CL-150066 Received: January 23, 2015 | Accepted: February 19, 2015 | Web Released: February 28, 2015

Production of Alkanes from Lignin-derived Phenolic Compounds over In Situ Formed Ni Catalyst with Solid Acid

Xinghua Zhang, Tiejun Wang, Qi Zhang, Ying Xu, Jinxing Long, Lungang Chen, Chenguang Wang, and Longlong Ma*
Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion,
Chinese Academy of Sciences, Guangzhou 510640, P. R. China

(E-mail: mall@ms.giec.ac.cn)

In situ formed Ni catalyst combined with added solid acids is highly active for the hydrodeoxygenation of lignin-derived phenolic compounds. In the heterogeneous catalysts, in situ formed Ni acts as the hydrogenation and hydrogenolysis catalyst and solid acid acts as the dehydration catalyst.

Lignin, the second most abundant natural organic polymer consisting of methoxylated phenylpropane units, can be effectively depolymerized into phenolic compounds.[1] A major challenge is that these complex phenolics are highly oxygenated, which limits their direct application as transportation fuel.[2] Therefore, hydrodeoxygenation (HDO) is necessary to make these lignin-derived phenolic compounds more suitable as high-grade fuel.

Sulfided CoMo and NiMo catalysts have been reported to be active for conversion of oxygenated compounds to hydrocarbons via HDO.[3] These catalysts contaminate products due to sulfur transfer. Thus, most hydrodeoxygenation studies have focused on non-sulfided supported catalysts, such as $Pt/SiO_2–Al_2O_3$,[4] Ni/HZSM-5,[5] Ni/ZrO_2, and $Ni/SiO_2–ZrO_2$.[6] Over these supported catalysts, hydrodeoxygenation of phenolic compound stems from the fact that the active metal can catalyze hydrogenation and the acid site of the supporter can catalyze dehydration and activate C–O bonds. Recently, the combination of hydrogenation catalysts (Pd/C) and liquid acid/solid acid (H_3PO_4 and HZSM-5) was also reported to be an effective method for the hydrodeoxygenation of phenolics to hydrocarbons.[7] However, the employment of noble metal-based catalysts could significantly raise production costs. The addition of liquid acid can lead to a corrosive reaction environment. Moreover, it is difficult to recover the liquid acid from the reaction mixtures. Herein we reported a new alternative method for hydrodeoxygeantion of phenolic compounds to hydrocarbons over an inexpensive non-sulfided bifunctional catalyst combining Ni derived in situ from decomposition of $(HCOO)_2Ni$ with solid acid, i.e., HZSM-5, SiZr ($SiO_2–ZrO_2$), and Nb_2O_5.

In this study, the hydrogenation of phenol was performed using $(HCOO)_2Ni$ as the precursor of Ni in an autoclave at elevated hydrogen pressure up to 3 MPa (initial pressure at RT). The thermal decomposition of nickel formate usually starts from about 260 °C.[8] However, the thermal decomposition temperature would be increased under the high pressure of H_2 due to the effect of reaction equilibrium. So, the decomposition of nickel formate is not complete at 260 °C in octane, resulting in a lower phenol conversion (Table 1, Entry 1). With the temperature increased, phenol conversion drastically increases since the decomposition of nickel formate is completed, resulting in the formation of in situ Ni. Moreover, cyclohexane selectivity also increases with temperature (Table 1, Entries 1–3), suggesting that hydrogenolysis of C–O over Ni catalyst can also be favored at higher temperature.

To investigate the catalytic performance in different solvent, octane, water, and dodecane were tested on the hydrogenation reactions of phenol over Ni derived in situ from decomposition of $(HCOO)_2Ni$, respectively (Table 1, Entries 2, 4, and 5). Alkanes are shown to be an efficient solvent for the hydrogenation of aromatic rings, obtaining a high phenol conversion.

Table 1. Hydrogenation and HDO of phenol with $(HCOO)_2Ni$ under different reaction conditions[a]

Entry	Catalyst precursor	Solvent	T/°C	Conversion /%	Selectivity/%		
					Cyclohexanol	Cyclohexane	Methylcyclopentane
1	$(HCOO)_2Ni$	Octane	260	34.6	90.6	9.4	—
2	$(HCOO)_2Ni$	Octane	280	96.0	100	—	—
3	$(HCOO)_2Ni$	Octane	290	98.1	84.4	15.6	—
4	$(HCOO)_2Ni$	H_2O	280	10.3	100	—	—
5	$(HCOO)_2Ni$	Dodecane	280	98.5	88.4	11.6	—
6	NiO[b]	Octane	280	83.4	93.9	6.1	—
7	$(HCOO)_2Ni$–HZSM-5	Octane	280	99	—	92.7	7.3
8	$(HCOO)_2Ni–Nb_2O_5$	Octane	280	100	—	82.6	17.4
9	$(HCOO)_2Ni$–SiZr	Octane	280	100	3.1	94.1	2.8
10	$(HCOO)_2Ni$–SiZr	Octane	280	98.6	10.2	89.8	—
11	$(HCOO)_2Ni$–SiZr	Octane	280	100	—	94.5	5.5
12	$(HCOO)_2Ni$/SiZr[c]	Octane	280	100	1.4	96.5	2.1
13	NiO/SiZr[d]	Octane	280	86.2	—	98.7	1.3

[a] Reaction conditions: Phenol: 4.7 g (0.05 mol); $(HCOO)_2Ni$: 1.48 g (0.01 mol); solvent: 143 mL; $P_{H_2} = 3.0$ MPa; $t = 5$ h; the mass of solid acid were 0.7 g for Entries 7–9, and 0.3 and 1.1 g for Entry 10 and Entry 11 respectively; Stirring rate: 800 rpm; $t = 5$ h. [b] Entry 6, the catalyst was NiO powders prepared by calcination of $(HCOO)_2Ni$ in air. [c] Entry 12, the catalyst was prepared by impregnation with $(HCOO)_2Ni$ (1.48 g) and SiZr (0.7 g). [d] Entry 13, the catalyst was prepared by calcination of the $(HCOO)_2Ni$/SiZr at 280 °C under air atmosphere.

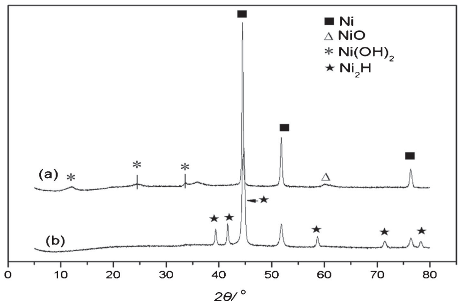
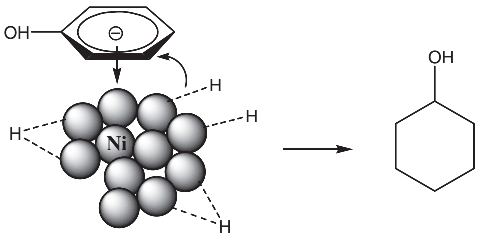


Figure 1. The XRD patterns of Ni obtained from pyrolysis of $(HCOO)_2Ni$ at 280 °C. (a) At solvent of H_2O; (b) at solvent of octane.



Scheme 1. Hydrogenation of phenol over in situ Ni catalyst.

However, the catalytic activity for phenol hydrogenation is deteriorated in the water solvent. Phenol conversions were only 10.3%.

To gain insight into the nature of solvent effects, XRD analysis of the used catalyst was carried out. Apart from the characteristic peaks of Ni ($2\theta = 44.45$, 51.81, and 76.32°), the peaks of NiO ($2\theta = 19.6$, 33.4, and 60.4°) and $Ni(OH)_2$ ($2\theta = 19.6$, 33.4, and 60.4°) were clearly observed for the catalyst used in water (profile of (a) in Figure 1). In aqueous solution, H_2O can coordinate with the Ni^{2+}, forming a complex compound $[Ni(H_2O)_6]^{2+}$, which can be decomposed into $Ni(OH)_2$. Thereafter, $Ni(OH)_2$ would be further decomposed into NiO.[8] To make matters worse, part of the Ni catalyst can be oxidized in the presence of H_2O. These lead to a decline of the catalytic activity for hydrogenation.

In octane, $(HCOO)_2Ni$ was directly decomposed into Ni, H_2, CO, etc. The hydrogen derived in situ from the decomposition of $(HCOO)_2Ni$ and the dissolved hydrogen in alkane solution[9] can be adsorbed on the surface of cluster Ni, forming an adsorption of linear H species (Ni–H). This is a weak and reversible adsorption with high catalytic activity for hydrogenation reaction. During the hydrogenation of phenol, Ni^0 accepts the delocalized aromatic ring electron, resulting in the activation of the ring,[10] which allows the nucleophilic addition reaction occurring through the adsorbed H attacking the aromatic ring, finally completing the conversion of phenol to cyclohexanol (Scheme 1).

However, linear adsorption is unstable. The adsorbed H atom tends to form the bridge adsorption species (Ni–H–Ni), which is stable and irreversible adsorption leading to lower activity for the hydrogenation of the aromatic ring.[11] Fortunately, bridge absorbed H can prevent the oxidation of Ni during the reaction process, giving the catalyst longer life with high catalytic activity for hydrogenation.

Ni powders (prepared by calcination of $(HCOO)_2Ni$ in air) were used as catalyst in the hydrogenation of phenol at 280 °C in octane. The phenol conversion (Entry 6, 83.4%) is lower than that of the in situ Ni catalyst derived from the decomposition of $(HCOO)_2Ni$ (Table 1, Entry 2, 96.0%), clearly suggesting an advantage for the in situ catalyst in phenol hydrogenation. The hydrodeoxygenation of phenol was performed over the combination of $(HCOO)_2Ni$ and different solid acid (Table 1, Entries 7–9). It could be found that the phenol conversion further increased with the addition of solid acids. Synergy effects between the hydrogenation and dehydration might be an important reason. In the reaction process, phenol is converted by hydrogenation over the in situ formed Ni to form the intermediates of cyclohexanol, then through dehydration catalyzed by solid acid and subsequent hydrogenation by Ni catalyst.

Over the combination of $(HCOO)_2Ni$ and SiZr, the major products for the phenol HDO were cyclohexane (94.1%), methylcyclopentane (2.8%), and cyclohexanol (3.1%). Cyclohexanol disappeared from the phenol HDO products when Nb_2O_5 and HZSM-5 were added into the reaction system (Table 1, Entries 7 and 8). The reason is that strong acidity favors dehydration of intermediate cyclohexanol. In addition, increased selectivity for the methylcyclopentane was also observed in the products when HZSM-5 and Nb_2O_5 were used as solid acids. This outcome may be also associated with the acidity of the solid acids because a strongly acidic catalyst favors the isomerization of intermediates formed during the process of phenol HDO.[12]

The effects of combination of nickel precursor and solid acid on the catalytic performance were investigated. The catalytic activity of a mechanical mixture of $(HCOO)_2Ni$ and solid acid SiZr is similar to that of the supported catalyst $(HCOO)_2Ni/SiZr$. Over the two catalysts, phenol can be converted into cyclohexane with a high conversion rate and selectivity (Table 1, Entries 9 and 12), suggesting an excellent synergy between in situ Ni and acid sites. However, the conventional supported catalyst Ni/SiZr exhibits a lower catalytic activity for the phenol HDO (Table 1, Entry 13). This result also indicates that the catalyst originating from the in situ method has an advantage for phenol HDO from another viewpoint.

Apart from phenol, more complex phenolic compounds, including guaiacol, vanillin, eugenol, anethole, *o*-cresol, 2,4-dimethylphenol, and acetylisoeugenol were investigated under the optimized conditions in octane at 280 °C (Table 2, Entries 1–7). The combination of in situ Ni and SiZr successfully converted these tested phenolic compounds to their corresponding C6–C9 cyclohexanes as expected. In addition, a small amount of arenes was also observed, which may result from the hydrogenolysis of the C–O bond of aryl ethers. The catalytic performance is comparable to the combined catalysts of Pd/C and liquid acid H_3PO_4, Pd/C and HZSM-5, Raney® Ni and Nafion/SiO_2.[7,13] The octane numbers of the obtained hydrocarbons mostly range from 80 to 120, indicating that it is suitable as a high-grade transportation fuel component.[5]

Furthermore, mixed phenolic compounds were also investigated over the combined catalyst with in situ Ni and SiZr (Table 2, Entry 8). Most of the phenolic compounds were transformed into hydrocarbons. The main products were cyclohexane, methylcyclohexane, and propylcyclohexane as expected, which were similar to the results in the HDO of single

Table 2. HDO reaction of phenolics over $(HCOO)_2Ni$ and SiZr[a]

Entry	Reactant	Conv./%	Selectivity/%
1	Guaiacol	96.8	Methylcyclopentane (2.84) Benzene (5.32) Cyclohexane (91.84)
2	Vanillin	93.1	Dimethylcyclopentane (1.41) Benzene (2.31) Cyclohexane (27.68) Methylcyclohexane (62.97) Toluene (5.62)
3	Eugenol	96.3	*n*-Propylbenzene (6.9) *n*-Propylcyclohexane (90.9) 1-Methyl-2-propylcyclopentane (2.2)
4	Anethole	94.1	*n*-Propylbenzene (11.25) *n*-Propylcyclohexane (88.1) 1-Methyl-2-propylcyclopentane (0.65)
5	O-cresol	98.8	Methylcyclohexane (93.8) Toluene (6.2)
6	2,4-dimethylphenol	92.8	1,3-Dimethylcyclohexane (89.7) *m*-Xylene (10.3)
7	Acetylisoeugenol	100	*n*-Propylbenzene (3.7) *n*-Propylcyclohexane (91.8) 2-Methoxy-4-propylphenol (4.3)
8	Mixture[b]	88.6	Cyclohexane (32.1) Methylcyclohexane (22.8) Toluene (5.8) *n*-Propylbenzene (2.1) *n*-Propylcyclohexane (37.2)

[a] Reaction conditions: reactant: 0.05 mol; $(HCOO)_2Ni$: 0.01 mol; the mass of SiZr were 0.7 g; octane: 143 mL; $P_{H_2} = 3.0$ MPa; $T = 280$ °C; $t = 5$ h. Stirring rate: 800 rpm. [b] Entry 8: the mixture consisted of phenol (0.01 mol), cresol (0.01 mol), eugenol (0.01 mol), *trans*-anethole (0.01 mol), vanillin (0.005 mol), and guaiacol (0.005 mol).

phenolic compounds. Interactions between components in the mixture were not observed. This is expected to be very meaningful because lignin depolymerization products are phenolic mixtures, including guaiacols and alkyl-substituted phenols.[6]

Finally, recycling of the in situ formed Ni combined with solid acid SiZr catalyst was investigated in the HDO of phenolic mixtures. The conversion of the phenolic mixtures decreased from 88.6% in the first run to 78.4% in the second run. Fortunately, the decline for the conversion of the phenolic mixtures is slight when the catalyst was further reused in the third run and the fourth run (Figure S1A and Table S2, Supporting Information (SI)). Repeatedly used catalysts were analyzed by TG method. Compared the catalyst used only once, the weight loss increased inconspicuously while the catalyst was reused four times (Figure S1B, SI). This result may strongly suggest that the catalyst shows excellent resistance to coking formation. Coke may not be the main reason for the decline of catalytic activity. However, the crystallite size of Ni increased when the catalyst was repeatedly reused (Figure S1C, SI). This might be a reason for the decline of catalytic activity. In addition, it can be also inferred that the absence of Ni and hydrogen derived in situ from the decomposition of $(HCOO)_2Ni$ might be another factor for the decline of catalytic activity in the HDO of phenolic compounds.

In summary, we have developed a highly efficient non-noble and non-sulfided catalyst for the hydrodeoxygenation of phenolic compounds in alkane solvent. The fully heterogeneous catalyst combination acts as a bifunctional catalyst yielding high activity and selectivity to alkane, in which, the Ni obtained in situ from thermal decomposition of $(HCOO)_2Ni$ acts as hydrogenation and hydrogenolysis catalyst when HZSM-5, Nb_2O_5, and SiZr acts as solid acid for dehydration. This approach provides a new alternative route for upgrading lignin-derived phenolic compounds to hydrocarbons.

This work was financially supported by grants from National Key Technology Support Program (No. 2014BAD02B01), National Basic Research Program of China (No. 2012CB215304) and Youth Innovation Promotion Association of CAS (No. 2015288).

Supporting Information is available electronically on J-STAGE.

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