

Catalytic Conversion of Guaiacol Catalyzed by Platinum Supported on Alumina: Reaction Network Including Hydrodeoxygenation Reactions

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S Supporting Information

ABSTRACT: The conversion of guaiacol catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ was investigated with a flow reactor at 573 K and 140 kPa. Dozens of reaction products were identified, with the most abundant being phenol, catechol, and 3-methylcatechol. The kinetically significant reaction classes were found to be hydrogenolysis [including hydrodeoxygenation (HDO)], hydrogenation, and transalkylation. Selectivity–conversion data were used to determine an approximate quantitative reaction network accounting for the primary products, and a more detailed qualitative network was also inferred. Catalytic HDO was evidenced by the production of anisole and phenol. The HDO selectivity increased with an increasing H₂ partial pressure and a decreasing temperature. Products formed by transalkylation reactions match those produced in the conversion catalyzed by HY zeolite, in which no deoxygenated products were observed.

1. INTRODUCTION

Lignocellulosic biomass, because of its abundance and relatively low cost, is potentially valuable as a renewable resource for the production of fuels and chemicals. Bio-oils obtained from lignocellulosic biomass, typically by fast pyrolysis, often have high oxygen contents (35–40 wt %), and consequently they are characterized by low heating values, instability, corrosiveness, and immiscibility with gasoline and diesel fuels.^{1,2} As a result, bio-oils lack applications as liquid fuels and require upgrading, with catalytic hydroprocessing being an appealing option. Sulfided hydroprocessing catalysts containing molybdenum with nickel or cobalt, commonly used for the removal of sulfur and nitrogen from fuels, have drawn significant attention for the removal of oxygen, as have other families of catalysts, including supported metals.^{2–7}

Although lignin-derived compounds typically constitute as much as 30 wt % of bio-oils^{8,9} and offer excellent potential as feedstocks for catalytic conversion processes,^{1,10} they have received less attention than feedstocks derived from cellulose in this regard. Thus, in contrast to the literature of catalytic upgrading of cellulose- and hemicellulose-derived carbohydrates,^{11–15} the literature characterizing the catalytic conversion of lignin-derived compounds is scarce. Most of the reported work is limited in quantitative information that characterizes the reaction pathways and kinetics.

Our goal was to provide such information and to begin unraveling the catalytic chemistry of conversion of compounds characteristic of lignin-derived bio-oils and, specifically, to characterize the crucial oxygen-removal reactions. 2-Methoxyphenol (guaiacol) was chosen as a prototypical compound because it may be considered to represent a large number of substituted phenols found in bio-oils derived from soft- or hardwood lignin.^{16–18} Oxygen removal from guaiacol can lead to important compounds that are useful as fuel components and chemical building blocks, such as benzene, toluene, and phenol.

The results presented here characterize the catalytic conversion of guaiacol; preliminary results have already been communicated.¹⁹ Experiments were performed with a supported metal catalyst and with an acid catalyst, Pt/ γ -Al₂O₃ and HY zeolite, respectively. The data determine a reaction network for the conversion of guaiacol with H₂ and identify and quantify the kinetically significant reactions, demonstrating the occurrence of hydrogenolysis [including hydrodeoxygenation (HDO)], hydrogenation, and transalkylation reactions and providing evidence of the effects of temperature and H₂ partial pressure on the catalyst selectivity.

2. MATERIALS AND METHODS

2.1. Materials. Guaiacol (2-methoxyphenol, 99.5 wt %) was purchased from Sigma-Aldrich. H₂ (99.999%), generated from deionized water by electrolysis in a Domnick Hunter gas generator (model 40H), was used as a co-reactant in the catalytic conversion experiments and in the flame ionization detectors (FIDs) of gas chromatographs (GCs). N₂ (99.997% purity, Praxair), purified by passage through a hydrocarbon trap (Agilent Technologies, BHT-4) to remove traces of hydrocarbon, was used as an inert carrier gas in the reactor and in the GCs. Helium (99.995%, Praxair) was purified by passage through Agilent Technologies traps to remove traces of hydrocarbons (BHT-4), moisture (BMT-4), and oxygen (BOT-4) prior to use as a carrier gas in the GCs. Zero-air [<0.1 ppm hydrocarbon (as methane)], generated from house air by use of a Domnick Hunter zero air generator (UHP-10ZAW), was used in the FIDs of the GCs.

2.2. Catalysts and Catalyst Treatments. The catalysts were powders, Pt/ γ -Al₂O₃ [1 wt % Pt; Sigma-Aldrich; Brunauer–Emmett–Teller (BET) surface area, 206 \pm 1 m²/g; Pt dispersion, 0.25] and HY zeolite (Si:Al atomic ratio, 15; Zeolyst CBV 720). Before the beginning of

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each catalytic reaction experiment, the HY zeolite catalyst was usually treated in flowing N_2 [100 mL at normal temperature and pressure (NTP)/min]. The $Pt/\gamma-Al_2O_3$ catalyst was treated in a 70:30 N_2/H_2 mixture flowing at 100 mL (NTP)/min; in some experiments, the HY zeolite was also treated in this mixture. In these treatments, the catalyst in the flowing gas was heated at a rate of 5 K/min to the desired reaction temperature and held at this temperature for 30 min prior to the start of reactant flow.

2.3. Characterization of Catalytic Reactions of Guaiacol.

The catalytic conversions were carried out in a continuous stainless-steel down-flow, once-through tubular reactor (outer diameter, 1.3 cm; wall thickness, 0.089 cm). The reactor was mounted in a well-insulated three-zone furnace (1530 W/115 V, Applied Test Systems Series 3210). Thermocouples were used to measure the temperatures at the outer reactor wall, in the vaporization zone near the reactor inlet, and in a well mounted slightly downstream of the catalyst bed.

In each experiment, the packed bed in the reactor consisted of fresh powder catalyst (10–100 mg) mixed with particles of inert, nonporous $\alpha-Al_2O_3$ (Fisher A634-3, 90 mesh size). This bed was typically 1.0–2.5 cm long and situated in the middle zone of the furnace.

Reactant guaiacol at room temperature was loaded into a syringe pump (Teledyne Isco model 500D), which was used as a feed reservoir. N_2 was used as the carrier gas and mixed with the vaporized reactant at the inlet of the reactor located in the top zone of the furnace. H_2 was cofed in some experiments. Mass flow controllers (Brooks SLA5850S) were used to measure and control gas flow rates. A water-cooled condenser downstream of the reactor was used to separate condensable from volatile products at approximately 285 K. The gas product stream flowed to an online refinery gas analyzer (RGA, a GC), as described below; the flow rate of this stream was monitored with a mass flow meter (Brooks SLA7860S). The liquid product stream flowing steadily from the separator was sampled periodically for analysis with an off-line GC, as described below. Each experiment was typically run for approximately 4 h on stream at a system absolute pressure of 140 kPa. Mass balance closures were typically $98.5 \pm 1.3\%$ (Table S2 in the Supporting Information).

Temperature and flow rate measurements and controls of the flow system were facilitated with a NI PXI-1050 controller (National Instruments).

2.4. Data Analysis. Values of the guaiacol conversion (X) were determined from the mass flow rate and analysis of the product stream. The yield of product i (Y_i) is defined as the molar formation rate of that product divided by the total molar flow rate of the organic reactant fed. Thus, the selectivity to product i (Y_i/X) was calculated as the product yield divided by the total conversion of the reactant guaiacol.

Our goal was to characterize the catalyst performance in the (near) absence of deactivation, and therefore our experiments were carried out at low conversions and for short enough times on stream to provide data characterizing the reaction networks in the presence of the fresh catalysts. In kinetics experiments, we used initial conversion and selectivity values by extrapolating data to zero time on stream to analyze catalyst performance prior to significant deactivation.

3. RESULTS

3.1. Conversion of Guaiacol Catalyzed by $Pt/\gamma-Al_2O_3$. *3.1.1. Major, Minor, and Trace Products.* Control experiments were performed in the absence of a catalyst (the reactor was packed with 5 g of particles of inert $\alpha-Al_2O_3$) at temperatures ranging from 523 to 623 K, with the feed being a 70:30 N_2/H_2 mixture flowing at 100 mL (NTP)/min. At the highest temperature, only minimal guaiacol conversions were observed ($X < 0.003$), demonstrating that noncatalytic reactions were negligible under our conditions.

When the $Pt/\gamma-Al_2O_3$ catalyst was present in the reactor, dozens of products were observed. Data were obtained at conversions as low as 0.01 to determine initial rates and the products of primary reactions. The system was also run to give higher conversions, up to $X = 0.13$, with the goal of identifying nonprimary products.

The most abundant products identified at a guaiacol conversion of approximately 0.075 are summarized in Table 1. Phenol, benzene-1,2-diol (catechol), and 3-methylbenzene-1,2-diol (3-methylcatechol) were the major products. Other products formed in relatively high yields (Table 1) include benzene, methoxybenzene (anisole), cyclohexanone, methylbenzene (toluene), 2-methylphenol (*o*-cresol), 2-methoxy-3-methylphenol (3-methylguaiacol), 2-methoxy-6-methylphenol (6-methylguaiacol), and 1,2-dimethoxybenzene (veratrole). All of these products were quantified.

Water and methanol were also observed, being identified by gas chromatography–mass spectrometry (GC–MS), but they were not quantified (Table 1). Any methanol that might have been present in the vapor product stream was undetectable with the GC–RGA. Water was only a trace product, whereas methanol was a minor product (Table 1).

Methane was the only product identified in the gas stream effluent with the GC–RGA.

Other trace products that were identified by GC–MS but not quantified include cyclohexene, cyclohexane, methoxycyclohexane, 1,4-dimethylbenzene (*p*-xylene), cyclohexanol, methylcyclohexanones, methylanisoles, 2-methoxy-4-methylphenol (4-methylguaiacol), 2-methoxy-5-methylphenol (5-methylguaiacol), dimethylphenols, and trimethylphenols (Table 1).

3.1.2. Conversion of Guaiacol as a Function of Time on Stream and Inverse Space Velocity. Data illustrating the conversion of guaiacol catalyzed by $Pt/\gamma-Al_2O_3$ as a function of time on stream at various values of weight hourly space velocity (WHSV) are shown in Figure 1A. Good reproducibility between replicated experiments was achieved, as shown by the error bounds. The data shown in Figure 1A also imply that the catalyst underwent deactivation more rapidly at lower space velocities than at higher space velocities. Initial conversions were determined by extrapolating the data to zero time on stream, as shown in Figure 1A. As expected, the data indicate that higher space velocities led to lower initial conversions.

The identities of the major products provide a basis for inferring the kinetically significant classes of reactions; for example, the removal of oxygen from guaiacol to form phenol or anisole suggests reactions with H_2 that should be classified as HDO reactions. The observation of cyclohexanone suggests the occurrence of hydrogenation, and the observation of methyl-substituted guaiacols suggests the occurrence of methyl group transfer (transalkylation). The observation of methane points to the occurrence of hydrogenolysis.

Thus, we infer that the major products catechol and 3-methylcatechol resulted from methyl group transfer (transalkylation) reactions. Catechol could also have been formed by hydrogenolysis of the C–O bond β to the aromatic ring in guaiacol; such a reaction should not be ruled out because of the observation of the product methane. Similarly, the products phenol and methanol are inferred to have been formed by hydrogenolysis of the C–O bond of the methoxy group α to the aromatic ring. The minor products *o*-cresol, 3-methylguaiacol, 6-methylguaiacol, and veratrole are inferred to have formed in transalkylation reactions. The minor products anisole and water are inferred to have been formed by HDO of the C–O bonds linking hydroxy groups to the aromatic rings.

Table 1. Most Abundant and Trace^a Products Formed in the Conversion^b of Guaiacol Catalyzed by Pt/ γ -Al₂O₃ (Liquid Samples)^c

classification based on			
product	abundance in product stream ^d	basis for identification of product	basis for quantification of product
benzene	minor	standard sample	FID calibration curve
anisole	minor	standard sample	FID calibration curve
cyclohexanone	minor	standard sample	FID calibration curve
toluene	minor	standard sample	FID calibration curve
phenol	major	standard sample	FID calibration curve
<i>o</i> -cresol	minor	standard sample	FID calibration curve
catechol	major	standard sample	FID calibration curve
3-methylcatechol	major	standard sample	FID calibration curve
3-methylguaiacol	minor	MS EI database	FID calibration curve (used 4-methylguaiacol)
6-methylguaiacol	minor	MS EI database	FID calibration curve (used 4-methylguaiacol)
veratrole	minor	standard sample	FID calibration curve
cyclohexene	trace	standard sample	n/a
cyclohexane	trace	standard sample	n/a
1-methoxycyclohexane	trace	MS EI database	n/a
<i>p</i> -xylene	trace	MS EI database	n/a
cyclohexanol	trace	standard sample	n/a
2-methylcyclohexanone	trace	MS EI database	n/a
3-methylcyclohexanone	trace	MS EI database	n/a
2-methylanisole	trace	standard sample	n/a
4-methylanisole	trace	standard sample	n/a
4-methylguaiacol	trace	standard sample	n/a
5-methylguaiacol	trace	MS EI database	n/a
2,3-dimethylphenol	trace	MS EI database	n/a
2,5-dimethylphenol	trace	MS EI database	n/a
2,6-dimethylphenol	trace	standard sample	n/a
3,4-dimethylphenol	trace	MS EI database	n/a
2,3,5-trimethylphenol	trace	MS EI database	n/a
2,3,6-trimethylphenol	trace	MS EI database	n/a
2,4,6-trimethylphenol	trace	MS EI database	n/a
3,4,5-trimethylphenol	trace	MS EI database	n/a
water	trace	MS EI database	n/a
methanol ^e	minor	MS EI database	n/a

^a Identifications of some trace products were not confirmed with standard samples; therefore, for example, substituted benzenes and substituted phenols other than those listed are possible products. ^b Conversion conditions: temperature, 573 K; WHSV, 19.8 ± 0.1 g of guaiacol (g of catalyst)⁻¹ h⁻¹; and initial conversion of guaiacol, approximately 0.075. ^c Compounds were identified using the National Institute of Standards and Technology (NIST) electron impact (EI) mass spectral database; some were confirmed using authentic standards. ^d A product was classified as “major” when its response in a chromatogram was greater than 1.2×10^7 pico-Amps (pA), “minor” when its response was between 1.0×10^6 and 1.2×10^7 pA, and “trace” when its response was less than 1.0×10^6 pA. ^e Methanol was observed in liquid samples; however, its concentration in the gas phase was not quantified.

Benzene could have been formed in sequential HDO reactions, for example. Cyclohexanone is inferred to have been formed by removal of a methoxy group from the aromatic ring of a guaiacol followed by hydrogenation.

Most of the trace products are inferred to have been formed in sequential reactions. These products can be accounted by the following reaction classes: (a) HDO and hydrogenation accounting for cyclohexene, cyclohexane, and methoxycyclohexane, (b) HDO and transalkylation accounting for *p*-xylene, (c) HDO and hydrogenation accounting for cyclohexanol, (d) HDO, hydrogenation, and transalkylation accounting for methylcyclohexanones, and (e) HDO with multiple transalkylation reactions accounting for methylanisoles and methylphenols having multiple methyl substituents. Other trace products, including 4-methylguaiacol and 5-methylguaiacol, are inferred to have been produced in transalkylation reactions.

3.1.3. Development of a Quantitative Reaction Network.

Plots of selectivity (molar flow rate of product divided by the molar flow rate of reactant consumed) as a function of initial conversion were used to identify which products are primary and which are not.^{20,21} For each product, data were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products by our criterion. The selectivity–conversion data observed for guaiacol (Figure 2) indicate (a) that (A) phenol, (B) anisole, (C) 3-methylcatechol, (D) catechol, (E) 3-methylguaiacol, (H) veratrole, and 6-methylguaiacol (data not shown for 6-methylguaiacol because of the similarity to 3-methylguaiacol; Figure S1 in the Supporting Information) were primary products and (b) that (F) cyclohexanone, (G) benzene, (I) toluene, and (J) *o*-cresol were nonprimary (higher order) products

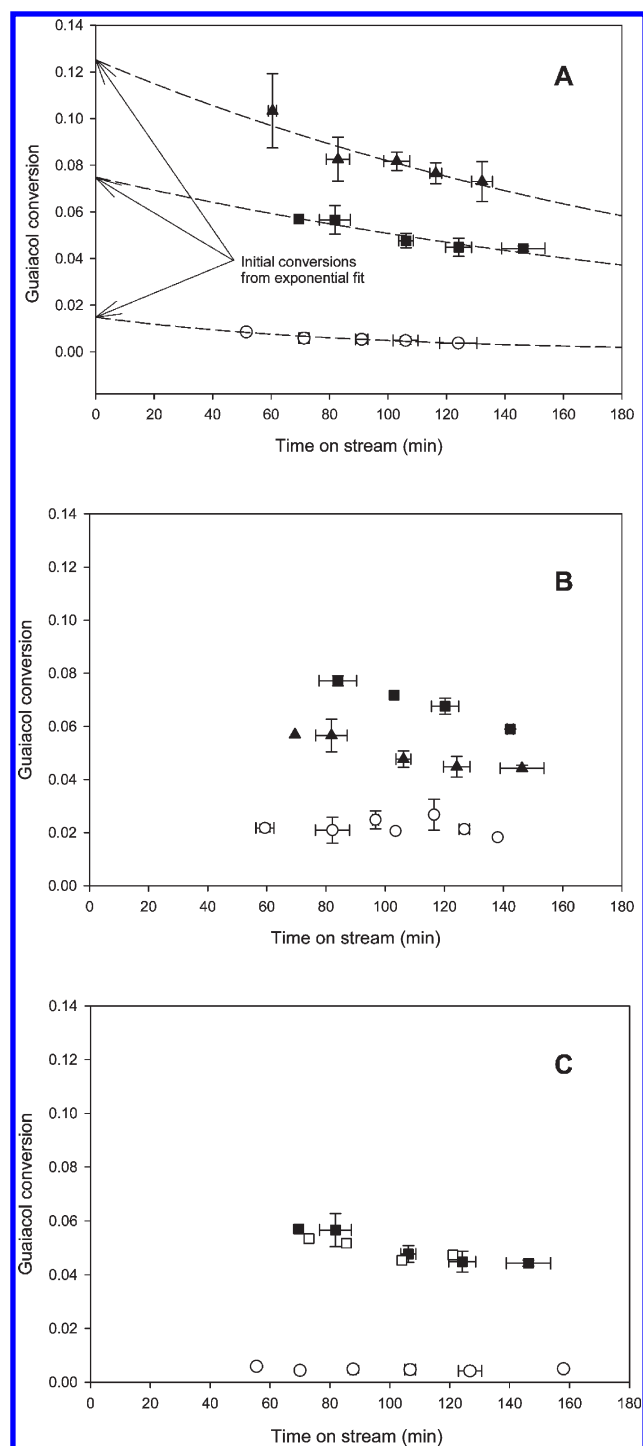


Figure 1. Guaiacol conversion during operation of the flow reactor (A) at 573 K at various values of WHSV [WHSV in units of g of guaiacol (g of catalyst)^{−1} h^{−1}]: (▲) 9.9 ± 0.1, (■) 19.8 ± 0.1, and (●) 99.6 ± 2.1; (B) at various temperatures: (○) 523 K at WHSV = 19.9 ± 0.2 g of reactant (g of catalyst)^{−1} h^{−1}, (▲) 573 K at WHSV = 19.8 ± 0.1 g of guaiacol (g of catalyst)^{−1} h^{−1}, and (■) 623 K at WHSV = 20.0 ± 0.2 g of guaiacol (g of catalyst)^{−1} h^{−1}; and (C) at various H₂ partial pressures (in kPa) at 573 K: (○) 0 at WHSV = 19.9 ± 0.2 g of guaiacol (g of catalyst)^{−1} h^{−1}, (■) 42 at WHSV = 19.8 ± 0.1 g of guaiacol (g of catalyst)^{−1} h^{−1}, and (□) 140 at WHSV = 19.7 g of guaiacol (g of catalyst)^{−1} h^{−1}. The error bars represent standard deviations when replicate data were obtained.

(we caution that primary products, such as catechol, might arise from more than one reaction).

Thus, we infer a partial statement of the reaction network, showing only the routes to the primary products, as summarized in Figure 3. Catechol is inferred to have been formed in more than one reaction pathway. The rate constant for the formation of catechol, calculated from the overall catechol yield, was 7.5 L (g of catalyst)^{−1} h^{−1}. The rate constant for the formation of catechol via hydrogenolysis shown above was approximated by subtracting rate constants for the formation of veratrole, 3-methylguaiacol, and 6-methylguaiacols from the overall rate constant for catechol formation; consequently, this value is less reliable than the others. A more complete statement of the reaction network is stated below, inferred on the basis of the identifications of the likely reaction classes, stated above to be HDO, transalkylation, hydrogenation, and hydrogenolysis.

The data allow for a quantitative characterization of the overall conversion of guaiacol catalyzed by Pt/γ-Al₂O₃ as well as the reactions giving primary products. A semi-logarithmic plot of the fraction of guaiacol unconverted as a function of inverse space velocity is nearly linear, indicating that the overall guaiacol conversion is well-represented by first-order kinetics over the conversion range that we investigated (Figure 4A). The pseudo-first-order rate constant for the disappearance of guaiacol was found to be 16.2 L (g of catalyst)^{−1} h^{−1} under the conditions stated in the caption of Figure 1A.

Data characterizing the conversion to individual primary products are also well-represented by first-order kinetics over the observed ranges of conversion, as shown in panels B and C of Figure 4. It is the information obtained from these plots that allows for the partially quantified statement of the partial reaction network, including the pseudo-first-order rate constants for the formation of the primary products (Figure 3).

3.1.4. Development of a Qualitative Reaction Network. According to the list of observed products (Table 1) and the inferred reaction classes, we infer an extended (but only qualitative) reaction network shown in Figure 5 for guaiacol conversion catalyzed by Pt/γ-Al₂O₃ in the presence of H₂. The network is based on not just the identification of the kinetically significant reaction classes (HDO, transalkylation, hydrogenation, and hydrogenolysis) but also our chemical judgment of the most likely pathways for the formation of the minor and trace compounds. For example, we infer that benzene (a minor product) was formed from guaiacol via sequential HDO reactions and that trimethylphenols (trace products) were formed from the primary product phenol by sequential transalkylation reactions. Thus, we emphasize that more detailed investigations could lead to modifications of the suggested reaction network.

3.1.5. Effect of the Temperature on Conversion of Guaiacol. Data characterizing the conversion of guaiacol catalyzed by Pt/γ-Al₂O₃ as a function of time on stream at various temperatures (523–623 K) are shown in Figure 1B. The error bars represent standard deviations determined in replicate experiments at each temperature. The data show that the initial conversions increased with an increasing temperature at WHSV ≈ 20 g of reactant (g of catalyst)^{−1} h^{−1}, as expected. The data of Figure 1B show that the catalyst deactivated more rapidly at the higher temperatures, as expected.

The temperature dependence of the product distributions is summarized in Table 2. The selectivity for the formation of primary products inferred to be formed in HDO reactions, including anisole and phenol, decreased as the temperature increased. The

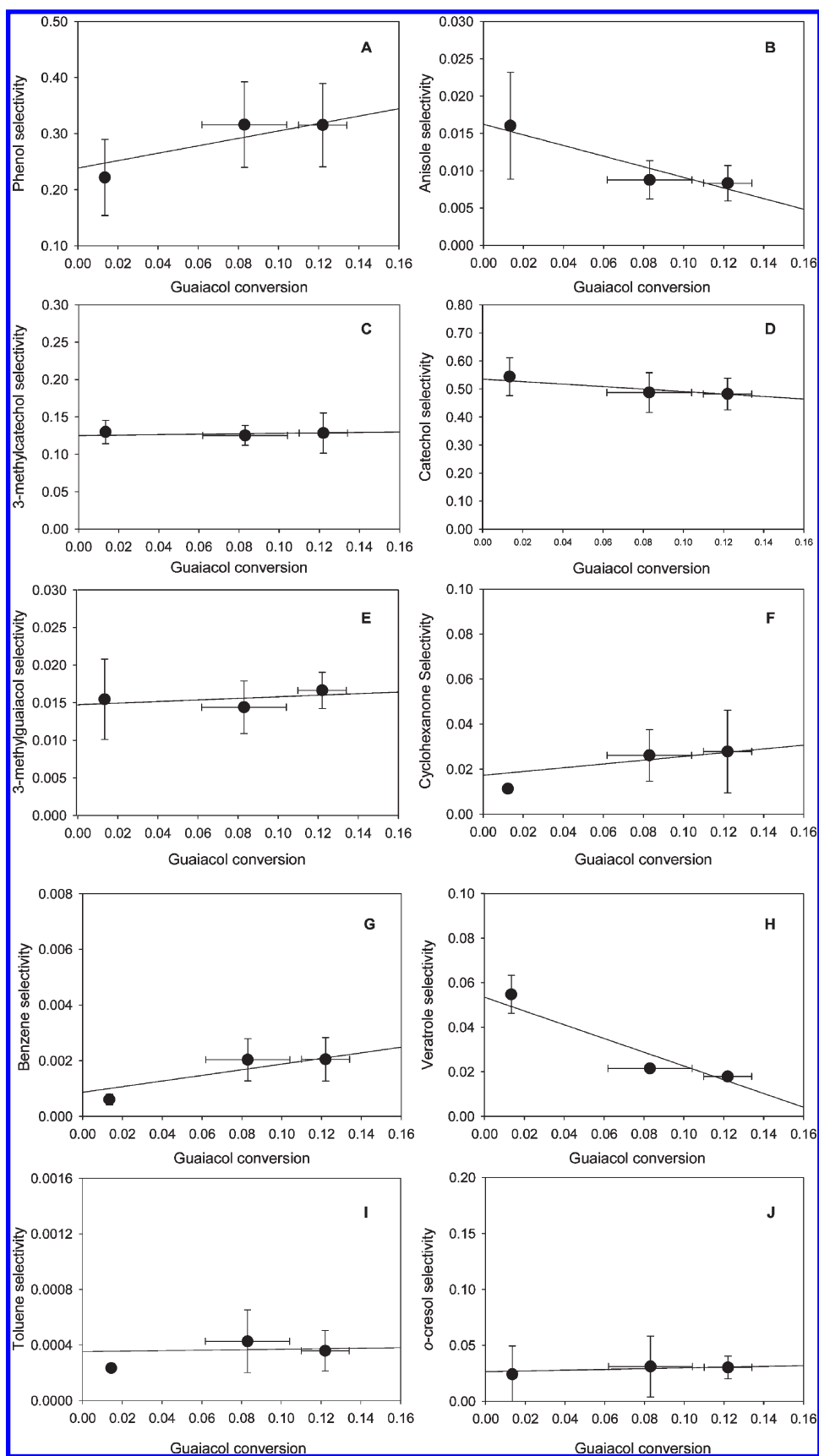


Figure 2. Selectivity for the formation of several products in the conversion of guaiacol catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ at 573 K; error bars were determined in replicate experiments at conversions of approximately 0.01, 0.08, and 0.12.

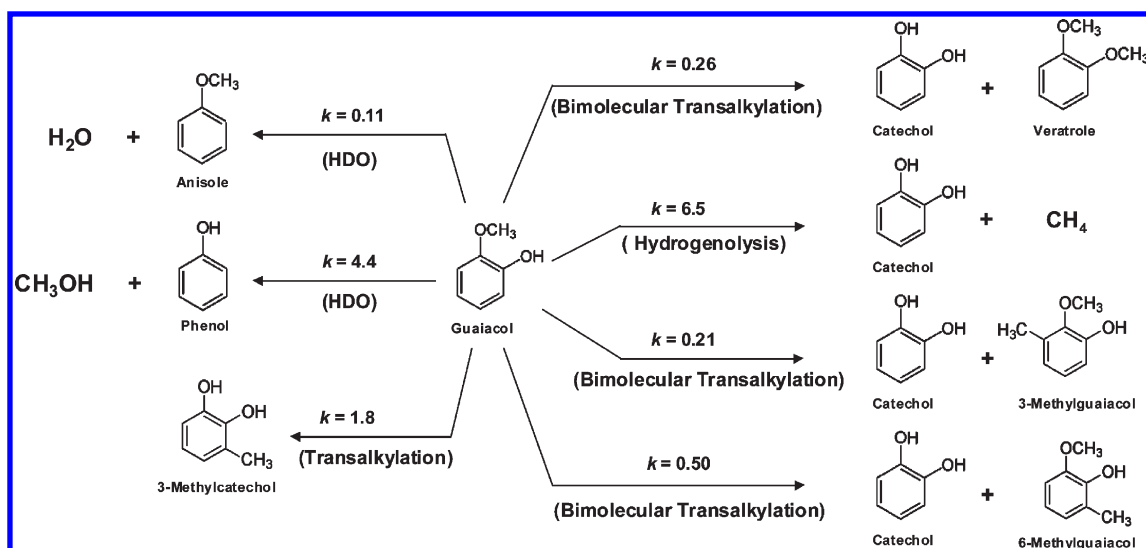


Figure 3. Reaction network accounting for the formation of primary products determined from analysis of selectivity–conversion plots for the conversion of guaiacol and H_2 catalyzed by $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ at 573 K. H_2 , as a reactant, is omitted for simplicity. Pseudo-first-order rate constants for the reactions giving the individual primary products formed in the conversion of anisole catalyzed by $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ are shown in units of $\text{L} \text{ (g of catalyst)}^{-1} \text{ h}^{-1}$.

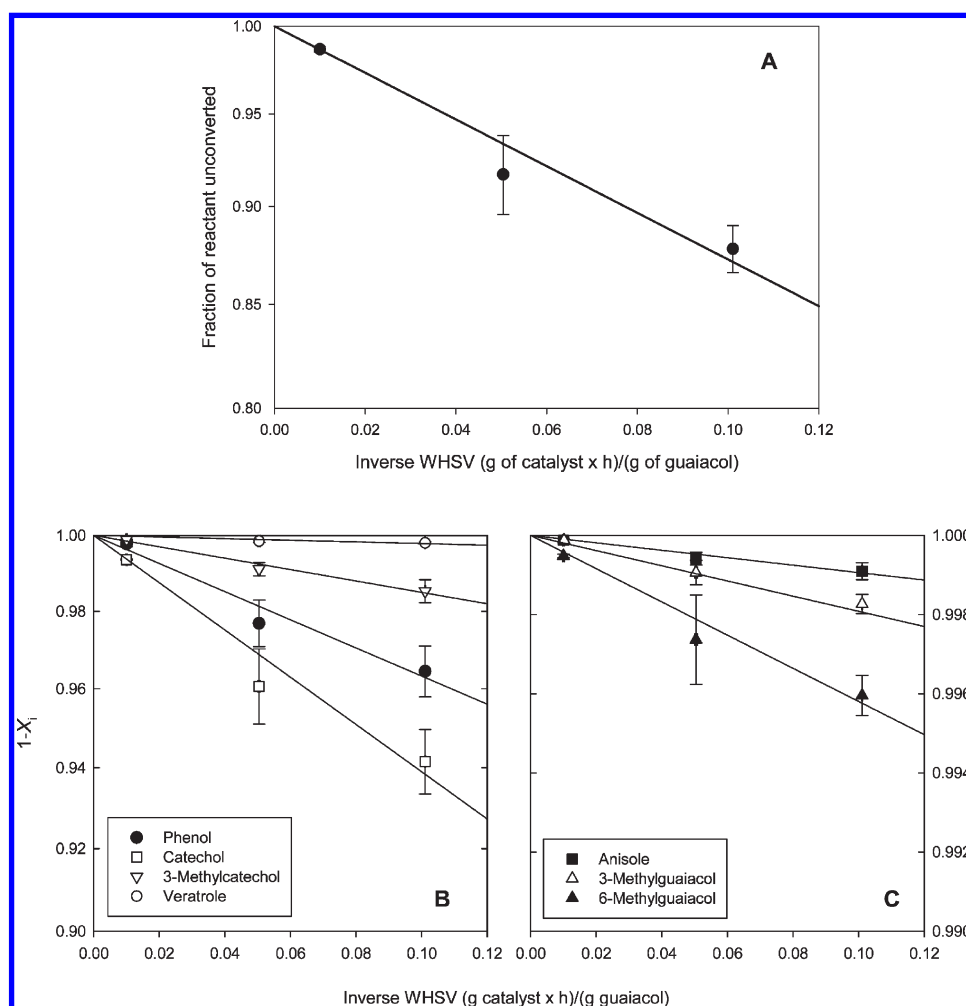


Figure 4. Demonstration of first-order kinetics of (A) overall conversion and (B and C) conversion to each primary product of guaiacol conversion catalyzed by $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ under the conditions stated in the caption of Figure 1A. The term X_i represents the conversion to product i . This value was calculated by dividing the number of moles of product i produced by the number of moles of guaiacol fed. Conversion was varied by changing the catalyst mass in the packed-bed reactor.

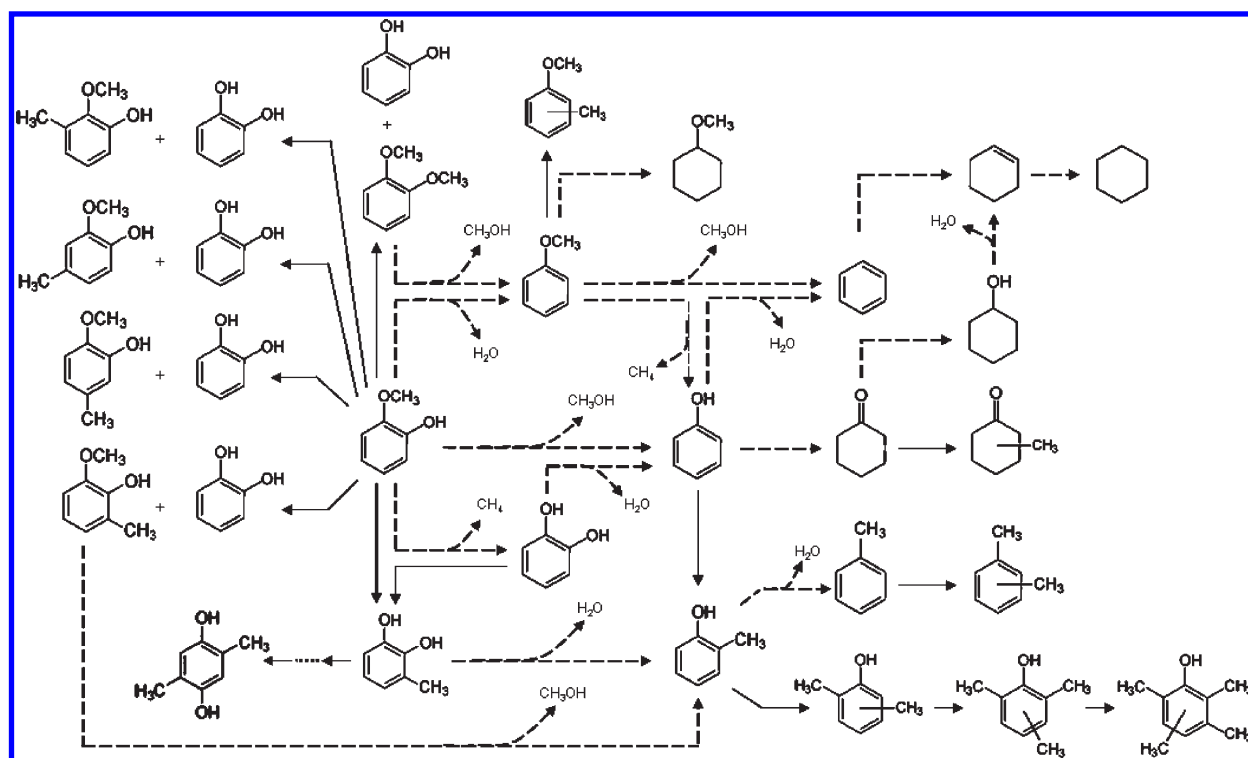


Figure 5. Reaction network for the conversion of guaiacol and H_2 catalyzed by $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ at 573 K. HDO, hydrogenolysis, and hydrogenation reactions are represented by dashed arrows, and methyl group transfer reactions are represented by solid arrows. H_2 , as a reactant, is omitted for simplicity. The representation in this network is simplified; for example, in transalkylation reactions in which two guaiacol molecules are involved (e.g., 2-guaiacol \rightarrow catechol + veratrole), the stoichiometry is not represented here.

Table 2. Products of Conversion of Guaiacol Catalyzed by $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ in the Presence of H_2 at Various Temperatures (Liquid Product Stream)^a

product	selectivity to product in reaction occurring in the presence of H_2 catalyzed by $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ at various temperatures (T , K)		
	$T = 523$	$T = 573$	$T = 623$
benzene	0.004	0.002	0.002
toluene	0.003	0.0004	0.0005
anisole	0.02	0.009	0.008
cyclohexanone	0.1	0.03	0.01
phenol	0.4	0.3	0.3
<i>o</i> -cresol	0.01	0.03	0.03
veratrole	0.05	0.02	0.02
3-methylguaiacol	0.005	0.01	0.02
6-methylguaiacol	0.04	0.03	0.03
catechol	0.3	0.4	0.3
3-methylcatechol	0.03	0.1	0.3

^a Data were extrapolated to zero time on stream and, thus, represent approximate initial selectivities determined at a WHSV of 20 g of guaiacol (g of catalyst)⁻¹ h⁻¹ and a pressure of 140 kPa. Selectivity is defined as yield (mol product formed/mol of organic reactant fed)/conversion (mol of organic reactant consumed/mol of organic reactant fed). The conversions are stated in the text. ^b The gas feed rate for 30% H_2 /70% N_2 was 100 mL/min, and the feed molar ratio of H_2 to the organic reactant was 10.

Table 3. Products of Conversion of Guaiacol Catalyzed by $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ at Various H_2 Partial Pressures (Liquid Product Stream)^a

product	selectivity to product in reaction catalyzed by $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ at various H_2 partial pressures (P_{H_2} , kPa)		
	$P_{\text{H}_2} = 0$	$P_{\text{H}_2} = 41^b$	$P_{\text{H}_2} = 127^c$
benzene		0.002	0.003
toluene		0.0004	0.001
anisole		0.009	0.04
cyclohexanone		0.03	0.2
phenol		0.3	0.5
<i>o</i> -cresol		0.03	0.03
veratrole	0.2	0.02	0.03
3-methylguaiacol	0.03	0.01	0.01
6-methylguaiacol	0.1	0.03	0.04
catechol	0.6	0.4	0.07
3-methylcatechol	0.06	0.1	0.002

^a Data were extrapolated to zero time on stream and, thus, represent approximate initial selectivities determined at WHSV of 20 g of guaiacol (g of catalyst)⁻¹ h⁻¹, a system pressure constant at 140 kPa, and a temperature of 573 K. Selectivity is defined as yield (mol product formed/mol of organic reactant fed)/conversion (mol of organic reactant consumed/mol of organic reactant fed). ^b The feed molar ratio of H_2 /guaiacol was 10. ^c The feed molar ratio of H_2 /guaiacol was 33.

selectivities to primary products that we infer to have been produced by transalkylation reactions (including 3-methylguaiacol

and 3-methylcatechol) increased with an increasing temperature. The selectivity for the formation of veratrole, however, decreased as

Table 4. Most Abundant and Trace^a Products Formed in the Conversion^b of Guaiacol Catalyzed by HY Zeolite: Liquid Sample^c

product	classification of product based on abundance in product stream ^d	basis for identification of product	basis for quantification of product
catechol	major	standard sample	FID calibration curve
3-methylcatechol	minor	standard sample	FID calibration curve
3-methylguaiacol	minor	MS EI database	FID calibration curve (used 4-methylguaiacol)
4-methylguaiacol	minor	standard sample	FID calibration curve
5-methylguaiacol	minor	MS EI database	FID calibration curve (used 4-methylguaiacol)
6-methylguaiacol	minor	MS EI database	FID calibration curve (used 4-methylguaiacol)
1,2-dimethoxy benzene	major	standard sample	FID calibration curve
anisole	trace	standard sample	n/a
toluene	trace	standard sample	n/a
phenol	trace	standard sample	n/a
<i>o</i> -cresol	trace	standard sample	n/a
<i>p</i> -xylene	trace	MS EI database	n/a
<i>o</i> -xylene	trace	MS EI database	n/a
2-methylanisole	trace	standard sample	n/a
4-methylanisole	trace	standard sample	n/a
1,2,3-trimethylbenzene	trace	MS EI database	n/a
1,2,5-trimethylbenzene	trace	MS EI database	n/a
1,2,3,4-tetramethylbenzene	trace	MS EI database	n/a
1,2,3,5-tetramethylbenzene	trace	MS EI database	n/a
pentamethylbenzene	trace	MS EI database	n/a
hexamethylbenzene	trace	MS EI database	n/a
2,3-dimethylphenol	trace	MS EI database	n/a
2,4-dimethylphenol	trace	MS EI database	n/a
2,5-dimethylphenol	trace	MS EI database	n/a
3,4-dimethylphenol	trace	MS EI database	n/a
3,5-dimethylphenol	trace	MS EI database	n/a
2,3,5-trimethylphenol	trace	MS EI database	n/a
2,3,6-trimethylphenol	trace	MS EI database	n/a
2,4,6-trimethylphenol	trace	MS EI database	n/a
3,4,5-trimethylphenol	trace	MS EI database	n/a
2,3,5,6-tetramethylphenol	trace	MS EI database	n/a
2,3-dimethoxytoluene	trace	MS EI database	n/a
3,4-dimethoxytoluene	trace	MS EI database	n/a
4-methylcatechol	minor	MS EI database	n/a
1,4-benzenediol-2,3,5-trimethyl	trace	MS EI database	n/a

^a Identifications of some trace products were not confirmed with standard samples; therefore, for example, other substituted benzenes and substituted phenols are possible products. ^b Conversion conditions: temperature, 573 K; WHSV, 20.0 ± 0.1 g of guaiacol (g of catalyst)⁻¹ h⁻¹; and initial conversion of guaiacol, approximately 0.11. ^c Compounds were identified using the NIST EI mass spectral database; some were confirmed in experiments with standard samples. ^d A product was classified as “major” when its response in a chromatogram was greater than 1.2×10^7 pA, “minor” when its response was between 1.0×10^6 and 1.2×10^7 pA, and “trace” when its response was less than 1.0×10^6 pA.

the temperature increased. The selectivity to catechol, which can possibly be formed by either hydrogenolysis or transalkylation reactions, first increased and then decreased as the temperature increased. A similar pattern was observed for catechol.

3.1.6. Effect of the H₂ Partial Pressure on Guaiacol Conversion. H₂ plays a crucial role as a co-reactant in numerous reactions leading to the removal of oxygen from organic compounds. To illustrate the importance of H₂ in the reactions of guaiacol catalyzed by Pt/ γ -Al₂O₃, data showing conversion as a function of time on stream at various H₂ partial pressures are shown in Figure 1C. The initial conversions were similar (approximately 0.08) when the reactant gas was 70% N₂/30% H₂ ($P_{N_2} = 95$ kPa; $P_{H_2} = 41$ kPa; $P_{\text{guaiacol}} = 4$ kPa) or 100% H₂ ($P_{H_2} = 127$ kPa; $P_{\text{guaiacol}} = 13$ kPa). In contrast, the removal of H₂

from the feed ($P_{N_2} = 134$ kPa; $P_{\text{guaiacol}} = 6$ kPa) resulted in a drastic drop in the initial conversion (to approximately 0.006).

As shown in Table 3, in the presence of H₂ in the feed stream, the selectivity for the formation of deoxygenated products, including benzene, toluene, anisole, cyclohexanone, and phenol, increased as the H₂ partial pressure increased. In contrast, the major transalkylation products, such as catechol and 3-methylcatechol, formed less selectively, and the selectivities for the formation of *o*-cresol and veratrole did not change significantly. The results imply that HDO was favored relative to methyl group transfers at higher H₂ partial pressures. Because the selectivity for the formation of cyclohexanone was also significantly higher at higher H₂ partial pressures, the results also indicate that hydrogenation is favored at higher H₂ partial pressures, as expected.

None of the products formed in oxygen-removal reactions (including methane, methanol, benzene, toluene, anisole, cyclohexanone, phenol, and *o*-cresol) was detected in the absence of H_2 in the feed.

The data shown in Figure 1C demonstrate similar trends in catalyst deactivation when H_2 was fed ($P_{H_2} = 41$ or 127 kPa).

3.2. Catalytic Conversion of Guaiacol Catalyzed by HY Zeolite. **3.2.1. Major, Minor, and Trace Products.** Dozens of products were observed and identified in the conversion of guaiacol catalyzed by HY zeolite. Data were obtained at only a single space velocity, approximately 20 g of reactant (g of catalyst) $^{-1}$ h $^{-1}$, with the goal of identifying the classes of reactions catalyzed by the solid acid. No deoxygenated products were observed when this catalyst was used.

The most abundant products identified at a guaiacol conversion of approximately 0.11 are summarized in Table 4. Catechol and veratrole were major products. Other products formed in relatively high yields include 3-methylguaiacol, 4-methylguaiacol, 5-methylguaiacol, 6-methylguaiacol, and 3-methylcatechol. Trace products include substituted benzenes, substituted phenols, and substituted veratroles. Guaiacol feed contaminants (present in only trace concentrations), including anisole and phenol, were also detected as trace components in the products, as were their alkylated products. Methane was not detected in the product gas stream, in contrast to what was observed when the catalyst was Pt/ γ - Al_2O_3 used in the presence of H_2 .

The most abundant products can be accounted for by methyl group transfer (transalkylation) reactions. Most of the trace products are inferred to have been formed by sequential transalkylation reactions of the abundant products and feed contaminants. For example, dimethoxytoluenes can be produced by transalkylation of veratrole, and methylguaiacols can be formed via transalkylation of guaiacol. These reactions are known to be catalyzed by solid acids under conditions similar to ours.^{22,23}

3.2.2. Conversion of Guaiacol as a Function of Time on Stream. Data showing the conversion of guaiacol catalyzed by HY zeolite as a function of time on stream at a space velocity of approximately 20 g of reactant (g of catalyst) $^{-1}$ h $^{-1}$ are shown in Figure 6. Good reproducibility was achieved in duplicate experiments, with typical deviations in conversions being $\pm 2\%$.

Initial conversions were determined by extrapolating the data to zero time on stream. The data shown in Figure 6 indicate that guaiacol conversion was higher with HY zeolite (0.11) than with Pt/ γ - Al_2O_3 (0.08) at WHSV ≈ 20 g of reactant (g of catalyst) $^{-1}$ h $^{-1}$. Selectivities of the two catalysts illustrated by data representing the most abundant products formed from guaiacol are compared in Table 5.

HY zeolite underwent deactivation more rapidly than Pt/ γ - Al_2O_3 under similar conditions, with a decrease in conversion of approximately 50% within 1 h on stream.

3.3. Comparison of Pt/ γ - Al_2O_3 and HY Zeolite Catalysts. The results allow for a comparison of the two catalysts, specifically allowing for an identification of the reactions catalyzed by the acidic function, namely, methyl group transfers, and those catalyzed by the metal function, including HDO and hydrogenation. Alumina supports, known to be acidic,^{24,25} are catalysts for reactions involving carbocationic intermediates. The data obtained from the guaiacol conversion catalyzed by HY zeolite identify the class of reaction, transalkylation, catalyzed by solid acids, and we therefore attribute such reactions occurring in the presence of Pt/ γ - Al_2O_3 to the acidic γ - Al_2O_3 . The data show that the metal

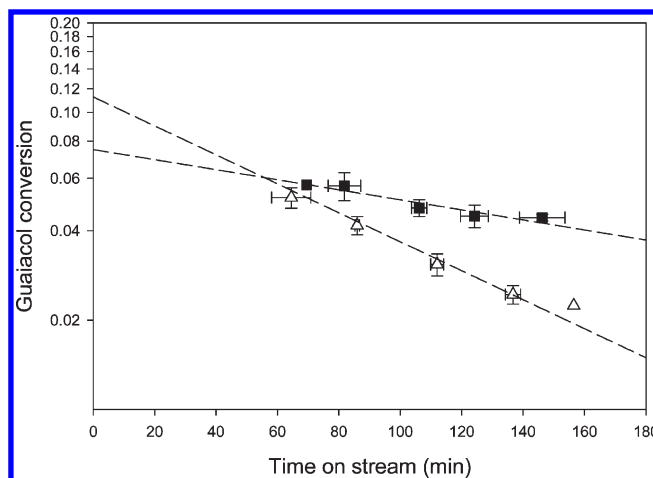


Figure 6. Conversion of guaiacol at 573 K catalyzed by (■) Pt/ γ - Al_2O_3 at WHSV = 19.8 ± 0.1 g of guaiacol (g of catalyst) $^{-1}$ h $^{-1}$ and (△) HY zeolite at WHSV = 20.0 ± 0.1 g of guaiacol (g of catalyst) $^{-1}$ h $^{-1}$. The feed to the reactor containing the former catalyst was 30% H_2 /70% N_2 , and the feed to the reactor containing the latter catalyst was N_2 .

function is necessary for the other observed reaction classes and specifically for oxygen removal from guaiacol under our conditions.

4. DISCUSSION

4.1. Catalytic Reactions of Guaiacol and Reaction Network Analysis. In the conversion of guaiacol catalyzed by Pt/ γ - Al_2O_3 , anisole and phenol formed as primary products along with water and methanol, and these products suggest the occurrence of HDO taking place via cleavage of the C–O bond α to the aromatic ring in guaiacol. This deoxygenation by removal of the methoxy group is more favorable than deoxygenation by removal of the hydroxyl group, as indicated by the higher selectivity for phenol formation than for anisole formation (Tables 2 and 3). As shown in Figure 3, the results also suggest that catechol can be produced in multiple reactions, including transalkylation reactions (e.g., being formed along with veratrole or methylguaiacols), and cleavage of the C–O bond β to the aromatic ring at the methoxy group. Low selectivities for the formation of veratrole and methylguaiacol relative to catechol imply that catechol is produced principally in the hydrogenolysis reaction. The formation of the primary products 3-methylcatechol and methylguaiacols indicates that intramolecular transalkylation (intramolecular rearrangement of guaiacol) and intermolecular transalkylation (transalkylation involving catechol and guaiacol) are reactions that occur in parallel.²⁶

Consistent with results characterizing the conversion of anisole,²² the data indicate methyl group transfers, and the data characterizing the HY-zeolite-catalyzed conversion imply that these reactions take place on acidic surfaces, which we infer to include the Al_2O_3 support of the Pt/ γ - Al_2O_3 catalyst.

The results show that, among the methylguaiacols, only 3-methylguaiacol and 6-methylguaiacol were formed in substantial yields (4-methylguaiacol and 5-methylguaiacol were observed only as trace products). We suggest that this selectivity is related to the interaction of guaiacol molecules with the Al_2O_3 surface. One might expect that, via bonding at the methoxy or hydroxyl group of guaiacol, methoxyphenate or hydroxyphenate species were formed, respectively,²⁷ facilitating methylation

Table 5. Products of Conversion of Guaiacol Catalyzed by Pt/ γ -Al₂O₃ and HY Zeolite (Liquid Product Streams)^a

product	selectivity to product in reaction catalyzed by Pt/ γ -Al ₂ O ₃ with H ₂ in feed ^b	selectivity to product in reaction catalyzed by Pt/ γ -Al ₂ O ₃ without H ₂ in feed ^c	selectivity to product in reaction catalyzed by HY zeolite without H ₂ in feed ^c
benzene	0.002		
toluene	0.0004		
anisole	0.009		
cyclohexanone	0.023		
phenol	0.3		
o-cresol	0.03		
veratrole	0.02	0.2	0.3
3-methylguaiacol	0.01	0.03	0.02
4-methylguaiacol			0.07
5-methylguaiacol			0.04
6-methylguaiacol	0.03	0.1	0.05
catechol	0.4	0.6	0.5
3-methylcatechol	0.1	0.06	0.03

^aData were extrapolated to zero time on stream and, thus, represent approximate initial selectivities determined at a WHSV of 20 g of guaiacol (g of catalyst)⁻¹ h⁻¹, a pressure of 140 kPa, and a temperature of 573 K. ^bThe gas feed rate for 30% H₂/70% N₂ was 100 mL/min, and the feed molar ratio of H₂ to the organic reactant was 10. ^cThe gas feed rate for 100% N₂ was 100 mL/min.

preferentially at the positions next to these groups and leading to the formation of 3-methylguaiacol and 6-methylguaiacol but not 4-methylguaiacol and 5-methylguaiacol.

The formation of cyclohexanone, a hydrogenation product in the reactions catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ (Table 1), is consistent with recent investigations of phenol conversion catalyzed by other supported metals; cyclohexanone was observed as an intermediate in the deoxygenation of phenol catalyzed by Pd/C⁴ and NiMo/ γ -Al₂O₃.²⁸

The reaction network presented in Figure 5 contains more detail than has been reported previously for the catalytic conversion of prototypical compounds of pyrolysis bio-oils,^{4,5,23,29–32} and the new results are broadly consistent with the earlier reports of guaiacol conversion catalyzed by supported metals.^{16,32} The classes of reactions indicated by our data, including HDO, hydrogenation, and transalkylation, account for the products observed in the earlier work, but the details of the reported product distributions differ from ours because the catalysts and operating conditions were different.

For example, in work with a Pt/ZrO₂ catalyst, Gutierrez et al.³² reported the conversion of guaiacol at 373 K and 8 MPa. Their products included some observed in our work, including veratrole, cyclohexanol, and cyclohexane, and some not observed in our work, including 1,2-dimethoxycyclohexane. Our reaction network (Figure 5) suggests that this compound was formed in a sequence of hydrogenation reactions as the aromatic ring in intermediate compounds (e.g., veratrole) became saturated.

The observations by Gutierrez et al. of higher yields of deoxygenated products (cyclohexanol, ~60 mol %; cyclohexane, ~1 mol %) than we found suggest the importance of the higher H₂ partial pressures that they used, but we do not exclude the influence of the lower reaction temperatures.

4.2. Influence of Operating Conditions. The product distribution in guaiacol conversion is affected substantially by temperature. The data show that higher temperatures result in lower selectivities for most products formed by HDO and in higher selectivities for products formed by transalkylation. However, the data do not allow for a simple general statement regarding how oxygen removal selectivity is affected by the temperature because of the occurrence of sequential reactions.

Gutierrez et al.³² suggested that the availability of hydrogen on the catalyst surface affected reactions with H₂. At higher temperatures, the coverage of the catalyst surface by hydrogen is expected to decrease,³³ which could lead to a decrease in the rates of HDO and hydrogenation with an increasing temperature. This suggestion is consistent with our observation of lower selectivities to deoxygenated products (including anisole and phenol) and hydrogenated products (including cyclohexanone) at the higher temperatures. The choice of the reaction temperature for optimum oxygen removal might be determined in part by the temperature dependence of the coverage of the catalyst surface.

Not surprisingly, the selectivity is affected significantly by the H₂ partial pressure. At a given temperature, oxygen removal reactions are significantly favored by higher H₂ partial pressures, as indicated by the selectivities for benzene, toluene, anisole, and phenol (Table 3). No deoxygenation was observed in the absence of H₂ in the feed. The results underline the importance of H₂ as a co-reactant for deoxygenation and point to the likely advantage of high-pressure operation when deoxygenation is a goal.

4.3. Importance of Metal Function for Oxygen Removal. The guaiacol conversion catalyzed by HY zeolite was similar to that observed with Pt/ γ -Al₂O₃ in the absence of H₂; transalkylation was the only kinetically significant reaction class. The pattern is consistent with those observed for anisole conversion catalyzed by HY zeolite²² and the zeolite HZSM-5.²³ Several other products expected to be formed in sequential transalkylation reactions (that were not observed when Pt/ γ -Al₂O₃ was used in the presence of H₂) were also observed (e.g., methylveratroles and dimethylbenzenediols), presumably as a consequence of the acidity of the HY zeolite. The results highlight the importance of the metal function in Pt/ γ -Al₂O₃ in hydrogenolysis, HDO, and hydrogenation. Bifunctional catalysts would offer further good opportunities for control of the selectivity.

5. CONCLUSION

An extensive reaction network for the conversion of guaiacol catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ has been developed, including rate constants for the formation of primary products.

Three major classes of reactions occurred: hydrogenolysis (including HDO), hydrogenation, and transalkylation. We infer that the metal function catalyzed the two former reaction classes and that the alumina support catalyzed the latter. Higher temperatures favored transalkylation, and the selectivity for HDO increased substantially as the H₂ partial pressure increased from 41 to 127 kPa. Without H₂, oxygen removal was negligible. These results suggest that an appropriate catalyst (e.g., a noble metal) and high H₂ partial pressures may be optimal for the catalytic oxygen-removal process.

The results presented here may provide a foundation for understanding the conversion of more complex mixtures of oxygen-containing compounds, such as those derived from lignin.

■ ASSOCIATED CONTENT

S Supporting Information. Product analysis methodology, gas chromatography instrumentation, mass balance data, and calculations of kinetics parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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