



Low-Temperature Catalytic Hydrogenolysis of Guaiacol to Phenol over AI-Doped SBA-15 Supported Ni Catalysts

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Abstract: Selective hydrogenolysis of aromatic carbon-oxygen (Carvi-O) bonds is a key strategy for the generation of aromatic chemicals from lignin. However, this process is usually operated at high temperatures and pressures over hydrogenation catalysts, resulting in a low selectivity for aromatics and an extra consumption of hydrogen. Here, a series of Al-doped SBA-15 mesoporous materials with different Si/Al molar ratios (AI-SBA-15) were prepared via a postsynthesis method using NaAlO2 as the Al source, and then Al-SBA-15 supported Ni catalysts (Ni/Al-SBA-15) were prepared by a deposition-precipitation method using urea as the hydrolysis reagent. The prepared supports and catalysts were extensively characterized using various techniques such as XRD, N2 adsorption/desorption, TEM, ²⁷AI NMR, NH₃-TPD, XPS, H₂-TPR, and pyridine-FT-IR, and the catalysts were evaluated in the hydrogenolysis of the Carvi-O bond in guaiacol and lignin derived compounds under mild conditions. The effects of the Si/Al ratio in catalyst and reaction parameters on guaiacol conversion and product distribution were investigated in detail, associated with solvent effect. The incorporation of Al into the framework of SBA-15 can improve the Lewis acidity and the dispersion of the supported Ni particles and yet modulate the metalsupport interactions, which are propitious to the hydrogenolysis of the Carvi-O bond in guaiacol. The catalyst Ni/Al-SBA-15 with a Si/Al molar ratio of 10 shows the best performance with a guaiacol conversion of 87.4% and a phenol selectivity of 76.9% under the mild conditions conducted, because of its proper acidity, suitable metal-support interactions, and high dispersion of the active species. The present study would stimulate research and development in multi-functional catalysts for the generation of valuable chemicals from biomass.

Introduction

Lignin is constructed from methoxylated phenylpropanoid subunits bridged by numerous ether linkages (C-O-C) as well as hydroxyl (–OH) and methoxyl (–OMe) side groups.¹ The utilization of lignin as a sustainable resource for the production of fuels and chemicals has garnered much attention in the last decade. Ligninderived oils, which contain aryl ether fragments (C_{aryl} -O bonds), are produced from lignin by thermal and catalytic processes of polymer fragmentation.² However, the wide application of ligninderived oils is limited due to several drawbacks such as low energy density and thermal stability, immiscibility with hydrocarbons and wide variation in boiling points, which are mainly caused by the high content of C_{aryl} -O bonds.³ Unfortunately, these molecules are much more refractory than sugar-derived oxygenates, and the cleavage of the C_{aryl} -O bonds in lignin currently represents one of the grand challenges due to the high C_{aryl} -O bond energy (218-314 kJ/mol).³ Hydrogenolysis is regarded as an effectively upgrading strategy to the cleavage of the C_{aryl} -O bonds in lignin and lignin-derived oils, rendering them closer in value to conventional fossil fuels or upgrading them to high valued aromatics.

As the complex composition of raw lignin-derived phenolic compounds, model compounds that have similar properties, such as eugenol, syringol, and guaiacol, are chosen for the initial screening of catalysts for the following upgrading of lignin-derived phenolic compounds.⁴ Among which, guaiacol is regarded as a model compound representing phenols derived from lignin, as there exists both -OH and -OCH₃ groups in guaiacol.⁵⁻¹⁰ Hydrogenolysis of guaiacol involves the direct removal of oxygen from bio-oil via C_{aryl}–O bond cleavage while it is challenging, since high yields of aromatic hydrocarbons can only be achieved by selectively cleaving the strong C_{aryl}–O bond without hydrogenating the aromatic ring.

Reports have shown that the catalyst property is a critical factor regulating the hydrogenolysis route, as shown in Table S1. Supported noble metals, such as Pd, Ru, Au, Rh, and Re, as well as base metals, such as Co, Ni, Fe, and their heterometallic alloys, are found to possess a high hydrogenolysis and hydrogenation activity, but some undesirable reactions, including the hydrogenation of benzene ring, C-C bond hydrogenolysis as well as methanation, also prevail on them, resulting in a low aromatics yield and a high H₂ consumption.⁵⁻¹⁰ Hydrodeoxygenation using H donors (e. g. alcohols, formic acid and water) has been considered as a promising method to improve the selectivity towards aromatic hydrocarbons over supported noble metals.5g, h Mo-based hydrotreating catalysts, e.g., CoMo sulfide, NiMo oxide, MoO₃, and Mo₂C catalysts, have been investigated for the hydrogenolysis of guaiacol, but demand high H₂ pressures and high temperatures. Besides, sulfur-containing reagents are required to add to the feedstock to keep sulfide catalysts from deactivation, consequently causing the sulfur contaminated products.⁷ Recently, supported Ni-based catalysts are recognized as efficient and low cost ones in the hydrogenolysis of guaiacol and a range of materials have been reported as catalyst supports, including y-Al₂O₃, mesoporous SiO₂, ZrO₂, zeolites, TiO₂, and activated carbons.⁸⁻¹⁰ Zhou et al.⁹ reported that guaiacol could be converted into cyclohexanol over Co-promoted Ni/y-Al2O3 catalysts at 200 °C and a H₂ pressure of 5 MPa and some proper acidity and interactions between metal species and support would

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be helpful for the hydrogenolysis of guaiacol. Broglia et al.¹⁰ investigated the effects of the support surface properties of Ni/Al₂O₃-SiO₂ on the hydrogenolysis of guaiacol into phenol and found that both guaiacol conversion and product distribution were markedly affected by the morphological and surface features of the support, and the high conversion of guaiacol was achieved up to 84% at a H₂ pressure of 5 MPa and 300 °C. As a general trend, the appropriate acidity of catalysts is favorable for enhancing their performance in the hydrogenolysis of guaiacol.^{5,6} In addition, the strong metal-support interactions could modulate the stacked morphology and degree of active species to produce more active centers with a high activity. Unfortunately, recent research has been mainly focused on pure oxides as supports and the hydrogenolysis has been mainly carried out at relatively harsh conditions like reaction temperatures higher than 200 °C and H₂ pressures higher than 5 MPa, resulting in the high consumption of H₂ and full aromatic-ring saturation. Thus, it is imperative to develop Ni-based catalysts with high catalytic activities for the hydrogenolysis of guaiacol that could be achieved at relatively low temperatures and H₂ pressures.

In this work, we report high selectivity and stability Ni supported catalysts with a high H₂-utilization efficiency for the hydrogenolysis of guaiacol to phenol at mild conditions. A series of Al-doped SBA-15 materials with various Si/Al ratios (Al-SBA-15) were prepared via a post-synthesis method with sodium aluminate (NaAlO₂) as the Al source for effectively incorporating tetrahedral aluminum species into pure silica SBA-15 in a basic condition, and the prepared AI-SBA-15 materials were used as supports to synthesize Ni/AI-SBA-15 catalysts via a depositionprecipitation method, and these prepared supports and catalysts were then characterized by different techniques. It is found that the incorporation of AI species into SBA-15 framework can increase the Lewis acidity and yet enhance the metal-support interactions to improve the catalytic activity. The synergistic effects of the incorporated AI species and Ni species on the hydrogenolysis were elucidated. Further, the effects of the reaction parameters, such as type of solvent, temperature, and initial H₂ pressure, on guaiacol conversion and product distribution were investigated in detail.

Results and Discussion

Characterization of Supports and Catalysts. The typical smallangle and wide-angle XRD patterns of the reduced Ni/SBA-15 and Ni/AI-SBA-15 with different Si/AI ratios are shown in Figure 1a1-2. Three strong diffraction peaks are observed with 2θ at around 0.85°, 1.42°, and 1.65°, respectively, indexed as (100), (110), and (200) diffractions of SBA-15, reflecting the presence of a typical well-ordered two-dimensional hexagonal P6mm mesostructured phase.¹¹ The intensity of (110) and (200) diffraction peaks increases while the (100) diffraction peak keeps constant with a slightly shift toward the low angle side with decreasing the Si/Al molar ratio from 50 to 10, demonstrating that the structural order is enhanced due to the incorporation of Al into the framework of SBA-15, in correspondence with the observation by Chang and Lin.¹² The shift corresponds to an increased length of the unit cell α_0 from 11.11 to 12.10 nm, calculated from the formula $a_0=2d_{100}\sqrt{3}$ as shown in Table S2. The shifting of the Bragg angle to a slightly low value indicates that some Al3+ species ($r_{Al^{3+}}$ =0.054 nm) enter the lattice of SiO₂ ($r_{Si^{4+}}$ =0.040 nm), leading to an increase in the lattice parameters and the formation of Al-O-Si structure to some extent. In all the catalysts, the weak diffraction peaks of metallic Ni are observed at 44.3°, 51.9°, and 76.4°, respectively, reflecting the high dispersion of Ni in the reduced catalysts. Additionally, the peaks at $2\theta = 35.2^{\circ}$ and 61.2°, ascribed to NiO species, respectively, are also observed in the XRD pattern, indicating that both metal Ni and NiO species appear on the surface of the support. It can be seen that the intensity of the diffraction peaks of metallic Ni decreases with increasing the incorporating amount of Al into SBA-15, suggesting that the incorporation of Al would lead to the better dispersion of metallic Ni species on the support. A similar behavior was also observed on Al-modified mesoporous SiO₂ supported NiMo catalysts.¹³ Consistently, the diffraction peaks that are characteristic for Al₂O₃ are not detected in the current samples.



Figure 1. (a) Small-angle and wide-angle XRD patterns of the reduced catalysts, (b) TEM image and particle size distribution of Ni/AI-SBA-15(10), (c) TEM image and particle size distribution of Ni/AI-SBA-15(30), and (d) TEM image and particle size distribution of Ni/AI-SBA-15(50).

The TEM images and size distributions of Ni species (including metallic nickel and nickel oxides) supported on Al-SBA-15 are shown in Figure 1b-d. For all the samples, the characteristic mesostructure of Al-SBA-15 is visible, and the particles of Ni species can be clearly differentiated ranging from 2.0 to 10.0 nm. According to the surface area weighted average diameter, the Ni particle sizes of the samples are further calculated as follows:

$$d_s = \sum n_i d_i^3 / \sum n_i d_i^2$$
 (1)

where n_i is the number of the counted particles of Ni species with diameter d_i , in which the total number of the counted particles of Ni species was more than 80.

The average Ni particle size is calculated to be 7.6 nm in diameter in Ni/AI-SBA-15(50). Additionally, the average particle size of Ni species in the catalysts remarkably decreases from 7.6 to 3.8 nm with decreasing the Si/AI molar ratio in AI-SBA-15 from 50 to 10, confirming that the incorporation of AI would improve the dispersion of Ni species on the support further, which is in good accordance with the XRD results presented in Figure 1a. Besides, with increasing the incorporated AI amount in SBA-15, the catalyst possesses a much narrower size distribution of the particles of Ni species on the support, implying that the interactions between Ni species and support become stronger.

The results on the N₂ adsorption–desorption isotherms and the corresponding pore size distributions of the supports and catalysts are presented in Figure S1 and Table S2. The hysteretic capillary condensation is observed in a relative pressure range from 0.66 to 0.9, suggesting the presence of characteristic mesopores in all the samples investigated. Additionally, Ni/SBA-15 has a narrow pore size distribution with the most probable pore diameter centered at 8.3 nm, nearly identical to that of SBA-15, reflecting that the incorporated Ni species onto the support do not markedly affect the mesostructure of SBA-15.



Figure 2 ²⁷Al MAS NMR spectra (a) of the reduced catalysts, H₂-TPR profiles (b) of NiO and the calcined catalysts, NH₃-TPD profiles (c) and pyridine adsorption FT-IR spectra (d) of the reduced catalysts.

²⁷Al-NMR spectroscopy was performed to analyze the existent states and distribution of AI species in SBA-15. In general, the chemical shifts at 0 and 53 ppm are assigned to octahedrally and tetrahedrally coordinated AI, respectively.^{12,13} As shown in Figure 2a, only one sharp peak at 53 ppm is observed, assigned to a tetrahedrally coordinated AI framework in AI-SBA-15. This indicates that all the AI atoms are located in a tetrahedral environment and covalently bound to Si atoms via oxygen bridges, confirming that AI species are successfully incorporated into the framework of SBA-15 via the post-synthesis method. Moreover, the tetrahedrally coordinated AI species, linking Si atoms via

oxygen bridges, the so-called "bridging hydroxyl groups", are helpful for improving the total acidity and yet creating the acidic sites.^{13,14}

The H₂-TPR study was carried out to investigate the reducibility of Ni oxides on the support, and these results are shown in Figure 2b. The H₂-TPR profile of the reference sample NiO shows a sharp H₂ consumption peak at ca. 340 °C, ascribed to the reduction of crystalline NiO. In contrast, there is a broad reduction peak in a temperature range of 400-600 °C in the H2-TPR profile of calcined Ni/SBA-15, suggesting the presence of the reducible Ni oxides that strongly interact with SBA-15. Interestingly, when AI-SBA-15 materials with different Si/AI ratios are used as the supports, there are the significant shifts of the H₂ consumption peaks in the H₂-TPR profiles of calcined Ni/Al-SBA-15 catalysts to higher temperature ranges, indicating that the Ni oxide species are more stable, compared to those in Ni/SBA-15. Besides, an up-shift of the reduction peak in terms of temperature is observed, when the Si/Al molar ratio in AI-SBA-15 is decreased. suggesting that the interactions between Ni oxide species and support would be enhanced because of more surface-attached hydroxyl groups and Al-O-Ni bonds available with increasing the incorporated amount of AI into SBA-15. These pronounced interactions between Ni oxide species and support, consequently, lead to an increase in the dispersion of Ni species in the catalysts, which could help to inhibit the thermal transmigration and sintering of the metal species during calcination and reduction. A similar observation is reported in Al-modified mesoporous SiO₂ supported Ni catalysts.12,13 Therefore, the effects of the incorporated AI in SBA-15 on the dispersion of Ni species on the support would inevitably contribute to the improvement in the catalytic activity.

The number and strength of the acid sites on SBA-15 and AI-SBA-15 supported Ni catalysts were measured by NH₃-TPD. The acid strength is classified to be weak (100-250 °C), medium (250-400 °C), and strong (>400 °C) in terms of the desorption temperature of NH₃.¹⁵ As shown in Figure 2c, only the weak acid sites are detected in Ni/SBA-15 at ca. 180 °C and 140 °C, respectively, while Ni/Al-SBA-15 catalysts show similar profiles with a main broad asymmetric NH3 desorption peak at ca. 280 °C and an additional wide, small shoulder centered at ca. 190 °C, corresponding to medium and weak acid sites, respectively, suggesting that the incorporation of AI species can improve the acid strength of the catalyst. The medium acid sites, corresponding to the desorption peak at ca. 280 °C, supply the active sites for the cleavage reaction of ether bonds in guaiacol and lignin model compounds.¹⁶ Moreover, the total acid numbers of the catalysts can be calculated by the desorbed amounts of NH₃, and these results are summarized in Table S2. A substantial improvement in the acid number of Ni/Al-SBA-15 is clearly observed, which is enhanced with increasing the incorporated AI amount into SBA-15.

Although it has been reported that the total number and strength of acid sites on various catalysts are closely related to their catalytic activities for the hydrogenolysis and/or hydrogenation of guaiacol, the contribution of separate acid sites, such as Brønsted and Lewis acid sites, to the ether bond cleavage reaction activities of guaiacol has not been well-characterized until now.^{3,10} Therefore, the pyridine adsorption IR measurements were performed to further determine the Brønsted and Lewis acidities of all the reduced catalysts, and these results are shown in Figure 2d. The peaks at 1454 and 1623 cm⁻¹ are assigned to

pyridine adsorbed onto the Lewis acid sites, suggesting that the coordinatively unsaturated Al³⁺ sites are present on the surface of SBA-15.¹⁷ The Brønsted acid sites are not observed on Ni/Al-SBA-15, due to the absence of the adsorption peaks at 1545 and 1640 cm⁻¹, respectively.¹⁸ These results are different from those in the literature,¹⁸ in which both Brønsted and Lewis acids are present on the surface of Al-doped SBA-15 prepared using aluminum isopropoxide or aluminum nitrate as the Al source. In the current case, the absence of the Brønsted acid sites in the catalysts is due to the compensated Na⁺ for the negative charges of the framework of Al-SBA-15.



Figure 3. Ni 2p XPS spectra (a), Al 2p XPS spectra (b) and the Ni²⁺/Ni⁰ atomic ratio versus the Si/Al molar ratio in the reduced catalysts, I: Ni/Al-SBA-15(50), II: Ni/Al-SBA-15(30), III: Ni/Al-SBA-15(10), and IV: Ni/SBA-15.

The surface element compositions of Ni/SBA-15 and Ni/Al-SBA-15 were analyzed by the in-situ XPS technique, and Ni 2p and AI 2p XPS spectra and corresponding binding energies of the catalysts are shown in Figure 3 and Table S3. The Ni⁰ 2p_{3/2}, Ni⁰ $2p_{1/2}$, and their satellite core level binding energies appear at ca. 853.1, 870.1, 862.4, and 881.8 eV, respectively.19 The peaks at 857.5 and 874.4 eV are assigned to Ni²⁺ $2p_{3/2}$ and Ni²⁺ $2p_{1/2}$, suggesting that both metallic Ni and NiO are present on the surface of support,¹⁹ in accordance with the analysis of the XRD patterns (Figure 1a-2). Compared with a binding energy of 852.8 eV (Ni⁰ 2p_{3/2}) of unsupported metallic Ni, the positive shift of the binding energy suggests the stronger interactions between Ni and support available, see the results shown in Table S3. It should be stressed that the different AI amounts incorporated into SBA-15 do not affect the Ni 2p binding energy shift, indicating that there is no electronic effect of AI on Ni. The Ni2+/Ni0 atomic ratio in Ni/AI-SBA-15 is increased, compared with that in Ni/SBA-15, indicating that the incorporation of AI into SBA-15 may have an adverse effect on the reduction of NiO species into metallic Ni. as shown in Figure 3c. The H₂-TPR results (Figure 2b) also confirm that the reducibility of Ni/AI-SBA-15 decreases because of its reduction peak at ca. 650 °C while that at 540 °C for Ni/SBA-15, which is in good accordance with the XPS results. Deconvolution of the Al 2p spectrum of Ni/Al-SBA-15 reveals one peak at a binding energy of 74.4 eV, corresponding to the tetrahedral Al³⁺ state, implying that the Al³⁺ is covalently bound to four Si atoms via oxygen bridges.13,20



Scheme 1. Possible reaction network for guaiacol conversion.

Catalytic Conversion of Guaiacol. Herein the primary products of guaiacol conversion over the Ni-based catalysts were determined at 120 °C in aqueous phase. The guaiacol conversion and product distribution are presented in Figure 4. Phenol and catechol are the primary aromatic products, and cyclohexanol, 2methoxy cyclohexanol, and cyclohexanone as hydrogenation products are the byproducts. Besides, methanol and a small amount of methane were also detected. This product distribution suggests that the selective hydrogenolysis of the Carvi-O bond forms phenol, the hydrolysis of guaiacol produces catechol, the hydrogenation of guaiacol and phenol forms 2-methoxy cyclohexanol, cyclohexanone, and cyclohexanol, see the reaction network shown in Scheme 1. The properties of the catalyst support used significantly affect both guaiacol conversion and product selectivity. The different Ni particle sizes and interactions between Ni species and support in the catalysts revealed by the TEM (Figure 1) and H₂-TPR (Figure 2b) characterizations are responsible for the difference in the catalytic activity, showing that the better dispersion of the metallic Ni on the support, the higher guaiacol conversion and phenol selectivity, and Ni/Al-SBA-15(10) shows the best catalytic performance in terms of guaiacol conversion and phenol selectivity. These results are in good accordance with those observed by Zhou and Schutlser.9,21



Figure 4. Guaiacol conversion and product distribution over (A) Ni/SBA-15, (B) Ni/Al-SBA-15(50), (C) Ni/Al-SBA-15(30), and (D) Ni/Al-SBA-15(10). Reaction conditions: guaiacol (3.00 g), catalyst (0.20 g), H_2O (100 mL), 120 °C, 3 h, initial H_2 pressure (0.1 MPa) and stirring at 700 rpm.

The acid sites could act as an H- radical acceptor and transferrer, which could greatly increase the reaction rate by the adjustment of the H- transfer length in the hydrogenolysis of guaiacol at low H₂ pressures over RuNi/HZSM-5 catalysts.⁸ Here, over Ni/SBA-15, the guaiacol conversion is only 42.5% and the main product is methoxy cyclohexanol with a selectivity of 72.8%, see Figure 4. When AI-SBA-15 materials are used as the supports, a significant change in the product distribution is observed. Over Ni/Al-SBA-15(50), the guaiacol conversion is increased up to 68.9%, meanwhile the main products are catechol and phenol with selectivities of 43.2% and 24.2%, respectively. When the incorporated amount of AI into SBA-15 reaches its maximum in the current investigation, i.e. a Si/Al molar ratio of 10 in Al-SBA-15, the highest conversion of guaiacol and the highest selectivity for phenol, 87.4% and 76.9%, respectively, are achieved. Combined with the results on the Lewis acid characterization (Figure 2c and d), where a substantial improvement on the Lewis acid number associated with a decrease in the Lewis acid strength is observed with increasing the incorporated AI amount into SBA-15, indicating that the strong acid sites would be responsible for the catalytic reaction to form catechol while the moderate Lewis acid sites would be favorable for the hydrogenolysis of guaiacol to produce phenol. This observation is in good accordance with Yu's results,²² in which the higher conversion of quaiacol could be obtained when the support Al-SBA-15 with a lower Si/Al molar ratio was used.

 Table 1. Effects of solvent on guaiacol conversion and product distribution^a

	Ni/Al-SBA-15(10)	ОН +	СССОН +		С + () +	\bigcirc°	
		1	2	3	4	1	5	
Entr	Solvent	Conv.	Product Sel. (%)					
У	Solvent	(%)	1	2	3	4	5	
1	Water	87.4	76.9	3.6	6.8	6.3	2.6	
2	Ethanol	48.2	5.8	3.2	21.3	57.8	6.5	
3	<i>n</i> -Hexane	31.2	2.6	2.7	24.8	61.2	5.3	
Boastion conditions: guaiacal (2.00 g) solvent (100 ml.) Ni/AL								

^a Reaction conditions: guaiacol (3.00 g), solvent (100 mL), Ni/Al-SBA-15 catalyst (0.20 g), initial hydrogen pressure (0.1 MPa), 120 °C, 3 h, and stirring at 700 rpm.

In this study, the effects of different solvents, such as water, ethanol, and n-hexane, on the conversion of guaiacol over Ni/Al-SBA-15(10) were investigated, and these results are shown in Table 1. The maximum guaiacol conversion is 87.4% with a phenol selectivity of 76.9% using water as the solvent. On the other hand, the guaiacol conversion is only 48.2% or 31.2% using ethanol or *n*-hexane as the solvent. This may be related to the relatively weak polarity of ethanol and *n*-hexane in comparison with that of water. These results on the effects of the used solvent are in good agreement with those observed by Ma et al.7b and Zhou et al.9 Differently, phenol, produced with a high selectivity of 76.9% in water as the solvent, is produced with a selectivity of only 3.8% (2.6%) using ethanol (n-hexane) as the solvent. Guaiacol is converted to 2-methoxy cyclohexanol and cyclohexanol with selectivities of 21.3% and 57.8%, respectively, using ethanol as the solvent, and when *n*-hexane is used as the solvent, a higher total selectivity of 86.0% for 2-methoxy cyclohexanol and cyclohexanol is obtained. Therefore, it seems that the aromatic-ring hydrogenation would dominate the reaction pathway, when either ethanol or *n*-hexane is used as solvent.

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Figure 5. Effects of reaction temperature on guaiacol conversion and product distribution over Ni/Al-SBA-15(10). Reaction conditions: guaiacol (3.00 g), Ni/Al-SBA-15(10) catalyst (0.20 g), H_2O (100 mL), 3 h, initial H_2 pressure (0.1 MPa) and stirring at 700 rpm.

The effects of reaction temperature on the guaiacol conversion and product distribution over Ni/Al-SBA-15 (10) are presented in Figure 5. The guaiacol conversion is significantly increased from 27.6 to 98.8% with increasing the reaction temperature from 80 to 160 °C. On the other hand, the guaiacol conversion is dramatically dropped to 4.7% as the reaction temperature is increased up to 200 °C. This is mainly due to the structure collapse of the catalyst under such harsh hydrothermal conditions, as shown in Figure S2. In a temperature range of 80-160 °C, an increase in the reaction temperature results in a decrease in the selectivity for phenol from 80.4% to 42.6% while an enhanced selectivity for cyclohexanol from 3.1% to 28.7%. These results indicate that low temperatures are favorable for the hydrogenolysis of guaiacol into phenol while high temperatures are favorable for the aromatic-ring hydrogenation, in good accordance with the observation by Zhou et al.9 and Nakagawa et al.¹⁷ In summary, in the current study, the hydrogenolysis of guaiacol over Ni/Al-SBA-15(10) has a conversion of 87.4% with a phenol selectivity of 76.9% at 120 °C and an initial H₂ pressure of 0.1 MPa, which can be considered as the best results in terms of phenol yield over a non-noble metal based catalyst under the mild conditions.





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guaiacol (3.00 g), Ni/Al-SBA-15(10) catalyst (0.20 g), H_2O (100 mL), 120 °C, 3 h, and stirring at 700 rpm.

The effects of initial H₂ pressures varying from 0.1 to 1.0 MPa on the guaiacol conversion and phenol selectivity were investigated at 120 °C over Ni/Al-SBA-15(10), see Figure 6. The guaiacol conversion increases slightly from 84.4% to 92.3% while the selectivity for phenol decreases dramatically from 76.9% to 2.1% with increasing the initial H₂ pressure from 0.1 to 1.0 MPa. On the other hand, the selectivity for cyclohexanol reaches its maximum at an initial H₂ pressure of 1.0 MPa. Moreover, the

selectivity for 2-methoxy-cyclohexanol increases with increasing the initial H_2 pressure, suggesting that excessive H_2 would contribute to the hydrogenation of the aromatic ring in phenol and guaiacol. In addition, increasing initial H_2 pressure would also enhance the solubility of H_2 into the reaction solution, promoting the hydrogenation of the hydrodeoxygenation products.

Table 2. Products distribution for hydrogenolysis of different model compounds over Ni/AI-SBA-15(10)^a

Entry	Substrate	Conv. (%)			Selectivity fo	r the main product	ts (%)	
1		94.3		OH			Others	
			83.6	3.4	4.5	5.2	3.3	
2		86.7		0	OH	НОСОН		Others
_			75.7	9.2	2.4	4.6	4.3	3.8
3		77.2		0		HO		Others
			65.8	17.3	6.2	2.7	4.8	3.2
4	OH O	80.2	OH	OH O	ОН	OH O O	OH O	Others
			62.1	26.6	2.2	4.6	1.8	2.7
5	OH C	82.8	OH	ОН	OH C	OH	Others	
			82.7	4.9	6.3	2.4	3.7	
6	OH O O O O O O O O O O O O O O O O O O	76.8	OH	OH OH	OH	OH O O O O O O O O O O O O O O O O O O	OH OH	Others
			63.6	25.4	2.1	3.8	1.9	3.2

^a Reaction conditions: substrate (3.00 g), H₂O (100 mL), catalyst (0.20 g), initial hydrogen pressure (0.1 MPa), 120 °C, 3 h, and stirring at 700 rpm.

On the basis of the understanding of the model reaction based on guaiacol that contains methoxy group and phenolic hydroxy group, it was nevertheless important to determine whether other varieties of C_{aryl} -O bonds can be cleaved over the currently developed catalysts under the same reaction conditions. Therefore, the hydrogenolysis reactions of other model

compounds over Ni/Al-SBA-15(10) were performed and the corresponding results are summarized in Table 2. As expected, 1,3-dimethoxybenzene and 1,3,5-trimethoxybenzene are converted into benzene with anisole as the intermediate, which is principally converted to benzene with a selectivity of 83.6%. On the other hand, 1,3,5-trimethoxybenzene has a lower conversion,

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compared to 1,3-dimethoxybenzene and anisole, which can be contributed to the enhanced C_{aryl} -O bond energy caused by the extra electron-donating group (-OCH₃).²³ For the conversion of syringol, partially deoxygenated products such as phenol, guaiacol, catechol, and methoxy cyclohexanol are identified by a liquid product analysis, among which phenol is the main product with a selectivity of 62.1% and guaiacol is as demethoxylation (removal of -OCH₃) product from the onset of the reaction with a selectivity of 26.6% by the end of the reaction. In addition, the hydrogenolysis reactions of 4-*n*-propylguaiacol and 4-*n*propylsyringol were also performed, and it is found that 4-*n*propylphenol is the main product via demethoxylation. Based on the above results, it can be concluded that Ni/Al-SBA-15(10) possesses some excellent catalytic properties for cleavaging the C_{aryl} -O bonds in lignin-derived compounds.

Table 3. Reusability of Ni/AI-SBA-15(10)^a

	NI/AI-SBA-15(10)	он + 💭	Сон +	ССОН	+ () ^{OH} +	$+ \bigcirc^{\circ}$	
	1	2		3	4	5	
Entry	Conv. (%)	Product Sel. (%)					
Entry		1	2	3	4	5	
1	87.4	76.9	3.6	6.8	6.3	2.6	
2	86.5	76.4	3.4	6.7	6.4	2.4	
3	84.7	75.8	3.3	6.8	6.2	2.7	
4	85.4	76.2	3.4	6.4	6.1	2.3	
5	84.7	76.5	3.5	6.2	6.5	2.5	

^a Reaction conditions: guaiacol (3.00 g), H_2O (100 mL), catalyst (0.20 g), initial hydrogen pressure (0.1 MPa), 120 °C, 3 h, and stirring at 700 rpm.

In addition, a five-run experiment of the selective hydrogenolysis of guaiacol over Ni/AI-SBA-15 was carried out to check the reusability (Table 3). The catalyst was filtered from the reaction medium after each run and dried at 80 °C after washed with ethanol. Then the used catalyst was reused in the next run for the hydrogenolysis of guaiacol under the same reaction conditions. Obviously, the recycling use of the catalyst for five runs shows no obvious change in the catalyst is stable enough during the hydrogenolysis.

Conclusion

In summary, the selective hydrogenolysis of the C_{aryl} –O bond in guaiacol was symmetrically carried out over Al-doped SBA-15 supported Ni catalysts under the relatively mild conditions. The results show that the incorporation of Al into the framework of SBA-15 can improve the Lewis acidity and the dispersion of the supported Ni particles and yet modulate the metal–support interactions, which are propitious to the hydrogenolysis of the C_{aryl}-O bond in guaiacol. When the incorporated amount of Al into SBA-15 reaches its maximum in the current investigation, i.e. a Si/Al molar ratio of 10 in Al-SBA-15, the highest conversion of guaiacol and the highest selectivity for phenol, 87.4% and 76.9%, respectively, are achieved. In addition, the type of the solvents used in the reaction would significantly affect the guaiacol conversion and phenol selectivity, and the strong polarity water

as the solvent helps the hydrogenolysis of guaiacol to form phenol while the weak polarity ethanol or *n*-hexane as the solvent enhances the hydrogenation of guaiacol to form 2-methoxy cyclohexanol and cyclohexanol. Low reaction temperatures are favorable for the hydrogenolysis of guaiacol into phenol while high reaction temperatures are favorable for the aromatic-ring hydrogenation. Furthermore, low initial H₂ pressures are favorable for the hydrogenolysis of guaiacol into phenol. In addition, the developed catalyst also show some excellent performance in the hydrogenolysis of other model compounds. The current work, therefore, indicates that the Al-doped SBA-15 supported Ni catalyst, showing a high activity, selectivity for phenol, and stability under the mild reaction conditions, would be alternatives of sulfide or noble-metal catalysts for the upgrading of lignin.

Experimental Section

Chemicals. All of the used reagents were of analytic purity grade and purchased from Sinopharm Chemical Reagent Co., Ltd. **Materials Preparation.** SBA-15 was prepared following the method reported in the literature.¹¹ Typically, 8.00 g of the surfactant P123 (EO₂₀PO₇₀EO₂₀, average molecular weight = 5800) was added to 300 mL of 1.6 M HCl at 40 °C until completely dissolved, and 18.00 g of tetraethyl orthosilicate (TEOS) was then added. The mixture was further stirred at 40 °C for 24 h. Afterwards it was charged into a Teflon-lined stainless autoclave and heated at 100 °C for 48 h. After the resultant precipitate was collected by filtration, the cake was washed with ethanol and deionized water, and finally dried in an oven at 80 °C for 10 h and calcined in static air at 550 °C for 6 h.

Al-SBA-15 supports with different molar ratios of Si/Al were synthesized via a post-synthesis method using sodium aluminate (NaAlO₂) as Al source and deionized water as solvent. A typical synthesis of Al-SBA-15 was performed as follows: a certain amount of NaAlO₂ was dissolved in 250 mL of deionized water under magnetic stirring. Then 2.00 g of the above-synthesized SBA-15 was added into the solution and the mixture was stirred for 12 h at 40 °C. All the synthesized Al-SBA-15 materials with different Si/Al molar ratios were obtained after calcination in static air at 550 °C for 6 h.

The supported Ni/AI-SBA-15 catalysts were prepared by a deposition-precipitation method with urea as the hydrolysis agent, according to the procedure reported in the literature.²² In a typical synthesis, 2.47 g of Ni(NO₃)₂.6H₂O was added to 250 mL of deionized water, and the mixture was divided into two parts: 6.30 g of urea was added into the first part with 50 mL of the mixture, and 2.00 g of AI-SBA-15 and the second part of the mixture were then together put into a flask at 90 °C, in which the pH was adjusted to 2 with diluted HNO3. The solution with urea was then added to the flask with AI-SBA-15 at a flow rate of 1 mL/min, after which the suspension was magnetically stirred for 12 h. The suspension was then cooled to room temperature, and the solid was filtered and washed with distilled water three times. Finally, the sample was dried at 120 °C for 24 h, calcined in flowing air at 550 °C for 6 h, and reduced in flowing H₂ at 400 °C for 2 h. The obtained sample was nominated as Ni/Al-SBA-15(x), in which x represents the molar ratio of Si/Al in Al-SBA-15.

Characterization. The powder X-ray diffraction (XRD) patterns of the samples were obtained on a D8 Advanced X-rav diffractometer (Bruker) using with a Cu K α radiation source (λ = 0.15406 nm) at a voltage of 40 kV and a current of 40 mA. The morphological and structural details of the samples were investigated using a FEI Talos-S transmission electron microscope (TEM) with an accelerating voltage of 200 kV. The textural properties of the samples were determined by N2 adsorption-desorption isotherms at -196 °C using a Micromeritics ASAP 2020 instrument. The H₂-TPR and NH₃-TPD measurements of the calcined samples were carried out on a Micromeritics AutoChem 2920 instrument with a thermal conductivity detector. The solid-state NMR spectra of the samples were recorded on a Bruker 400 MHZ Ultra-Shield spectrometer with a resonance frequency of 104.3 MHz for ²⁷Al detection. The adsorption of pyridine was performed on a Thermo Fisher iS 50 FT-IR spectrometer equipped with a DTGS detector at an optical resolution of 4 cm⁻¹ by carrying out 64 scans. The surface analysis of the reduced catalysts was conducted with an X-ray photoelectron spectrometer (XPS) (ESCALAB 250, Thermo Fisher) equipped with a monochromatized AI Ka X-ray source (hv = 1486.6 eV) and a pass energy of 40 eV.

Catalytic Hydrogenolysis. The catalytic reaction was carried out with a 300 mL batch reactor (Parr 4566, made of Hastelloy) equipped with a temperature controller (Parr 4848). In a typical run, 3.00 g of guaiacol, 0.20 g of catalyst, and 100 mL of deionized water were loaded into the reactor. The reactor was then evacuated and purged with high-purity nitrogen for five times and finally pressurized to the desired pressure with hydrogen. The sealed reactor was then heated to 120 °C with a stirring speed of 700 rpm. After the reaction, the reactor was quenched to ambient temperature using piping water, and the liquid products were collected using ethanol as solvent and analyzed by an Agilent 7890B gas chromatography (GC) with a flame ionization detector and an Agilent 7890-5975 GC-mass spectroscopy (GC-MS). Sym-trimethylbenzene was used as an internal standard to calibrate the liquid product concentrations. Two HP-5 MS capillary columns (30 m \times 0.25 mm \times 0.25 µm) were used in the two GCs for the analysis. For the reusability test, after the reaction, the catalyst was separated from the reaction medium, repeatedly washed with ethanol twice, and then dried overnight in a vacuum oven at 80 °C.

Equations (2) and (3) were used to calculate the conversion of guaiacol and the selectivities for the products, respectively. The carbon balances were typically within $\pm 5\%$, calculated by comparing the total mole of carbon in the reactant with the one in the products. Hence, the selectivities were calculated, based on the GC observable products.

Conversion of guaiacol: Conv. _{GUA} =
$$\frac{n_{GUA}^0 - n_{GUA}}{n_{GUA}^0} \times 100\%$$
 (2)

Selectivity for product: Sel.=
$$\frac{n_i}{n_{GUA}^0 - n_{GUA}} \times 100\%$$
 (3)

where n_{GUA}^0 and n_{GUA} depict the carbon moles of guaiacol before and after the reaction, respectively, and n_i is the mole number of product *i*. All the experiments were repeated five times for each fresh catalyst, and the conversion and selectivity were calculated based on the average of the five-times measurements and relative error was within 1%.

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The developed Al-doped SBA-15 supported Ni catalyst shows some excellent performance in the selective cleavage of the C_{aryl} -O bonds in guaiacol under mild conditions, because of its proper acidity, suitable metal-support interactions, and high dispersion of the active species. The present study would stimulate research and development in multi-functional catalysts for the generation of valuable chemicals from biomass.