm/TiO\textsubscript{2}-A-40 nm and 0.4Au/TiO\textsubscript{2}-R indicated different interactions between Au particles and the supports.

After loading gold particles on the TiO\textsubscript{2}-A-40 nm (0.4Au-19 nm/TiO\textsubscript{2}-A-40 nm) and TiO\textsubscript{2}-R (0.4Au/TiO\textsubscript{2}-R), the 0.4Au/TiO\textsubscript{2}-R showed only a small improvement over TiO\textsubscript{2}-R, but the 0.4Au-19 nm/TiO\textsubscript{2}-A-40 nm displayed a striking vaunt in performance in guaiacol hydrogenation. The performance of 0.4Au/TiO\textsubscript{2}-A became even better than the 0.4Au/TiO\textsubscript{2}-R. The products with 0.4Au/TiO\textsubscript{2}-A-40 nm were mainly phenolics. Fernando et al.\textsuperscript{42} compared activity of Au/TiO\textsubscript{2}-A and Au/TiO\textsubscript{2}-R on hydrogenation of m-dinitrobenzene in the same Au particle size range, the pseudo-first-order rate constant on Au/TiO\textsubscript{2}-A was higher than that on Au/TiO\textsubscript{2}-R.

The interactions between Au and the supports have been reported to be dependent on the nature of the support. Okazawa et al. observed charge transfer from electron-rich Au particles to TiO\textsubscript{2} (110, anatase) by a positive shift of XPS.\textsuperscript{43} Chen et al.\textsuperscript{44} found that Au particles bind first on the oxygen vacancy sites on the highly defective rutile TiO\textsubscript{2} (110) surface. Reduced rutile was found to enhance the binding of Au with Ti sites with electron donation from reduced TiO\textsubscript{2} (x < 2) to Au. The electron-rich Au showed enhanced CO bonding. TiO\textsubscript{2} in proximity to the supported metal could be reduced, and defects could be created on the anatase surface.\textsuperscript{45} The defects on the TiO\textsubscript{2} support may also affect the adsorption of guaiacol and catechol on the surface of this work. In other studies, Fe/SiO\textsubscript{2} and Pt/SiO\textsubscript{2} were shown to be active in hydrogenation of guaiacol and m-cresol, respectively. Although interactions exist between Au particles and the SiO\textsubscript{2} surface defect,\textsuperscript{46} 0.4Au/SiO\textsubscript{2} did not show any activity in this work. The TiO\textsubscript{2}-A support has been observed to play an important role in the physical, chemical, and catalytic properties of supported Au particles.\textsuperscript{22} Strong metal support interaction between Au and TiO\textsubscript{2} has been found.\textsuperscript{47} The ultrafast hot electron transfer from electron-rich Au nanoparticles to TiO\textsubscript{2} was determined by Furube et al. with femtosecond-resolved IR probe.\textsuperscript{39} Because the interface Schottky barrier in Au/ZrO\textsubscript{2} and Au/SiO\textsubscript{2} were larger than that in Au/TiO\textsubscript{2}, there was essentially no hot electron injection in these systems.\textsuperscript{48,49} Xiangchao et al.\textsuperscript{51} demonstrated that strain can decrease the interfacial n- and p-type Schottky barrier height of the Au/TiO\textsubscript{2} (001) interface mainly.
by changing the intrinsic properties of Au (Fermi level) and TiO₂ (valence band maximum and band gap). Strain was suggested to be an effective way to improve performance of readily interfacial electron exchange in plasmonic photocatalysis and nanoelectronics over Au/TiO₂. As gold alone does not catalyze guaiacol hydrogenation, the hydrogenation of guaiacol on 0.4Au-19 nm/TiO₂-A-40 nm either take place at the interface between the Au nanoparticles and the TiO₂-A or by on the TiO₂ surface by hydrogen spilt over23 from metal sites. The dissociation of H₂ over Au/TiO₂ has been observed at room temperature.53 Dimitar et al.54 observed the spillover of atomic hydrogen from supported Au particles onto TiO₂ at 22 °C.

### 3.2. Effect of Anatase Particle Size and Gold Loading.
We further studied the effect of TiO₂-A support particle size, by comparing the TiO₂-A-40 nm with a TiO₂-A of 45 μm. The performances of the catalysts with different support particle size are shown in Figure 2 (0.1Au/TiO₂-A-40 nm and 0.1Au/TiO₂-A-45 μm). The TiO₂-A in 45 μm still showed rather poor performance for this reaction. The 0.1Au/TiO₂-A-45 μm showed a visible improvement in the performance. However, its performance was much inferior as compared to the 0.1Au/TiO₂-A-40 nm. Because the 0.1Au/TiO₂-A-45 μm has a much lower surface area (27 m²/g) than that of 0.1Au-TiO₂-A-40 nm (88 m²/g), and the Au loading is low on both catalysts, the difference in the catalytic performance between the two catalysts may be ascribed to the difference in the surface area of the supports. Even though the 0.1Au/TiO₂-A-45 μm also showed considerably increased guaiacol hydrogenation activity over that of TiO₂-A-45 μm, the lower activity of 0.1Au/TiO₂-A-45 μm as compared to that of the 0.1Au/TiO₂-A-40 nm at the same low Au loading suggests that the TiO₂-A surface also plays an important role in this reaction. When the gold loading was increased from 0.1 wt % to 0.7 wt %, the conversion of guaiacol increased from 20% to 72% with the TiO₂-A-40 nm support.

### 3.3. Effect of Gold Particle Size.
In accordance to the characterization results on the Au particle size (Figure S-3 in Supporting Information), the catalytic performances of these samples with gold particle sizes ranging from 2.7 nm (Table S-1) to 41 nm (Table 3) at the same Au loading (0.4 wt %) in the hydrogenation of guaiacol were evaluated, and the results are shown in Figure S-4 (Supporting Information). The 0.4Au-3 nm/TiO₂-A-40 nm with the smallest gold particles shows the highest conversion of guaiacol (about 65%). The conversions of guaiacol over 0.4Au-19 nm/TiO₂-A-40 nm, 0.4Au-32 nm/TiO₂-A-40 nm and 0.4Au-41 nm/TiO₂-A-40 nm catalysts were 43%, 37% and 36%, respectively, decreasing with increasing gold particle size, but appeared more sensitive to smaller Au particle size. At the same Au loading, this change reflects a reduced Au surface area or the interface area between Au particles and the TiO₂-A on large Au particles. Though the conversions of guaiacol hydrogenation varied about 7% in a range of Au particle size from 19 to 41 nm, these TiO₂-A supported Au catalysts showed similar selectivity in guaiacol hydrogenation to form phenolic compounds. Various other hydrogenation reactions were studied for Au particles of different size.55,56 The relationship between gold particle size and the activities of some catalysts has been observed. Shi et al.57 reported reduced conversion of cinnamaldehyde over increased Au nanoparticles among 3.0, 4.9, and 16.3 nm Au on the SiO₂ support in the hydrogenation of cinnamaldehyde. In the hydrogenation of p-chloronitrobenzene to p-chloroaniline, similar Au

### Figure 2
Effect of support particle size on guaiacol hydrogenation. Reaction conditions: catalyst 0.30 g, guaiacol 1.50 g, toluene 25 mL, 6.5 MPa initial H₂ pressure at 300 °C, 700 rpm, 3 h.

### Table 3. Average Particle Size

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Distribution (nm)</th>
<th>Amount (%)</th>
<th>Mean Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4Au-19 nm/TiO₂-A-40 nm</td>
<td>17–18</td>
<td>18.2</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>18–19</td>
<td>36.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19–20</td>
<td>18.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20–21</td>
<td>18.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21–22</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>0.4Au-32 nm/TiO₂-A-40 nm</td>
<td>24–28</td>
<td>9.5</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>28–30</td>
<td>14.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30–33</td>
<td>38.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>33–35</td>
<td>33.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35–36</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>0.4Au-41 nm/TiO₂-A-40 nm</td>
<td>35–37</td>
<td>16.7</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>38–40</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40–42</td>
<td>38.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>42–44</td>
<td>22.2</td>
<td></td>
</tr>
</tbody>
</table>

The distributions of Au particles size were measured using Nano Measure 1.2.
particle size (from 1.5 to 9.0 nm) dependence was observed in the activities of the catalysts. The number of guaiacol converted over the gold surface atoms (mol/mol) for several samples are calculated and shown in Table S-2. Although the number of surface Au atoms increases with decreasing Au particle size for samples from 0.4Au-3 nm/TiO2-A-40 nm to 0.4Au-41 nm/TiO2-A-40 nm, resulting in the increased product yield in guaiacol hydrogenation (Figure S-4), the number of converted guaiacol molecules per surface Au atom actually decreased in this order (Table S-2). It should be emphasized that the reaction of guaiacol hydrogenation did not just take place over the gold particle surface. We do not have evidence that all Au surface atoms are fully interfaced with TiO2-A. The results are consistent with the hypothesis that catalysis took place at the interface between Au and TiO2-A, rather than on the Au surface. The interface area does not appear to be proportional to the number of surface Au atoms. In this work, the Au particle sizes (between 19 and 41 nm) are close to that of the support (TiO2-A-40 nm) (Figure 3d). The effect is considerably more pronounced as compared to the literature.

The TiO2-A-40 nm interfaced with a low loading of Au particles of similar size showed an strikingly improved performances on guaiacol hydrogenation, both in activity and in product selectivity. The catalyst bearing smaller Au particles (19 nm) delivered a higher activity in the conversion of guaiacol. The increased catalytic activity with the decrease of Au particle size from 41 to 19 nm may be attributed to the increased interface areas between the Au particles and the anatase support. While the loadings of gold over the 0.4Au-19 nm/TiO2-A-40 nm, 0.4Au-32 nm/TiO2-A-40 nm, and 0.4Au-41 nm/TiO2-A-40 nm were nearly the same, ranging from 0.411 to 0.427 wt % (see Table 1), the total Au surface area for the smaller Au particle size can be expected to be larger than that of larger Au particles due to more Au small particles. Therefore, the interface area between small gold particles and the support is expected to be larger than that between large Au particles and the support. While small Au particles alone could be active for the reaction, the study for the performance of Au particles in a few nanometer size range is out the scope of this work and will be a subject of future study. This work is mainly focused on the effect of inactive large Au particles on the activation of anatase TiO2 for the hydrodeoxygenation of guaiacol with the sole selectivity to phenolic products.

### 3.4. Mechanism Study of Guaiacol Hydrogenation on the 0.4Au-19 nm/TiO2-A-40 nm Catalyst

Gold nanoparticles on all other supports showed very little catalytic function. The superior catalytic performance of the TiO2-A-40 nm support in guaiacol hydrodeoxygenation with high activity and selectivity to phenolics is uncharacteristic of either gold nanoparticles or the support for the reaction.

In the hydrogenation of guaiacol over the 0.4Au-19 nm/TiO2-A-40 nm, methane was not detected as a product. The methyl group in guaiacol forms either methanol or migrates to the aromatic ring of the phenolics. To determine the dominant methyl transfer mechanism, the concentration of guaiacol was varied, as shown in Table 4. When the concentration of guaiacol was decreased from 0.48 mol/L to 0.16 mol/L, the methanol and phenol yields were increased, and the yield of methyl transfer products in the phenolics was decreased. There are three possible mechanisms for the methyl transfer in this reaction. The formation of high concentration of phenol and the presence of methanol in the products suggests a possible mechanism involving methylation by methanol.

<table>
<thead>
<tr>
<th>concentration of guaiacol (mol/L)</th>
<th>0.48</th>
<th>0.16</th>
</tr>
</thead>
<tbody>
<tr>
<td>conversion of guaiacol (%)</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

The 0.4Au-19 nm/TiO2-A-40 nm catalyst was evaluated for the possible reaction of methanol with phenol at methanol/phenol = 10 mol/mol under the reaction conditions. Neither methylation of phenol by methanol nor dehydration product between methanol and phenol took place in the system. The absence of acid sites in 0.4Au-19 nm/TiO2-A-40 nm was responsible for the stability of methanol and phenol under the reaction conditions.

The second possible mechanism could involve intramolecular methyl group transfers to the same aryl ring; the products distribution will not be expected to change by varying the concentration of guaiacol. Experimentally, no methylcatechol was found in our products. Therefore, this mechanism can be ruled out as an important one in this catalytic system.

The third one may involve bimolecular cross methyl group transfer from one guaiacol molecule to another molecule, such as phenolic products. When the concentration of guaiacol was decreased, the rate of bimolecular reaction may be expected to decrease, resulting in decreased yield of methylated products. The high concentration of xyleneols and trimethylphenols in Table 4 arising from the conversion of a high concentration of guaiacol supports this mechanism of bimolecular methylation. Catechol is a product of the bimolecular methylation between guaiacol and a phenolic compound. Therefore, the bimolecular methylation is indicated as the dominant methylation mechanism involved in the hydrogenation of guaiacol over the 0.4Au-19 nm/TiO2-A-40 nm catalyst under our reaction conditions.

Recently, Gao et al. investigated the reaction pathways of guaiacol hydrodeoxygenation over Pt/C. It was confirmed that phenol was formed using catechol as a reactant. To determine the prevailing reaction pathway of phenol formation on whether it is formed via direct hydrodeoxygenation of guaiacol or via hydrodeoxygenation of catechol intermediate, the reaction rates of guaiacol hydrogenation ($k_{\text{gua}}$) and catechol hydrogenation ($k_{\text{cate}}$) over the 0.4Au-19 nm/TiO2-A-40 nm catalyst were determined (Figure 4). The comparison of reaction rates between guaiacol and catechol helps to determine the possible pathways in guaiacol hydrogenation, by using the same catalyst and identical reaction conditions. The product of catechol hydrogenation is phenol. The $k_{\text{gua}}$ value is 0.91 (min$^{-1}$ g-cat$^{-1}$ cm$^{-3}$), while that of guaiacol hydrogenation ($k_{\text{gua}}$) is 0.26 (min$^{-1}$ g-cat$^{-1}$ cm$^{-3}$). Therefore, catechol hydrogenation proceeds much faster than guaiacol hydrogenation over this
catalyst. The reaction rate \( k \) of guaiacol hydrogenation over CoMo/C\(^{\text{P}}\) was 0.22 \((\text{min}^{-1} \cdot \text{g-cat}^{-1} \cdot \text{cm}^{-2})\), a little lower than on the 0.4Au-19 nm/TiO\(_2\)-A-40 nm catalyst. Because catechol was formed as an intermediate that coexisted with the guaiacol feed, an experiment was carried out to assess the competitive hydrogenation between guaiacol and catechol on the 0.4Au-19 nm/TiO\(_2\)-A-40 nm catalyst (Table 5). When the reaction system contained both guaiacol and catechol, conversion of catechol was evidently faster than that of guaiacol, consistent with the measured kinetics as shown in Figure 4. During guaiacol hydrogenation, catechol was detected in the products (Figure 1, 0.4Au-19 nm/TiO\(_2\)-A-40 nm), as a result of transmethylation reaction from guaiacol. Therefore, catechol seems a major intermediate product to form phenol in guaiacol hydrogenation over 0.4Au-19 nm/TiO\(_2\)-A-40 nm.

No methane was observed in the reaction products. The guaiacol molecule possesses three types of C–O bonds: \( C_{\text{Me}}=\text{OC}_A \) (methoxy C–O), \( C_{\text{Ar}}=\text{OC}_{\text{Me}} \) (aryl C–O) and \( C_{\text{Ar}}=\text{OH} \) (aryl hydroxyl) with bond energies of 247, 356, and 414 kJ/mol, respectively.\(^{38}\) The demethylation by \( C_{\text{Me}}=\text{OC}_A \) cleavage would be the easiest reaction among the three C–O bonds according to the bond energies. As a weak hydrogenation catalyst and due to the lack of acidity on the TiO\(_2\)-A support, the 0.4Au-19 nm/TiO\(_2\)-A-40 nm did not catalyze the formation of methane. The formation of a high concentration of phenol and methanol suggests that the hydrogenation of guaiacol on the 0.4Au/TiO\(_2\)-A-40 nm surface is favored for the cleavage of the \( C_{\text{Ar}}=\text{OC}_{\text{Me}} \) bond. Anisole was not detected, suggesting that the formation of anisole directly from guaiacol via hydrodehydroxylation is difficult, in agreement with the high \( C_{\text{Ar}}=\text{OH} \) bonding energy. Transmethylation appears to be the major pathway leading to the formation of catechol as the initial products. The facile hydrogenation of catechol leads to the formation of phenol. The absence of methylated catechol and methylated guaiacol suggests that cresols is not formed from the hydrogenation of methylcatechols. Instead, they may be formed as products of transmethylation between guaiacol and phenol. Details involved in the mechanism of bimolecular transmethylation will be a subject of future study.

3.5. Catalyst Stability and Effect of Water. The stability of 0.4Au-19 nm/TiO\(_2\)-A-40 nm was evaluated in guaiacol hydrogenation by reuse of the catalyst in three consecutive tests. Figure 5 shows that the 0.4Au-19 nm/TiO\(_2\)-A-40 nm remained active throughout the three consecutive runs at the same reaction conditions. No substantial changes in activity and selectivity were found over the three tests.

Water is a byproduct of catechol hydrogenation to phenol. Excess water may inhibit the catechol hydrodehydroxylation. Therefore, the effect of water on the guaiacol hydrogenation over the 0.4Au-19 nm/TiO\(_2\)-A-40 nm was studied. As shown in Table 6, a decrease in the conversion of guaiacol was observed with the presence of an increased amount of water. While the selectivity to phenol did not vary appreciably as the amount of water was increased relative to guaiacol, the selectivity to methylsubstituted phenols decreased with the increased amount of water. The results indicate that the presence of a moderate amount of water, at the level corresponding to \( H_2O/\text{guaiacol} = 1/4 \), does not significantly affect the guaiacol conversion, but a higher amount of water (the molar ratio of 0.37/1) does. Importantly, higher water concentration appears to suppress the relative rate of intermolecular methyl transfer over that of hydrogenation. In all cases, no anisole was detected in guaiacol hydrogenation over the 0.4Au-19 nm/TiO\(_2\)-A-40 nm catalyst.

3.6. Catalytic Pathways of Guaiacol Hydrogenation over 0.4Au-19 nm/TiO\(_2\)-A-40 nm. Two possible pathways for the conversion of guaiacol to phenol over 0.4Au-19 nm/TiO\(_2\)-A-40 nm (Scheme 1) are investigated in this work. The absence of anisole in the products rules out the pathway of guaiacol hydrodehydroxylation to form anisole. In a separate experiment, anisole was found to be stable under our reaction conditions.
condition over the 0.4Au-19 nm/TiO₂-A-40 nm catalyst. The absence of CH₄ and benzene in the products rules out the possibility of anisole as a short-lived intermediate. It is particularly interesting to note that hydrodehydroxylation of catechol and hydrodemethoxylation of guaiacol proceeded well over the 0.4Au-19 nm/TiO₂-A-40 nm catalyst. The observed catalytic hydrogenation activity of guaiacol and catechol is therefore facilitated by the presence of the OH at the adjacent carbon in the aromatic ring. Cresols and other phenolic compounds were mainly formed via transmethylation followed by hydrodehydroxylation. Phenolates on alumina was proposed to form through the coordination of guaiacol on Lewis sites followed by cleavage of the PhO–CH₃ bond and migration of the CH₃ to surface oxygen. The cationic CH₃ group in guaiacol also transferred to the surface of CoMo catalyst and further to the aromatic ring of absorbed catechol. As methylguaiacol and methycatechol were not detected in the products over the 0.4Au-19 nm/TiO₂-A-40 nm with few acid sites, methyl groups are most likely transferred to phenolic compounds to form alkylated phenolic species. The lack of Lewis acidity on the TiO₂-A makes it unlikely to have the cationic methyl transfer. On the basis of our results above, we establish that the hydrogenation of guaiacol on the 0.4Au/TiO₂-A-40 nm catalyst proceeds via both pathway 1 and pathway 2 (Scheme 1). The measured reaction rates (kₐ and kₐₑ) indicate that pathway 1 prevails through bimolecular mechanism.

Table 6. Effect of Water on Guaiacol Hydrogenation with 0.4Au-19 nm/TiO₂-A-40 nm

<table>
<thead>
<tr>
<th>reaction conditions</th>
<th>no water</th>
<th>water:guaiacol =0.14:1 mol/mol</th>
<th>water:guaiacol =0.37:1 mol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>conversion of guaiacol (%)</td>
<td>43.1</td>
<td>42.4</td>
<td>32.2</td>
</tr>
<tr>
<td>yield of products (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>25.6</td>
<td>26.2</td>
<td>19.4</td>
</tr>
<tr>
<td>cresols</td>
<td>5.8</td>
<td>5.2</td>
<td>3.4</td>
</tr>
<tr>
<td>xylensols</td>
<td>4.2</td>
<td>3.9</td>
<td>1.9</td>
</tr>
<tr>
<td>trimethylphenols</td>
<td>1.8</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>tetramethylphenols</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>catechol</td>
<td>4.9</td>
<td>5.4</td>
<td>5.8</td>
</tr>
<tr>
<td>others</td>
<td>0.6</td>
<td>0.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

*Reaction condition: 0.3 g of 0.4Au-19 nm/TiO₂-A-40 nm, 1.50 g of guaiacol, 25 mL of toluene, 6.5 MPa initial H₂ pressure at 300 °C, 700 rpm, 3 h.

Scheme 1. Possible Pathways in Guaiacol Hydrogenation

The striking catalytic activity arising from the synergism between gold and the anatase TiO₂ support and the high selectivity of the 0.4Au-19 nm/TiO₂-A-40 nm for phenol and methyl substituted phenolics from guaiacol suggests that the three primary monomers of lignin, p-coumaryl, coniferyl, and...
sinapyl alcohols, could be converted to desirable phenolic compounds following depolymerization of lignin materials.\(^6^3\)

The nature of the active sites for the selective hydrogenation of guaiacol and catechol remains the subject of future study, although early works suggest the spillover hydrogen on TiO\(_2\) surface may play a role.\(^5^7\)\(^3^8\)

4. CONCLUSIONS

Presynthesized gold nanoparticles are not active catalyst for hydrodeoxygenation of guaiacol as a lignin model compound over most supporting materials, including ZrO\(_2\), Al\(_2\)O\(_3\), SiO\(_2\), activated carbon, and even rutile TiO\(_2\). The effect of gold nanoparticles on these supports for the reaction is marginal as compared to the supports alone for this reaction. While anatase TiO\(_2\) showed the poorest performance for the hydrogenation of guaiacol among all the supporting materials, it is most striking to observe that a low Au loading with Au nanoparticle in size similar to the inactive anatase TiO\(_2\) (TiO\(_2\)-A-40 nm) produced the most active catalyst with intriguingly desirable selectivity to phenolics. Even when the average gold particle size has grown from 3 nm to 19–41 nm during the catalyst preparation, the large gold nanoparticles are capable of inducing and maintaining the superior performance on the surface of anatase TiO\(_2\) for stable performance in selective hydrogenation of guaiacol to phenolics. The selectivity of the 0.4Au-19 nm/TiO\(_2\)-A-40 nm catalysts is manifested by the results that it does not catalyze the hydrogenation of phenols, anisole, and aromatics, but it hydrogenates catechol and guaiacol to phenol. Gold particle size and anatase TiO\(_2\) particle size have an effect on the catalyst activity, but it does not affect the phenolic product selectivity. While the nature of the active sites on the 0.4Au-19 nm/TiO\(_2\)-A-40 nm for the hydrodeoxygenation reaction catalysts remains a subject of further study, the inhibition of water on the reaction, together with the low contact area by the very large gold particles with the support, suggests that the active sites are likely associated with the support surface. Phenolics are formed from guaiacol hydrogenation via two major pathways over the 0.4Au-19 nm/TiO\(_2\)-A-40 nm catalyst: (1) direct hydrogenation of guaiacol to form phenol and methanol and (2) hydrodeoxygenation of catechol, which is formed from the transmethylolation between guaiacol and phenol. The rate of catechol hydrogenation is much faster than that of guaiacol hydrogenation.

ASSOCIATED CONTENT

\* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02368.

X-ray diffraction (XRD) of samples and supports; preparation method of 0.4Au-3 nm/TiO\(_2\)-A-40 nm; XPS spectra of 0.4Au-19 nm/TiO\(_2\)-A-40 nm (Au 4f); TEM of 0.4Au-3 nm/TiO\(_2\)-A-40 nm; average particle size of 0.4Au-3 nm/TiO\(_2\)-A-40 nm; effect of gold particle size on guaiacol hydrogenation; gold surface atoms of Au NPs (PDF)

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Notes

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