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Vapor-Phase Hydrodeoxygenation of Guaiacol to Aromatics over Pt/HBeta: Identification of the Role of Acid Site and Metal Site on the Reaction Pathway

Lei Nie,[a,b] Bo Peng,[b] and Xinli Zhu*[a]

Abstract: A comparative study of hydrodeoxygenation of guaiacol, a phenolic compound derived from lignin fraction of biomass with both hydroxyl and methoxyl functional groups, was performed on HBeta, Pt/SiO_2 and Pt/HBeta at 350 °C and atmospheric pressure. The reaction pathway and the role of acid site and metal site were studied. Acid sites catalyze transalkylation and dehydroxylation reactions, producing mono-hydroxyl phenolics (phenol, cresols and xylenols) as the major final products. Pt sites catalyze demethylation reaction resulting in catechol as the primary product, which can either be deoxygenated to phenol followed by phenol to benzene, or decarbonylated to cyclopentanone and further to butane. The close proximity of Pt and acid site in bifunctional Pt/HBeta improves transalkylation and deoxygenation (or dehydroxylation) reactions while significantly inhibits demethylation and decarbonylation reactions, producing aromatics as the major final products with a total yield > 85%. Both activity and stability of bifunctional Pt/HBeta during hydrodeoxygenation of guaiacol are improved compared to HBeta and Pt/SiO_2. The addition of water to the feed further improves the activity and stability via hydrolysis of O-CH_3 bond of guaiacol on acid site and removing coke around Pt.

Introduction

Production of transportable liquid fuels from renewable and abundant biomass may provide a sustainable energy process that reduces both the dependency on fossil fuels and CO_2 emissions. Bio-oil derived from biomass via fast pyrolysis is composed of many fragments that contain significant amount of oxygen.[1,2] Efficient oxygen removal and building up the carbon chain of these oxygenates into target molecules with desired fuel properties rely on novel catalyst with appropriate operating conditions. The high complexity of bio-oil makes model compound study a crucial role on obtaining preliminary understanding of the catalytic chemistry.

As lignin is a major component (up to 30%) of biomass, phenolic compounds (phenol, guaiacol, syringol and their derivatives) derived from lignin represent an important fraction of bio-oil. Hydroxyl (–OH) and methoxyl (–OCH_3) groups connected to the phenyl ring are the major functional groups of phenolics (Scheme 1 in reference [3]). Compared to other groups of molecules in bio-oil, phenolics have relatively long carbon chain and low oxygen content.[1-4] A direct deoxygenation process of phenolics could produce gasoline range hydrocarbon molecules. However, the delocalization effect of the lone pair electron of O (in both hydroxyl and methoxyl) onto the π bond of phenyl ring strengthens the $C_{aromatic}$-O bond, leading to a significantly higher activation barrier for oxygen removal from phenolics than that for aliphatic alcohols.[5] Hence, development of active and stable catalyst for conversion of phenolic-rich bio-oil remains a challenge.

Guaiacol (2-methoxyphenol) is one of the most abundant phenolics in bio-oil.[4,6] It has both hydroxyl and methoxyl functional groups. Therefore, it has been used as a model compound representing phenolics in bio-oil and been extensively studied over various catalytic materials.[6-11] Among those catalysts, bifunctional zeolite-supported metal catalysts have attracted significant attention.[12-29] Most of the works on hydrodeoxygenation (HDO) of guaiacol over metal/zeolite catalysts were performed in liquid phase, *i.e.* at low temperature (< 250 °C) and high pressure of H_2 (several MPa).[14,17-20] Under these conditions, the reaction proceeds through hydrogenation-deoxygenation (HYD) path in a bifunctional manner: saturation of the phenyl ring on metal sites, followed by dehydration on acid sites.[12,13] The methoxyl group is lost as methanol either by demethoxylation on metal site or hydrolysis on acid site.[14] The advantage of liquid phase HDO is that it may be coupled in a single step with liquefaction of biomass.[30-32]

On the other hand, relatively fewer works have been performed in vapor phase at high temperatures (> 250 °C) and atmospheric pressure on zeolite and metal/zeolite catalysts to simulate direct upgrading of phenolics right after pyrolysis before its condensation. Co-conversion of guaiacol with n-heptane over acidic HZSM-5 and HY zeolites were investigated at 450 °C under fluid catalytic cracking conditions.[33] It was found that hydrogen transfer is the major reaction path to produce methane and phenol. And guaiacol has a negative effect on heptane conversion due to coke formation. Foo et al. reported HDO of guaiacol on HBEA and Pt/HBEA at 400 °C and atmospheric pressure.[34] Isomers of methylcatehol were found as the major products on bare HBEA with low conversion of <5%. A wide range of products was observed on Pt/HBEA with only 3-5% was deoxygenated to aromatics. Similarly, on Fe-Ni/HBeta at 250-400 °C and atmospheric pressure,[29] and Ni-Fe/zeolite catalysts at 350-450 °C and 1.5-17 bar,[35] low degree of deoxygenation to aromatics was achieved. These preliminary

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works suggested guaiacol undergoes transalkylation and demethylation followed by deoxygenation to benzene and toluene. However, cyclopentanone was surprisingly found to be an important product besides catechol and phenol over Pt/MgO [36,37] and Pt/C [38] catalysts at 300 °C and atmospheric pressure. It is evident that very different product distributions were observed on metal, zeolite, and metal/zeolite catalysts at different temperatures. Although significant efforts have been made, the complex product distributions as a result of multiple functional groups (-OH, -OCH_3, phenyl ring) of guaiacol conversion on different active sites at different temperatures makes rigorous analysis of the reaction pathway on metal/zeolite catalysts not available. Furthermore, identification of the individual role of metal and acid site of zeolite is essential to understand the reaction pathway and to design efficient catalytic process.

In this work, we compared the conversion of guaiacol on HBeta, Pt/SiO_2, and Pt/HBeta catalysts at identical reaction conditions (350 °C and atmospheric pressure), to explore the reaction pathway and to identify the role of acid site and metal site in the bifunctional Pt/HBeta catalyst. Such optimized reaction conditions were applied in order to avoid non-catalytic thermal decomposition of guaiacol at higher temperatures, or complete hydrogenation of the phenyl ring at lower temperatures.[39,40] To investigate the reaction pathway, the conversion of possible intermediates of catechol and cyclopentanone was also studied. Compared to anisole (–OCH_3 group only) and m-cresol (–OH group only),[3,41,42] very different reaction chemistry was found for guaiacol (both –OH and –OCH_3 groups) over monofunctional acidic zeolite or metallic Pt/SiO_2. Besides transalkylation reactions observed for anisole and m-cresol,[3,41,42] dehydroxylation of one –OH is important for guaiacol and catechol feeds over bare HBeta. While no decarbonylation reaction was observed for feeds of anisole and cresol on Pt/SiO_2,[3,41,42] decarbonylation reaction was a major reaction for guaiacol. The close proximity between metal site and acid site in bifunctional Pt/HBeta inhibits the decarbonylation reaction on bare Pt while dramatically improves deoxygenation (or dehydroxylation) on bare Pt site or bare acid site, resulting in aromatics as the major final products. Aromatics of benzene, toluene, xylenes and C_{9+} with yield higher than 85% were achieved at low space time on bifunctional Pt/HBeta catalyst. The alkyl-aromatics have high octane numbers, which can be used as blends for gasoline.

Results and Discussion

Catalyst Characterizations

The detailed characterizations of the catalysts have been reported in previous works.[3, 39] Loading of 1% Pt has little effect on the structure, acidity and surface area of the supports. The dispersions of Pt (*i.e.*, the percentage of surface Pt atoms of the total Pt atoms loaded) on SiO_2 and HBeta are 20% and 71%, corresponding to average Pt size of 5.5 and 1.6 nm, respectively.[3] The TEM observation revealed that a large fraction of Pt particles is located inside of the micropores of HBeta. Brønsted acid site (BAS) densities of HBeta and Pt/HBeta, measured by IPA-TPD, are 695 and 674 μmol/g, respectively.[39] These values are in good agreement with that estimated from the Si/Al ratio of 19, indicating that the samples mainly contain BAS of bridging Al-OH-Si. The slight reduced BAS density originated from Pt loading suggests that Pt and BAS sites are in close proximity. The molar ratio of BAS to surface Pt site (estimated by CO chemisorption) is ca. 17.

Guaiacol conversion over HBeta

The conversion of guaiacol (Gua) as a function of W/F and the major products evolution (plotted versus guaiacol conversion) over zeolite HBeta are shown in Figure 1A and B, respectively. The conversion of guaiacol increased linearly to 36% for W/F less than 1.5 h. However, it steeply increased to 100% when W/F increased to 2 h.

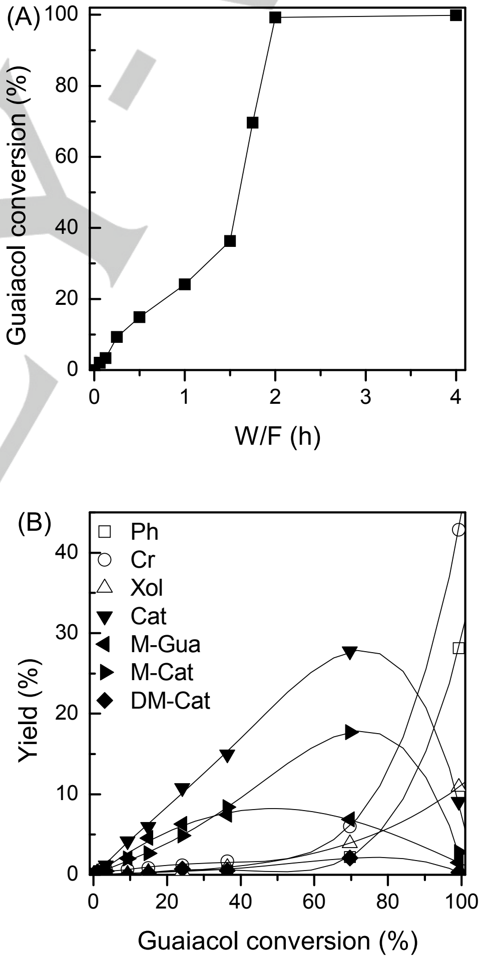
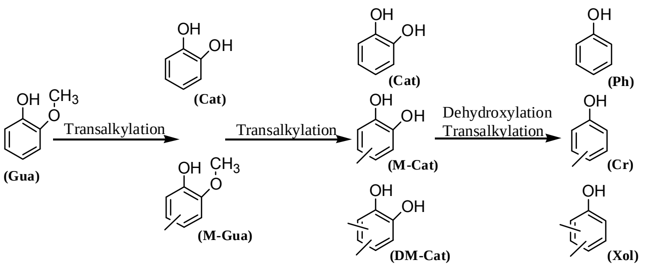


Figure 1. Guaiacol conversion over HBeta: (A) Effect of W/F on guaiacol conversion; (B) major products distribution as a function of guaiacol conversion. Reaction conditions: T = 350 °C, P = 1 atm, H_2/guaiacol = 50, TOS = 0.5 h for each W/F.

When guaiacol conversion is close to zero, only catechol (Cat) and methylguaiacols (M-Gua, 4 isomers) show notable yield, accompanied with negligible product of veratrole (1,2-dimethoxybenzene, yield < 1%). The yield of catechol is equal to the sum of those of methylguaiacols and veratrole, indicating that transalkylation reactions between guaiacol molecules are the primary reaction (C-alkylation to methylguaiacols and minor O-alkylation to veratrole) (Scheme 1). The observed significantly lower O-alkylation than C-alkylation may be a result of the relatively larger size of veratrole than that of methylguaiacol, leading to low diffusion rate of veratrole inside the pore channel of HBeta (0.67 nm). In addition, the $–CH_3$ in $–OCH_3$ is easily activated in transalkylation reactions.[38,39] Therefore, once veratrole is formed inside the pores, it quickly converts by denoting $–CH_3$.



Scheme 1. Major reaction path of guaiacol conversion over HBeta.

At intermediate conversions, the formation of methylcatechols (M-Cat, 2 isomers) and dimethylcatechols (DM-Cat, 3 isomers) at the expense of methylguaiacols is evidenced. A number of transalkylation reactions could account for such product evolutions: (1) M-Gua and Cat to two M-Cats; (2) Gua and Cat to another Cat and M-Cat; (3) M-Gua and M-Cat to another M-Cat and DM-Cat. The yield of dimethylcatechols in guaiacol conversion is significantly lower than the corresponding xylenols (dimethylphenols) in anisole conversion.[3,41] This could be a result of shape selectivity effect of the zeolite HBeta on products distribution, *i.e.*, the larger size of dimethylcatechols than dimethylphenols makes the formation of dimethylcatechols less favorable in the confined zeolite pore channel.[3,41] The transition state of bimolecular transalkylation intermediate is expected to have larger size than that of monomolecular isomerization. Here, the product distributions are similar to bimolecular transalkylation instead of monomolecular isomerization. Thus, the observed transalkylation may be attributed to the dissociation of $O–CH_3$ to leaving $–CH_3$ on the surface of zeolite. The $–CH_3$ left over the catalyst surface is preferentially reacting with another molecular through C-alkylation.[41]

At conversions >80%, yields of cresols (methylphenols, Cr, 3 isomers), phenol (Ph) and xylenols (Xol, 6 isomers) increase at the expense of Cat, M-Gua, M-Cat, DM-Cat. At such high conversion levels, the dehydroxylation reactions catalyzed by BAS of zeolite take place: (1) Cat to Ph; (2) M-Cat to Cr; (3) DM-Cat to Xol. However, one should note that the order of yields before dehydroxylation (Cat > M-Cat > DM-Cat) does not follow the corresponding order of dehydroxylated products (Cr > Ph > Xol). Such difference implies that besides the direct dehydroxylation, the transalkylation takes place simultaneously between the reactant (Gua), intermediate products (M-Gua, M-Cat, and Cat), and the dehydroxylated products (Ph and Cr). It is as expected that the activated $–CH_3$ on the surface preferentially alkylates the relatively smaller molecules due to shape selectivity of the zeolite. For example, phenol would be easier to be alkylated than catechol or methlycatechol, leading to different distributions in phenols (Ph, Cr, Xol) and catechols (Cat, M-Cat, DM-Cat).

The dehydroxylation may evolve protonation of the O atom of a hydroxyl of catechols over BAS, breaking the C-O bond, forming water and hydroxyphenyl ions on the surface. Hydrogenation of the hydroxyphenyl ions (to Ph, Cr, Xol) can take place by hydride transfer reactions, where coke precursors (phenolic oligomers) formed in the channel of zeolite may act as the source of hydride donor.

Small amounts (<1%) of aliphatic hydrocarbons and aromatics (xylenes, toluene, benzene, and C_{9+}) are produced when the conversion is approaching 100%. Further increase in W/F (> 2 h) when guaiacol conversion is 100% leads to a slight increase of aromatics' yield to < 5%. The formation of aromatics may be resulted from further dehydroxylation of phenols (Ph, Cr, Xol). In comparison with previous studies of cresol and anisole conversion on acid zeolite,[3,41,42] it is suggested that the dehydroxylation of catechols (Cat, M-Cat, DM-Cat) to phenols (Ph, Cr, Xol) has much lower activation barrier than further dehydroxylation of phenols to aromatics.

Table 1. Products distribution during catechol and cyclopentanone conversion over HBeta, Pt/SiO_2 and Pt/HBeta catalysts. [a]

Catechol						Cyclopentanone	
HBeta		Pt/SiO_2		Pt/HBeta		Pt/SiO_2	
Product	Yield (%)	Product	Yield (%)	Product	Yield (%)	Product	Yield (%)
Benezene	0.2	C_4	15.8	C_1	0.05	C_{1-3}	0.1
Phenol	5.5	Cyclopentane	0.2	C_2	0.1	C_4	22.9
Catechol	87.8	Benzene	0.8	C_3	0.2	C_{5+}	2.9
Heavies	6.5	Cyclohexene	0.2	C_4	3.4	Cyclopentane	16.9
		Cyclopentanone	16.4	C_5	1.4	Cyclopentanol	1.3
		Phenol	28.2	Cyclopentane	5.4	Cyclopentanone	52.7
		Catechol	36.4	C_{6+}	3.4	Others	1.8
				Benzene	40.8		
				Cyclohexane	0.8		
				Cyclopentanol	1.0		
				Cyclopentanone	0.1		
				Phenol	32.6		
				Catechol	7.0		
				Heavies	1.2		

[a] Reaction conditions: T = 350 ºC, P = 1 atm, H_2/organic feed = 50, TOS = 0.5 h, W/F = 1.75 h for catechol feed on HBeta, W/F = 0.25 h for other catalysts and feeds.

In summary, both transalkylation (at full W/F range) and dehydroxylation (only at high W/F) reactions are the main chemistry for guaiacol conversion over the zeolite HBeta (Scheme 1). To confirm whether the zeolite acid site is able to catalyze the dehydroxylation of phenolics, aqueous catechol was fed onto the zeolite HBeta at a W/F of 1.75 h. Phenol is the major product with trace amount of benzene produced (Table 1). The result clearly demonstrates that catechol undergoes dehydroxylation under current reaction condition. The significantly lower yield of benzene than phenol suggests that, again, catechol is easier to be dehydroxylated to phenol. But sequentially phenol is difficult to be dehydroxylated to benzene. The yield of unidentified heavy products (oligomers) shows comparable yield as that of phenol, suggesting that condensation reaction occurs. These heavy products could act as the coke precursors and hydride donors. The former deactivates the catalyst quickly, while the latter hydrogenates the phenyl or hydroxyphenyl species formed from phenolics' dehydroxylation.

Guaiacol conversion over Pt/SiO$_2$

Compared to guaiacol conversion on HBeta, the conversion curve is much smoother on Pt/SiO$_2$ (Figure 2A). Guaiacol was 100% converted at a W/F of 0.5 h, however, 100% oxygen removal was not achieved even at a W/F of 4 h.

The major products evolution as a function of W/F is shown in Figure 2B. To demonstrate the primary reactions, the major products yield is drawn as a function of guaiacol conversion for its conversion less than 100% (W/F < 0.5 h), as shown in Figure 2C. When the conversion is close to zero (Figure 2C), equal amounts of catechol (Cat) and phenol are produced, accompanied with evolution of methane (C$_1$). This might imply that demethylation to catechol and demethoxylation to phenol are the parallel primary reactions over Pt/SiO$_2$ (Scheme 2). However, notable amount of methanol was not detected, suggesting that direct demethoxylation can be neglected. Furthermore, ~15% methane is produced when guaiacol conversion is 100% (Figure 2B), which is in good agreement with the value estimated from demethylation of guaiacol, suggesting that the formation of methane is mainly from demethylation (hydrogenolysis of O-CH$_3$) of guaiacol. These results indicate that direct removal of methoxyl from guaiacol to phenol and methanol is a minor path. Therefore, demethylation of guaiacol to catechol and subsequent fast deoxygenation to phenol are the primary reactions (Scheme 2). It should be noted that the yield of anisole (methoxybenzene) is less than 2% under all tested conditions, suggesting that direct hydroxyl removal from guaiacol is a minor path. Hence, direct oxygen removal from either hydroxyl or methoxyl of guaiacol is not favored over Pt/SiO$_2$, as compared to hydrogenolysis of O-CH$_3$ bond (demethylation) of guaiacol to catechol and methane. Because of the delocalization effect between the lone pair electron of O and the π bond of phenyl ring, the bond of C$_{aromatic}$-O is much stronger than that of O-CH$_3$ bond. Thus, the initial step of guaiacol conversion is demethylation on Pt. This result is consistent with recent DFT calculations, showing that the removal of –CH$_3$ is the first step of guaiacol conversion over metal surface, such as Pt and Ru.[43-45]

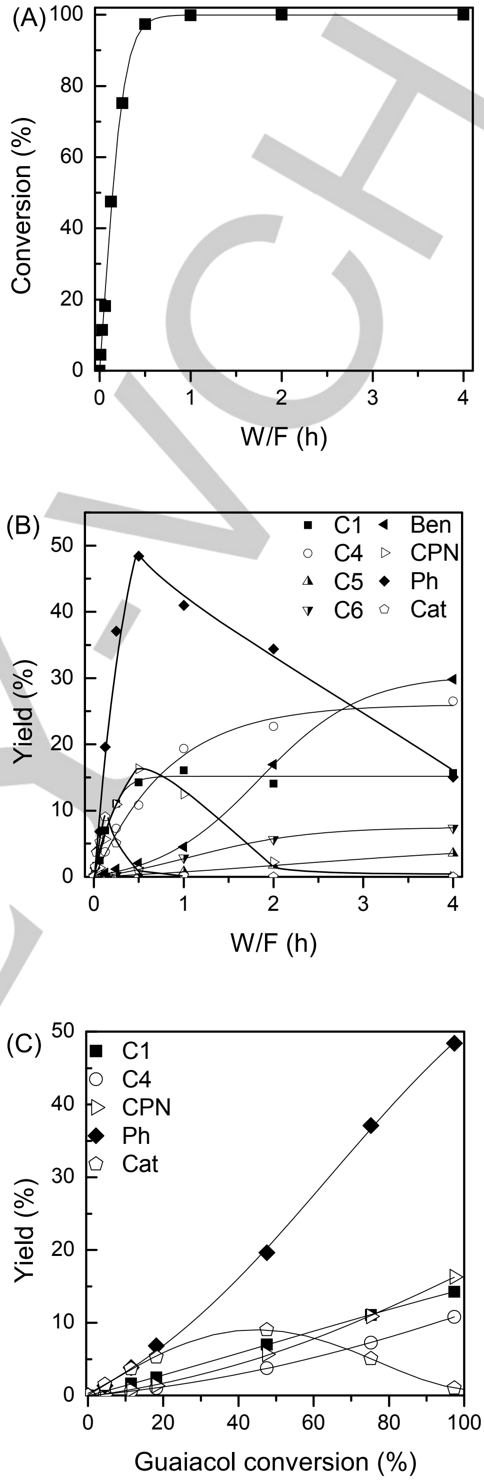
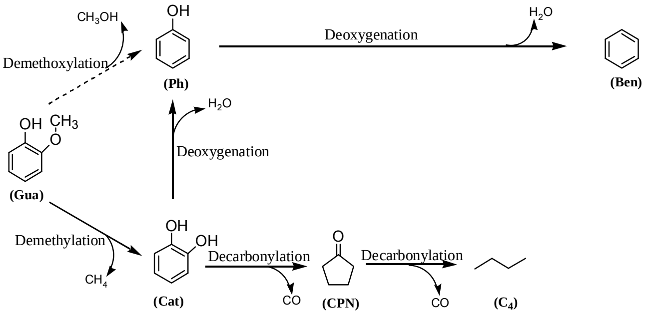


Figure 2. Guaiacol conversion over Pt/SiO$_2$: (A) Effect of W/F on guaiacol conversion; (B) major products distribution as a W/F; (C) Major products distribution as a function of guaiacol conversion for guaiacol conversion < 100%. Reaction conditions: T = 350 ºC, P = 1 atm, H$_2$/guaiacol = 50, TOS = 0.5 h for each W/F.

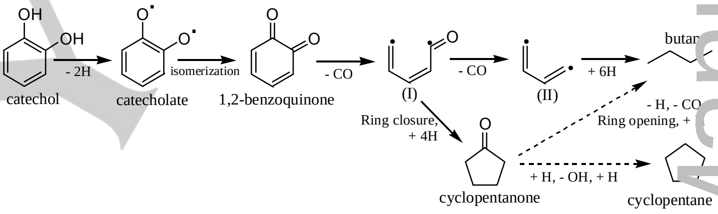


Scheme 2. Major reaction path of hydrodeoxygenation of guaiacol over Pt/SiO_2.

The yield of phenol continues increasing as guaiacol conversion, while catechol yield starts to decrease at intermediate conversion, accompanied by the appearances of cyclopentanone (CPN) followed by C_4 (Figure 2C). When the yield of catechol drops to zero at W/F of 0.5 h, the yields of cyclopentanone and phenol reach their maximum (Figure 2B). Further increase of W/F to ~2 h leads to the yield of cyclopentanone decreases to zero, while C_4 increases to ~26% (Figure 2B). On the other hand, benzene starts increasing at W/F of 0.5 h at the expense of phenol. At the highest W/F tested (4 h), phenol was not fully deoxygenated to benzene. The yield of cyclohexanone + cyclohexanol is less than 1%, implying full hydrogenation of the aromatic ring appears to be a minor path. C_5 and C_6 paraffins are produced at higher W/F (Figure 2B), probably from hydrogenation and cracking of benzene and cyclopentanone. Such product evolution indicates two parallel reaction paths (Scheme 2): (1) catechol direct deoxygenation to phenol and then to benzene in sequence, and (2) catechol decarbonylation to cyclopentanone and further to C_4 (releasing CO in each step) in sequence. The yield ratio of (Ben+Ph)/C_4 at W/F of 4 h is 9/5, which implies the ratio between the apparent direct deoxygenation path and the decarbonylation path. This ratio depends on the initial selectivity of phenol and cyclopentanone during catechol conversion.

To confirm the proposed reaction path, the intermediate products, catechol and cyclopentanone, were fed over Pt/SiO_2 catalyst under identical conditions. Catechol was mainly converted to phenol, cyclopentanone and C_4 (Table 1), indicating that two main reaction paths are in competition: direct deoxygenation of catechol to phenol and decarbonylation of catechol to cyclopentanone and further to C_4 (Scheme 2). This also confirms the initial fast conversion of the produced catechol to phenol during guaiacol conversion. Note that the yield of benzene is trace (Table 1), suggesting that deoxygenation of phenol to benzene is less reactive than decarbonylation of cyclopentanone to C_4 under current reaction conditions.

When cyclopentanone was fed onto Pt/SiO_2, C_4 and cyclopentane are the major products (Table 1), implying decarbonylation to C_4 and hydrogenation-hydrogenolysis to cyclopentane are the parallel major reaction paths. The conversion of intermediates on Pt/SiO_2 confirmed the proposed major pathway of guaiacol conversion (Scheme 2). The consecutive decarbonylation of catechol to cyclopentanone and butane may contain multiple steps, which is not clear so far. In an earlier work, Sakai and Hattori reported that pyrolysis of catechol at 500-600 °C in He or H_2 atmosphere primarily results in the formation of C_4 (mainly butadiene) and CO through decarbonylation reactions.[46] Later, Arends et al. studied decomposition of anisole in hydrogen at 520-750 °C. They found that anisole and phenol could be decarbonylated to cyclopentadiene, and suggested several radical reactions.[47] These observations suggest that decarbonylation of catechol is thermodynamically and kinetically possible over a catalyst. Recently, Nimmanwudipong et al. found that cyclopentanone is an important product in guaiacol conversion on a Pt/MgO catalyst at 300 °C.[36,37] They suggested that the reaction involves sequential reactions of ring hydrogenation, ring opening and closing, decarbonylation. And the basic support plays an important role on the formation of cyclopentanone. Since cyclopentanone and butane are also observed as important intermediate and final products in the conversion of guaiacol on inert silica supported Pt catalyst in present work, it thus can be concluded that the decarbonylation reaction is mainly related with metallic Pt itself instead of basic or inert support.



Scheme 3. Possible reaction mechanism of hydrodeoxygenation of catechol over Pt/SiO_2.

Scheme 3 shows possible surface steps for decarbonylation of catechol on Pt surface. Catechol is adsorbed flatly on Pt surface through its phenyl π bond. Similar to phenol dissociation,[48] the dissociation of catechol leads to catecholate formation on the surface,[43-45] which could be further isomerized to 1,2-benzoquinone [49] with carbonyl groups away from the surface. Cleavage of two C-C bonds leads to CO and surface species I. Further cleavage of C-C bond results in surface butadiene (species II), which is quickly hydrogenated to butane. Alternatively, the species I could go through ring closure and hydrogenation to cyclopentanone. Once cyclopentanone is formed and desorbed from the surface, the decarbonylation requires multiple steps including: dehydrogenation and adsorption through the cyclopenta-carbon ring on the surface, breaking the two C-C bonds releasing CO, and finally hydrogenation to butane. Such reaction pathway was confirmed by using cyclopentanone as the reaction feed. This process must be competed by the adsorption of cyclopentanone on the surface through its carbonyl group, followed by hydrogenation of carbonyl group, hydrogenolysis of the C-OH bond, and forming cyclopentane as the final product. It is evident that decarbonylation of species I is easier than that for adsorbed cyclopentanone, since the former includes cleavage of one C-C bond while the latter requires two. This difference may result in the different product distribution when catechol and cyclopentanone were used as reaction feed, respectively.

Note that a recent report suggested that the decarbonylation of catechol starts with hydrogenation of the phenyl ring over Pt/C.[38] However, in the current work, hydrogenation is thermodynamically constrained over group VIII metals when temperature is > 350 °C at atmospheric pressure.[39,40] And dehydrogenation from carbon instead of hydrogenation normally favors C-C hydrogenolysis. Indeed, the proposed surface reaction is consistent with high vacuum temperature programmed desorption studies of phenol and anisole on Pt(111) surface, which showed that surface phenoxy could be decomposed to CO and hydrocarbon species (C_xH_y) in the absence of hydrogen.[50,51]

Guaiacol conversion over Pt/HBeta

In contrast to guaiacol conversion on HBeta, a smooth conversion curve as a function of W/F is achieved over Pt/HBeta catalyst (Figure 3A), with 100% conversion at a W/F of 0.5 h and complete deoxygenation at a W/F of 0.75 h. It is obvious that Pt/HBeta is much more active for deoxygenation than either Pt/SiO_2 or HBeta, since significantly lower W/F is required for complete deoxygenation.

At low W/F and conversions, the major oxygenated products observed on Pt/HBeta are similar to those on HBeta, including: catechol (Cat), methylguaiacol (M-Gua) isomers, methylcatechol (M-Cat) isomers, dimethylcatechol (DM-Cat) isomers, phenol (Ph), cresol (Cr) isomers, xylenol (Xol) isomers (Figure 3B). The yields of primary products (Cat, M-Gua, M-Cat) from transalkylation of guaiacol firstly increase to the maximum and then decrease to zero. At intermediate W/F, the yields of secondary products (Ph, Cr and Xol), produced from removal of a hydroxyl from the primary products (Cat, M-Cat, DM-Cat), increase to the maximum and then decrease to zero. Similar to over HBeta, the transalkylation plays an important role on the distribution of secondary products. For example, the yield of DM-Cat is low, while the yield of Xol (formed from DM-Cat by removing one hydroxyl) is high, which indicates that Xol is generated from transalkylation between $-CH_3$ donating compounds (Gua, M-Gua, veratrole) and Cr.

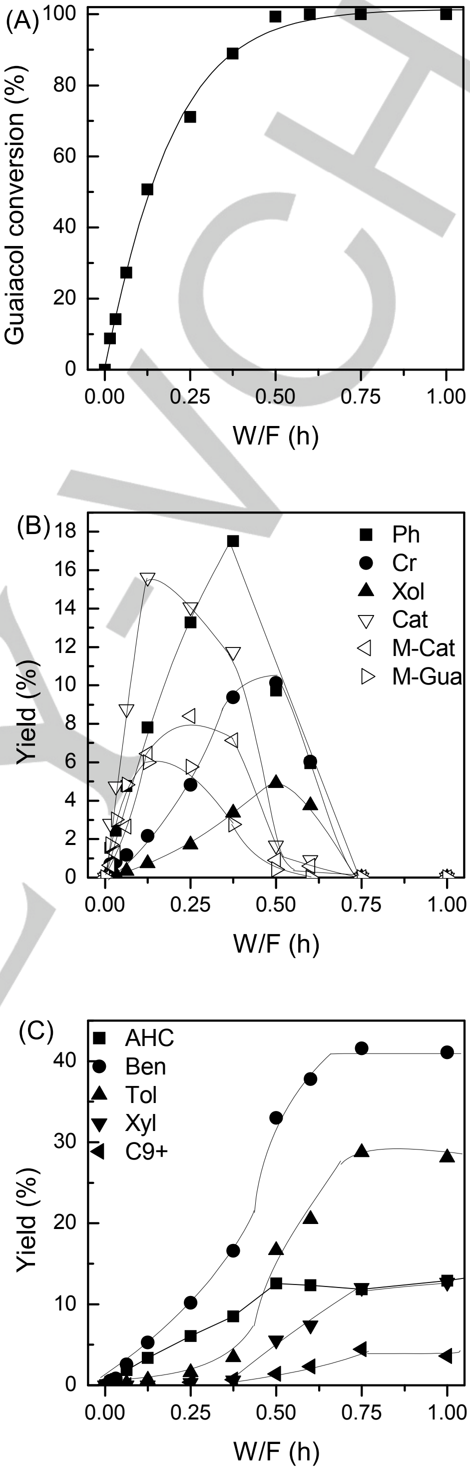


Figure 3. Guaiacol conversion over Pt/HBeta: (A) Effect of W/F on guaiacol conversion; (B) major oxygenated products distribution as a function W/F; (C) Major hydrocarbon products distribution as a function of W/F. Reaction conditions: T = 350 ºC, P = 1 atm, H_2/guaiacol = 50, TOS = 0.5 h.

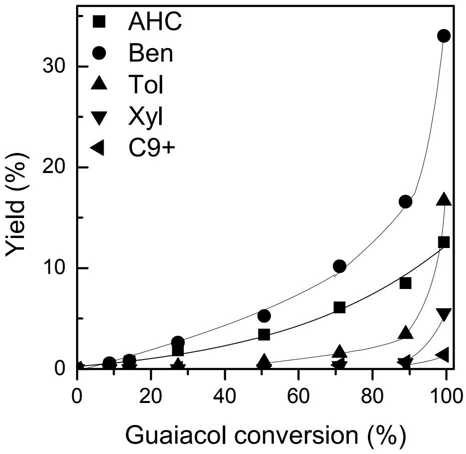
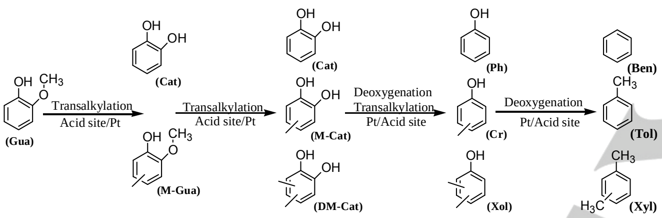


Figure 4. Effect of guaiacol conversion (< 100%) on aromatics distribution on Pt/HBeta. Reaction conditions: *T* = 350 °C, *P* = 1 atm, H_2/guaiacol = 50, TOS = 0.5 h.



Scheme 4. Major reaction path of hydrodeoxygenation of guaiacol over Pt/HBeta.

The fully deoxygenated products are benzene (Ben), toluene (Tol), xylenes (Xyl), multiple methylated aromatics (C_{9+}), as well as aliphatic hydrocarbons (AHC, sum of C_1 to C_6). As shown in Figure 3C, at low W/F, only the yield of benzene is noticeable among aromatics. However, its yield is significantly lower than the yields of the primary (Cat, M-Gua, M-Cat) and secondary (Ph, Cr, Xol) products. The yields of aromatics increase slowly with W/F before the secondary products (Ph, Cr, Xol) reach the maximum and increase significantly after the yields of secondary products reaching the maximum. It indicates complete deoxygenation of secondary products to aromatics is a tertiary reaction. Such conclusion is further verified by plotting the yields of aromatics as a function of guaiacol conversion (Figure 4). It is clear that the yields of aromatics only increase significantly when the guaiacol conversion is higher than 90%, at which the primary and secondary reactions are mostly converted to tertiary products. The complete deoxygenation is achieved at W/F of 0.75 h, with Ben, Tol, Xyl, and C_{9+} yields of 42%, 29%, 12% and 5%, respectively. The AHC may be produced from demethylation, hydrogenation, decarbonylation, ring opening, isomerization and cracking reactions. And the C_{9+} aromatics may be formed from hydrodeoxygenation of multiple-methylated phenols and/or alkylation of C_7/C_8 aromatics. Such products evolution indicates the major reactions evolved on Pt/HBeta catalyst are transalkylation over acid sites and apparent direct deoxygenation over Pt sites, as shown in Scheme 4.

Catechol, the major intermediate product in guaiacol conversion, was fed onto Pt/HBeta at a W/F of 0.25 h to verify the proposed major reaction path. It is seen that the major products are phenol and benzene (Table 1), suggesting removal of hydroxyls from phenyl ring by direct deoxygenation to phenol and subsequent to benzene is the major path over Pt/HBeta. Note that the yield of benzene is higher than phenol. Moreover, the benzene yield is also significantly higher than that on Pt/SiO_2 under the same conditions, indicating that Pt/HBeta is much more effective in removing both hydroxyls from catechol. In contrast to Pt/SiO_2, only small amounts of C_4 and cyclopentane were produced on Pt/HBeta (Table 1), which indicates that decarbonylation of catechol is a minor path. In other words, decarbonylation reaction on bare Pt was dramatically inhibited in bifunctional Pt/HBeta. On the other hand, compared to HBeta, the heavy products on Pt/HBeta were reduced significantly, suggesting that Pt helps hydrogenating surface carbon species and retards condensation reactions.

The major fully deoxygenated products (Ben, Tol, Xyl) of guaiacol conversion on Pt/HBeta are different from those (Ben, C_4 and C_1) on Pt/SiO_2. Apparently, being different from mainly demethylation and decarbonylation on Pt/SiO_2, the presence of BAS and the close proximity between BAS and Pt on Pt/HBeta led the reaction path to transalkylation and direct deoxygenation. For Pt/SiO_2, the Pt has an average particle size of ~5.5 nm,[3] which contains mainly Pt(111) surface. Guaiacol is preferably adsorbed on the Pt(111) as a flat configuration, *i.e.*, phenyl ring adsorption on a bridge site with –OH and –OCH_3 tilted away from the surface.[43,45] The reaction initiates with the hydrogenolysis of the weakest bond O-CH_3, resulting in the formation of CH_4 and catechol. Direct deoxygenation and decarbonylation may occur competitively for further conversion of surface catechol. Similar to dissociation of phenol on Pt,[48] the dissociation of catechol to catecholate (with O atoms away from the surface) and H atoms on the surface is readily to take place due to the low activation barrier.[43,45,48] The conversion of catecholate may facilitate the decarbonylation to cyclopentanone and further to C_4. In contrast, the Pt has a significantly smaller average particle size of ~1.6 nm for Pt/HBeta, and a notable fraction of Pt particles are located inside the micropores with close contact with BAS. In addition, the high BAS/Pt ratio of 17 suggests BASs are in large excess. A significant fraction of guaiacol is expected to adsorb on BAS through protonation of the O atoms and dissociate of the –CH_3 onto the surface, which is readily to react with a phenolic molecule nearby. The presence of Pt helps the hydrogenolysis of O–CH_3 of guaiacol and therefore accelerates the overall transalkylation reaction rate, as evidenced by a significantly lower W/F required for complete conversion of guaiacol on Pt/HBeta (0.5 h) than on bare HBeta zeolite (2 h). Besides deoxygenation on Pt, dehydroxylation of the first –OH from primary products (Cat, M-Cat, DM-Cat) by proton of BAS may also take place at relatively slower rates. In this case, the Pt plays a role on dissociation of H_2. And the activated H atoms diffuse to and regenerate the

BAS. On the other hand, these primary transalkylation products (Cat, M-Cat, DM-Cat) and secondary products (Ph, Cr, Xol) diffuse to Pt-BAS neighboring sites and adsorb on Pt through phenyl ring and on adjacent BAS by protonation of O of hydroxyl. With this configuration, one may expect the deoxygenation occurs in a bifunctional way: Pt hydrogenates the phenyl ring partially to reduce the deoxygenation barrier [52] and concerted dehydration readily happens on vicinal BAS,[3] forming aromatics directly or through further dehydrogenation. Since few large Pt particles exists in Pt/HBeta catalyst, the probability for catechol adsorption only on Pt(111) surface is low. Therefore, the decarbonylation to cyclopentanone and further to C_4 takes place to a minor extent. As a result, the decarbonylation reaction path was significantly reduced and not observable on Pt/HBeta.

Due to different reactivities of the two hydroxyl groups of catechol toward direct deoxygenation, and different reaction pathways (direct deoxygenation and decarbonylation) are involved during hydrodeoxygenation of guaiacol, it is not straight forward to direct compare the turnover frequency (TOF) of hydrodeoxygenation over Pt/SiO_2 and Pt/HBeta. Considering the facts the W/F for complete deoxygenation of guaiacol (~6 h and 0.75 h for Pt/SiO_2 and Pt/HBeta, respectively) and the dispersion of Pt in Pt/SiO_2 and Pt/HBeta, the roughly estimated TOF of hydrodeoxygenation of guaiacol is about 3 times higher for Pt/HBeta than for Pt/SiO_2. This improved deoxygenation activity could be ascribed to concerted participation of Pt and BAS in the reactions.

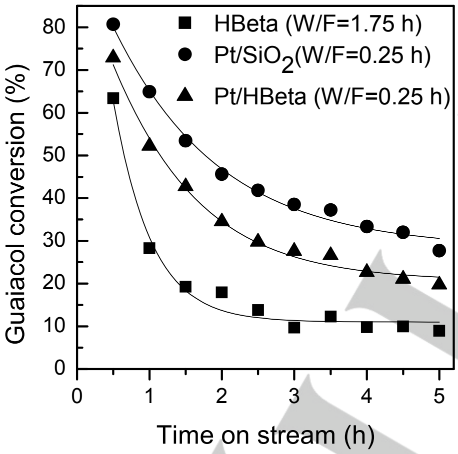


Figure 5. Stability of HBeta, Pt/SiO_2 and Pt/HBeta catalyst during hydrodeoxygenation of guaiacol. Reaction conditions: T = 350 °C, P = 1 atm, H_2/guaiacol = 50, W/F is 1.75, 0.25 and 0.25 h for HBeta, Pt/SiO_2, and Pt/HBeta catalysts, respectively, to achieve a similar initial conversion.

Stability test and coke analysis

Figure 5 compares the stability of different catalysts as a function of time-on-stream. The W/F for each catalyst was adjusted to achieve a similar initial conversion of guaiacol. The deactivation of HBeta catalyst was fast in the first hour, and maintained a stable and low conversion after 3 h reaction, suggesting that the BASs in micropores have been almost inaccessible by the reactant and only those on the external surface were available for the reaction. This could be a result of pore blockage due to the strong adsorption of guaiacol and its products. It has been suggested that guaiacol adsorbs on BAS through protonation of the O, and may form bidentate species on to two adjacent acid sites.[34] Pt/SiO_2 and Pt/HBeta deactivated with a similar rate, which is noticeable slower than that on bare HBeta. This indicates that addition of Pt to HBeta increased the stability of the catalyst, possibly due to improved deoxygenation activity (so that lower the concentration of phenolics in the stream) as well as hydrogenation of coke precursors that strongly adsorbed on BAS.

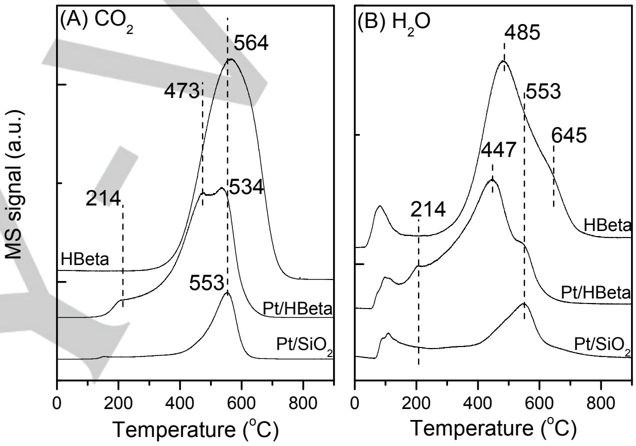


Figure 6. Temperature programmed oxidation profiles of (A) CO_2 and (B) H_2O evolution of spent HBeta, Pt/SiO_2 and Pt/HBeta catalysts. The spent catalyst samples were taken after stability test with reaction conditions shown in Figure 5.

The coke deposition on the spent catalysts was evaluated by temperature programmed oxidation. Note that both CO_2 and CO were produced on bare HBeta, while only CO_2 was produced on Pt/SiO_2 and Pt/HBeta. CO signal was calibrated and lumped with CO_2 signal for better comparison. As shown in Figure 6A, an intense CO_2 evolution peak was centered at 564 °C for bare HBeta, corresponding to 14.6 wt.% carbon. Its H_2O evolution profile (Figure 6B) showed a major peak at 485 °C and a shoulder peak at 645 °C. Comparison of CO_2 and H_2O profiles may indicate that two types of carbon species were deposited on the catalyst: reactant and products adsorbed strongly on the BAS with richer H for peaks at lower temperatures, while graphite carbon deeply inside of micropores with leaner H for peaks at higher temperatures. Only a small CO_2 evolution peak (2.6 wt.% carbon) was observed for Pt/SiO_2, accompanied with H_2O evolution at the same temperature. This suggests that only graphite type carbon was deposited around Pt, with very few reactant and products adsorbed on the inert SiO_2 support. For Pt/HBeta, the CO_2 profile was split into three peaks at 214, 473, and 534 °C, with corresponding H_2O peaks at 214, 447 and 553 °C, respectively. The former two peaks may be assigned to combustion of reactant and products adsorbed on the external surface and in the micropores, while the latter one may be related to graphite carbon inside of the pores. Importantly, the total amount of carbon decreased significantly to 9.1 wt.%, with respect to bare HBeta. This indicates that Pt plays an important role on cleaning the catalyst surface by hydrogenating the coke precursors.

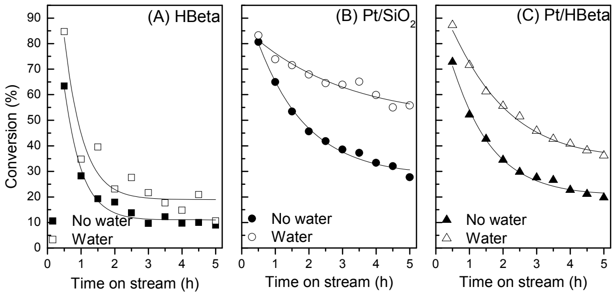


Figure 7. Effect of water addition on the conversion of guaiacol over (A) HBeta, (B) Pt/SiO_2 and (C) Pt/HBeta catalysts. Reaction conditions: $T = 350$ ºC, $P = 1$ atm, H_2/guaiacol = 50, W/F is 1.75, 0.25 and 0.25 h for HBeta, Pt/SiO_2, and Pt/HBeta catalysts, respectively, to achieve a similar initial conversion. The mass ratio of guaiacol/H_2O is 4/1.

Water effect

The effect of water on the activity and stability of the catalysts during hydrodeoxygenation of guaiacol was reported in Figure 7. Addition of water to the feed improved the reactivity of guaiacol on HBeta (Figure 7A), which can be attributed to that water helps hydrolysis of the ether bond of O-CH_3 on BAS and, therefore, improves the overall reaction rate of transalkylation.[38] H_2O addition seems to have little effect on the stability of HBeta. In contrast, the addition of H_2O has little effect on the activity of Pt/SiO_2 but improves its stability remarkably (Figure 7B). This suggests that Pt does not catalyze the hydrolysis of O-CH_3 bond, while H_2O plays a role on cleaning the surface of Pt during hydrodeoxygenation. Interestingly, addition of H_2O improves both the activity of Pt/HBeta and its stability moderately (Figure 7C). Obviously, this improvement is due to a combination of H_2O enhancing the BAS catalyzed hydrolysis of O-CH_3 bond of guaiacol and cleaning the Pt surface.

Conclusions

Through comparative study of hydrodeoxygenation of guaiacol and the intermediate products (catechol and cyclopentanone) over HBeta, Pt/SiO_2 and Pt/HBeta catalysts at 350 °C under atmospheric hydrogen pressure, the roles of Brønsted acid sites and Pt sites were identified. The Brønsted acid sites of HBeta catalyze transalkylation and dehydroxylation reactions, resulting in phenol, cresols, and xylenols as the major final products for hydrodeoxygenation of guaiacol. The Pt sites catalyze hydrogenolysis of guaiacol to catechol, which could be either directly deoxygenated in sequence to phenol and benzene or decarbonylated sequentially to cyclopentanone and butane. The combination of Pt site and Brønsted acid site with close proximity in Pt/HBeta enables both transalkylation and deoxygenation reactions with significantly improved activity toward direct deoxygenation (or dehydroxylation). Moreover, the demethylation and decarbonylation reactions observed on bare Pt/SiO_2 were dramatically inhibited on Pt/HBeta, due to the adsorption of catechols on Pt/HBeta through both phenyl ring on Pt and oxygen on Brønsted acid site. Such adsorption configuration facilitates the apparent direct deoxygenation. Being different from the carbon loss due to demethylation and decarbonylation over Pt/SiO_2, bifunctional Pt/HBeta retains most carbon in liquid products. The major final products are benzene, toluene, xylenes and C_{9+} aromatics with yields >85%. Addition of Pt to HBeta significantly improved the stability of catalyst through hydrogenating coke precursors. The presence of water in the feed improves the activity of Pt/HBeta by enhancing hydrolysis of O-CH_3 bond of guaiacol and moderately improves its stability in hydrodeoxygenation of guaiacol.

Experimental Section

Catalyst preparation and characterization

The catalysts used in this study were HBeta zeolite (Si/Al=19, Zeolyst, S_{BET}=710 m^2/g), 1 wt.% Pt/SiO_2, and 1 wt.% Pt/HBeta. The supported Pt catalysts were prepared using incipient wetness impregnation of HBeta or SiO_2 (HiSil 210, S_{BET}=135 m^2/g) with an aqueous solution of $H_2PtCl_4 \cdot 6H_2O$ (Aldrich) overnight, followed by drying at 110 °C for 12 h and calcination at 400 °C for 4 h. The samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), CO chemisorption, temperature programmed desorption of NH_3 (NH_3-TPD) and isopropylamine (IPA-TPD), which have been reported in previous work.[3,39] The spent catalyst samples were characterized by temperature programmed oxidation.[3]

Catalytic performance

Catalytic conversion of guaiacol was investigated in a fixed-bed quartz tube (6 mm o.d.) reactor at atmospheric pressure. The catalyst sample (40-60 mesh) was packed in the reactor between two layers of quartz wool, and was reduced in H_2 at 300 °C for 1 h prior to reaction. The reaction was carried out at 350 ºC to avoid non-catalytic thermal reactions at higher temperatures and saturation of phenyl ring at lower temperatures. H_2 flow was controlled by mass flow controllers (Porter). Guaiacol was fed using a syringe pump (Kd scientific), and was vaporized before entering the reactor. Ultra-high pure hydrogen was used as the reactant and carrier gas. The H_2/guaiacol molar ratio was kept at 50 in all runs. All lines were heated to avoid any condensation. The products were quantified online by a gas chromatograph (GC 6890, Agilent), equipped with a DB-5 capillary column (30 m) and a flame ionized detector (FID). The effluent was trapped in methanol using an ice-water bath, and qualified by an offline GC-MS (Shimadzu QP2010s). Standard samples were injected to GC for isomer identification.

To derive the major reaction path from product evolution, the W/F was adjusted from 0 to 4 h, by varying both catalyst amount (0-240 mg) and organic feed flow rate (0.03-0.48 mL/h). The W/F is defined as the ratio of catalyst mass (g) to organic feed flow rate (g/h). For an example, the H_2 flow rate, guaiacol flow rate, and catalyst amount were 20 scm^3/min, 0.12 mL/h and 68 mg, respectively, for W/F of 0.5 h. The conversion and yield were reported in mol_{carbon}%. The carbon balance was higher than 95% for each run. The absence of external and internal mass transfer limitations were confirmed by the same conversion was achieved by varying catalyst particle sizes and by varying feed flow rate at constant W/F.

The major intermediates (cyclopentanone and catechol (1,2-dihydroxybenzene)) during the guaiacol conversion were also fed to investigate the reaction pathway. To feed catechol, a solid at room temperature, an aqueous solution of 30 wt.% catechol was used. The effect of water on the guaiacol conversion was tested by co-feeding H_2O with a guaiacol/H_2O mass ratio of 4/1.

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Keywords: Guaiacol • Hydrodeoxygenation • Pt/HBeta • Transalkylation • Decarbonylation

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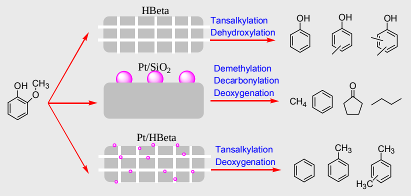

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Vapor-Phase Hydrodeoxygenation of Guaiacol to Aromatics over Pt/HBeta: Identification of the Role of Acid Site and Metal Site on the Reaction Pathway

Layout 2:

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