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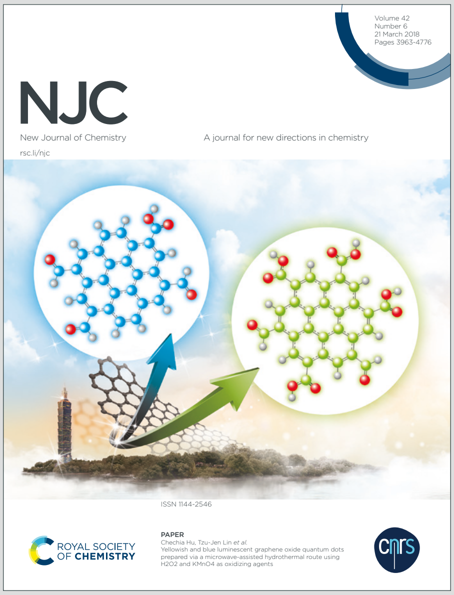

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ARTICLE

In-situ hydrogenation of phenolic compounds over Ni-based catalysts: upgrading of lignin depolymerization products

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A series of Ni-based catalysts were prepared to obtain H_2 from the aqueous phase reforming (APR) of methanol for the in-situ hydrogenation of phenolic compounds for bio-fuel, including Ni/SiO_2-ZrO_2, Ni/HZSM-5, Ni/Al_2O_3, Ni/SiO_2, Ni/AC and Ni/CMK-3. The promotion effect was investigated with the addition of Co, La, Fe and Cu in Ni/ CMK-3 catalyst and which were analyzed using BET, XRD and SEM. The results showed that Ni/SiO_2, Ni/AC and Ni/CMK-3 exhibited better performance on the yield of hydrogen, which were chosen for further investigation on the in-situ hydrogenation of phenol, guaiacol and lignin depolymerization products (LDP). Over these Ni-based catalysts,the APR of methanol could provide hydrogen for the hydrogenation of phenolic compounds.. Among the modified Ni/CMK-3 catalysts, La-Ni/CMK-3 exhibited the highest activity for the conversion of phenol (80.88%) with the satisfactory cyclohexanol yield (76.64%) at 240℃ for 4h without H_2. Over La-Ni/CMK-3, the content of phenolic compounds in LDP decreased from 75.25% to 25.38%, while the content of saturated alcohols increased from1.34% to 31.19%. It's possible to use the APR of methanol for the hydrogenation of LDP over Ni/CMK-3 catalysts.

Introduction

Inedible plant biomass in the form of lignocellulose, as one kind of bioenergy, could meet these essential criteria including being renewable, CO_2-neutral, widely available, and not competing with food production [1]. Lignin, as one of the main components of biomass and for its methoxylated phenylpropane structure, is a kind of potential fossil fuels' resource [2, 3]. However, as a kind of three-dimensional amorphous polymer [4], the depolymerization of lignin is a hot and difficult topic.

Lignocellulosic biomass is composed of cellulose (50%), hemicellulose (25%) and lignin (25%)[5]. One of the most prevalent strategies for lignin utilization is the direct hydrogenolysis of native lignin in biomass. However, the single lignin depolymerization has been shown to be higher in efficiency. Lignin extracted by Organosolv methods are among the most user-friendly and economically, because many solvents can be easily recycled[6]. The lignin extraction process depends on their chemical solubilization in the presence of an acid (proton donor). The process is generally carried out in hot situation to promote hydrolysis reactions between the ligno-cellulosic sub-fractions. Finally, the extracted lignin fractions are solubilized in a solvent solution (acetic acid or ethanol).Organosolv pretreatment affords sulfur-free lignin with high purity, which makes it a suitable precursor for depolymerization[7-9].Owing to the corrosivity, instability and other drawbacks, the unprocessed bio-oil need further upgrading for utilization. Because there are many kinds of phenolic compounds in the liquid product from the lignin and the content of each is not high, there are a lot of study on the hydrogenation of phenolic compounds to high-grade biofuels [10, 11].

Phenols, specially phenol and guaiacol, are popular model compounds for phenolic monomer valorization study [12,13]. Liu[14] studied selective hydrogenation of phenol to cyclohexanone over dual supported Pd-Lewis acid catalysts. Long[15] used Ni/MgO as catalyst to hydrogenate guaiacol for cyclohexanol production. The research group of Kou[16, 17] found that guaiacol could be completely converted into cycloalkane with Pd/C and H_3PO_4 catalysts. Yinet[18] reported that Ru/CMK-3 showed superior catalytic performance on the hydrogenation of levoglucosan, which gave essentially quantitative yields of sugar alcohols. Huang[19] reported that over Pd/N-CMK-3, various nitroarenes could be hydrogenated highly efficiently and selectively to the corresponding aromatic amines. Besides, the Pd/N-CMK-3 catalyst could be recovered easily for multiple recycling reactions without a loss of catalytic performance. Pang[20] used sulfonated CMK-3 as a catalyst, the results showed that the cellulose could be selectively hydrolyzed into glucose and the yield of glucose reached 74.5%.

But among the hydrogenation researches, hydrogen energy, as a kind of very expensive and high-level energy, must be used during the hydrogenation process. Is there any other lower cost chemical could afford hydrogen without hydrogen? In our previous work, we found that raw bio-oil could be converted into saturated alcohol at 220°C over Raney Ni catalyst in the methanol-water solvent without hydrogen. We also found that the conversion of methanol in aqueous phase reforming (APR)

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reaction, hydrogen selectivity were promoted and the side reaction for producing methane was restrained while the in-situ hydrogenation happened in the same reactor[9]. Later, Guan[21] found that in the upgrading fast pyrolysis bio-oil reaction, 0.25-10wt.% Mg doping in Al-MCM-41 could improve the in-situ catalytic activity.

In this paper, different carriers, such as SiO_2-ZrO_2, HZSM-5, Al_2O_3, SiO_2, AC and CMK-3, were chosen to load Ni activity in the APR of methanol for the hydrogen. The catalysts of Ni/SiO_2, Ni/AC, Ni/CMK-3 and the Ni/CMK-3 with different promoters were chosen for further investigation on the in-situ hydrogenation of model compounds and LDP.

Experimental

Materials

Methanol (P99.5%, analytical reagent) was purchased from Tianjin Fuyu Fine Chemical Co. Ltd. Phenol (P99.5%, analytical reagent) and guaiacol (P99.5%, analytical reagent) were purchased from Tianjin Fuchen Chemical Reagents Factory. $Co(NO_3)_2·6H_2O$ and $Ni(NO_3)_2·6H_2O$ were purchased from Guangzhou Chemical Co. Ltd. $Cu(NO_3)_2$, $La(NO_3)_3·6H_2O$ and $FeCl_3$ were purchased from Guangzhou Chemical Reagents Factory. Other chemicals were supplied by Jinhuada Chemical Reagent Co., Ltd. CMK-3 was prepared in the way shown in the literatures [22, 23].

The lignin depolymerization product was depolymerized from organicsolve lignin in methanol over 0.5g organicsolve lignin, 0.12g $MgCl_2$ (calcining before using) and 40 mL methanol were charged into a 100 mL 316L stainless autoclave. After the air was changed with H_2, the pressure was set to 0.5 MPa and the reaction was set at 260 °C for 0.5 h. After reaction, the autoclave was cooled down to the room temperature, the product mixture was filtered, and the liquid product was obtained as feedstock in the in-situ hydrogenation process.

Preparation of catalysts and characterization

The Ni/CMK-3 catalyst was prepared using wet impregnating method. After impregnating CMK-3 in $Ni(NO_3)_2·H_2O$ aqueous solutions, the water was evaporated and the residue was dried at 120^{o}C. The catalysts of 20 wt% Ni was obtained after calcined at 450^{o}C at N_2 atmosphere and reduced at 550°C in the flow of 5vol% hydrogen mixed with 95vol% nitrogen [24]. We also got the catalysts of Ni/SiO_2-ZrO_2, Ni/HZSM-5, Ni/Al_2O_3, Ni/SBA-15, Ni/AC, Ni/SiO_2 and Ni/CMK-3 in the same method.

Co-Ni/CMK-3 catalyst was prepared by wet impregnating method. The CMK-3 was impregnated in the $Ni(NO_3)_2·6H_2O$ and $Co(NO_3)_2·6H_2O$ mixed aqueous solution and the content of Ni and Co addition were 20wt% and 1wt% respectively. After calcined at 450^{o}C at N_2 atmosphere and reduced at 550°C in the flow of 5vol% hydrogen mixed with 95vol% nitrogen, the Co-Ni/CMK-3was obtained. In the same way, we got the catalysts of La-Ni/CMK-3, Fe-Ni/CMK-3 and Cu-Ni/CMK-3.

The surface area and pore size distribution of the catalysts were determined by the Brunauer–Emmet–Teller (BET) method using Quantachrome. The average pore diameter and pore volume were calculated with the Barret–Joyner–Halenda(BJH) model. X-ray diffraction(XRD) patterns were recorded using a RigakuD/max-rC with a CuKα radiation source. Scan step was 0.02°, scanning in 5-80° over catalysts. Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 instrument operated at 20 kV.

Typical procedure and products analysis

The APR of methanol was carried out in a 100 mL stainless autoclave. 1.5g catalyst, 36g water and 16g methanol (water/methanol =20/5, molar ratio) were charged into the autoclave. After the air was changed with N_2, the pressure was set to 0.1 MPa and the reaction was set at 220°C for 4 h with the revolution of 400rpm. After reaction, the autoclave was cooled down to the room temperature and then sampled the gas products for GC analysis with FID detector.

The in-situ hydrogenation of phenolic/gualacol and the lignin depolymerization product was also carried out in the 100 mL stainless autoclave respectively. Based on the APR reaction system of methanol, the reactants of 0.08mol(model compounds) or 14 mL(raw lignin depolymerization product) were added in the reactor. The in-situ hydrogenation reaction was set at 240°C for 4 h under 1 Mpa pressure of N_2 atmosphere. The gas product was sampled for analysis by Shimadzu GC20B gas chromatograph and the liquid product was sampled for analysis by Shimadzu GC 2010. The raw lignin depolymerization product and the upgraded product were also measured by gas chromatography/mass spectrometry (GC–MS, Trace 2000, Thermo-Finnigan Inc., USA). The separation was realized on a column of HP-INNOWAX, 30 m*0.25 mm*0.25 mm, and the oven temperature program was 40 ^{o}C (holding for 8 min) at 6/min to 280^{o}C (holding for 30 min). The content of each compound was evaluated based on GC data using the internal standard method. The conversion of reactant (mol%) was calculated as below.

$$\text{Conversion}=\left(1-\frac{\text{Moles of reactants after reaction}}{\text{Moles of reactants loaded initially}}\right)\times 100\% \quad (1)$$

$$\text{Selectivity of product}=\left(\frac{\text{Moles of product}}{\sum\text{Moles of product}}\right)\times 100\% \quad (2)$$

Results and discussion

Aqueous phase reforming of methanol

The APR of methanol was carried out over the Ni-based catalysts with different carriers. The amount of each gas in products was shown in Fig. 1.

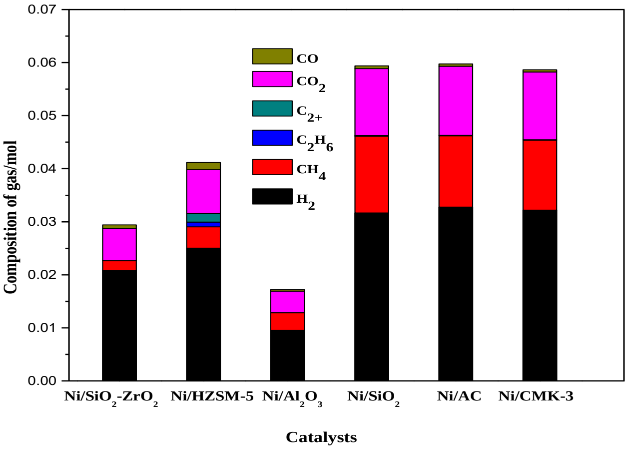

Fig.1 The gas distribution from the APR of methanol over Ni catalysts on different supports (0.1MPa (N_2), 220 °C, 4 h, 1.5g catalyst, 36g water and 16g methanol)

In all the products, H_2, CO_2 and CH_4 were the main products. Over Ni/HZSM-5 catalyst, there was some C_2H_6 and C_{2+} in the products. Grarcia[25] studied the APR reaction of methanol, acetic acid and glycerol over Ni-La/Al_2O_3 catalyst, the gas phase was made up of H_2, CO_2, CO and CH_4. Tsiakaras[26] used Ni/SiO_2-Al_2O_3 as catalyst in the APR of crude glycerol, the main gas products were H_2, CH_4 and CO_2. While using Pt/Al_2O_3 as catalyst [27], except for the three kinds of gas, CO was one of the main gas products in the products.

From Fig. 1, the gas product distributions over Ni/SiO_2, Ni/Ac and Ni/CMK-3 were quite similar with each other and the amount of H_2 was all above 0.03 mol. The distributions of gas products varied greatly after APR reaction over Ni/SiO_2-ZrO_2, Ni/HZSM-5 and Ni/Al_2O_3. Naito[28] used NaY zeolite, Al_2O_3, SiO_2, and SiO_2-Al_2O_3 to load ruthenium as catalysts for the aqueous phase reforming of acetic acid and found that the amounts of products changed a lot over different supports. The gas product distributions might depend not only on the activity centers but also on the supports. In consideration of the better performance on the APR of methanol, the catalysts of Ni/SiO_2, Ni/Ac and Ni/CMK-3 were selected as the catalysts to investigate the in-situ hydrogenation of lignin-derived compounds and the raw lignin depolymerization products.

The characterization of Ni-based catalysts

Table 1 Textural and structural properties of the catalysts

Catalysts	A_{BET}/m^2·g^{-1}	Average pore size/nm	Pore volume /cc·g^{-1}
Ni/SiO_2	450.75	1.06	0.31
Ni/AC	846.36	0.54	0.76
Ni/CMK-3	1001.15	3.83	0.75

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The BET of Ni/SiO_2, Ni/AC and Ni/CMK-3 were shown in Table 1. The carbon carriers had relative higher specific surface area. CMK-3, as one of typical mesoporous materials, has the biggest specific surface area and average pore size among the three catalysts, as well as high hydrothermal stability and biocompatibility [29, 30].

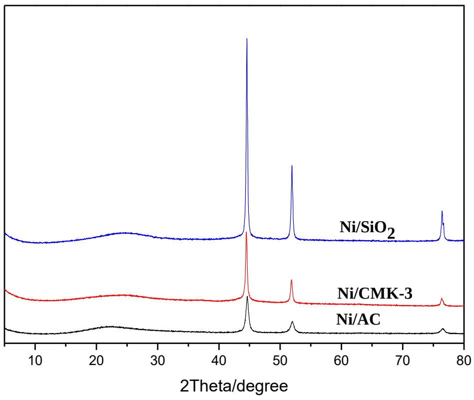

Fig. 2 XRD patterns of Ni/SiO2, Ni/Ac and Ni/CMK-3

The XRD patterns of Ni/SiO_2, Ni/AC and Ni/CMK-3 were shown in Fig. 2. In the three XRD patterns, the three strong diffraction peaks were all in 44.51°, 51.85°, and 76.37°, which belonged to the characteristics peak of Ni(111), Ni(200) and Ni(220) respectively[31]. Although the Ni load in the three catalysts was the same, the strength of the diffraction peak varies greatly, which represented the difference in Ni particle size[32]. Therefore, it can be indicated that Ni dispersion varies greatly on different carriers, and the order of approximate particle size is Ni/SiO_2 was bigger than that of Ni/CMK-3 and Ni/AC.

Although in the three catalysts the position of the characteristic diffraction peak was almost the same, the intensity of the peaks varied greatly, which meant that the crystal sizes of these three samples were quite different. From the characteristics peak of Ni, the crystal size of Ni of Ni/SiO_2 >Ni/CMK-3>Ni/AC.

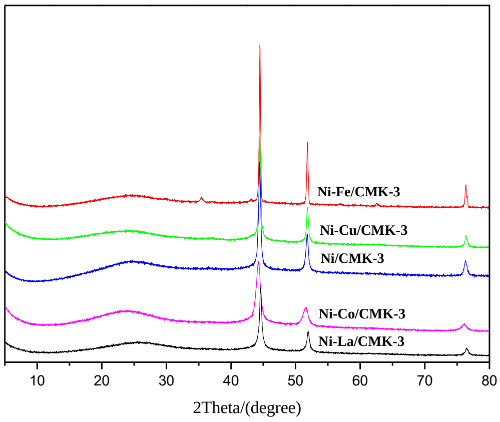

Fig.3 XRD patterns of Ni/CMK-3 catalysts with different promoters

XRD patterns of Ni/CMK-3 with promoters were shown in Fig. 3. Similar with the XRD pattern of Ni/CMK-3, thetypical peaks indexed with 2θ = 44.51°, 51.85° and 76.37° were attributed to Ni(111), Ni(200) and Ni(220). The characteristic peaks of promoters were not obvious for its low content.

Using Scherrer formula, the grain size of Ni particles in catalyst samples modified by various additions were calculated. The textural properties and the Ni particle grain size of Ni/CMK-3 catalysts with different promoters were shown in Table 2.

Table 2 Physical properties of Ni/CMK-3with promoters

Catalysts	A_{BET}[a]/ ($m^2 \cdot g^{-1}$)	Average pore size[a]/nm	FWHM	Average metal size[b]/nm
Ni/CMK-3	1001.15	3.83	0.18	46.15
Ni-Fe/CMK-3	922.68	3.86	0.13	63.47
Ni-La/CMK-3	925.95	3.84	0.23	36.26
Ni-Co/CMK-3	955.84	3.83	0.22	39.05
Ni-Cu/CMK-3	1018.04	3.85	0.15	56.39

FWHM: full width half maximum;

[a] Evaluated from N2 adsorption-desorption isotherms.

[b] Estimated by XRD.

The surface area of the catalysts was all in the range of 920 to 1020 $m^2.g^{-1}$ and all the modified catalysts kept the characteristic of high surface areas. The pore diameters of the catalysts were all about 3.8 nm, which had little difference with each other. The average Ni size in catalysts with different additives were calculated by the Scherrer formula estimated by XRD. The results exhibited that the Ni/CMK-3 catalysts modified by La and Co, in which the average Ni size was 36.26 nm and 39.05 nm, exhibited better dispersibility with smaller metal particle size than the Ni/CMK-3 catalysts with other promoters. The introduce of La and Co would help to increase the dispersibility of metal particles and contribute to restraining the aggregation of metal particles during the thermal treatment which might be due to the strong interaction between Co/La and/or Ni species and support. Similar behaviors were reported in the Ni catalysts after the addition of other metal components to improve the dispersibility of metal particles [33-35]

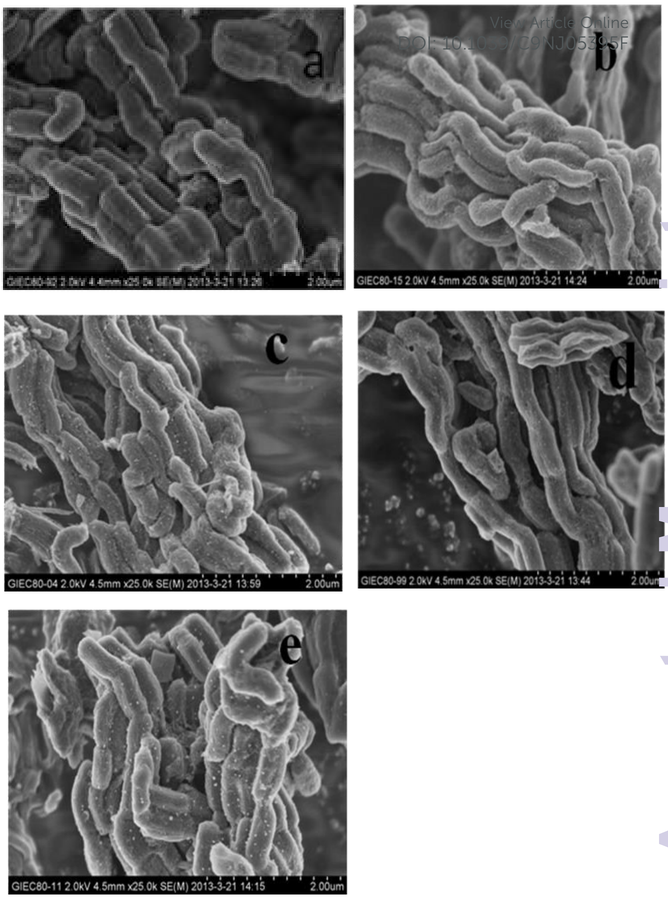

Fig.4 SEM imagines of Ni/CMK-3 with promoters（a:Non, b:La, c:Cu, d:Co, e:Fe）

The SEM of these Ni/CMK-3 catalysts were shown in Fig. 4. All the catalysts maintained the mesoporous rod structure of CMK-3[36]. Moreover, the voids all kept well, even if the Ni active center was loaded. The Ni activity was uniformly dispersed in the surface and pore channels of the catalysts. In Fig. 5,we could see a lot of white dots on the CMK-3 carrier which were the Ni particle. The difference between Ni/CMK-3(Fig.4a), Ni-La/CMK-3(Fig.4b) and Ni-Co/CMK-3 (Fig. 4d) was not particularly obvious, but the dots in Fig. 4c(Ni-Cu/CMK-3) and Fig.4e (Ni-Fe/CMK-3) were significantly larger than those mentioned above. The results were consistent with the average metal size estimated by XRD above.

The in-situ hydrogenation of model compounds over Ni-based catalysts

The experimental results of the hydrogenation of phenol and guaiacol over Ni-based catalysts were showed in Fig. 5. From Fig.5, over different catalysts, the conversions of model compounds, the selectivity and the yield of cyclohexanol were quite different. The experimental results indicated that, the in-situ hydrogenation rate of phenol and guaiacol over Ni/CMK-3 was higher than Ni/SiO_2 and

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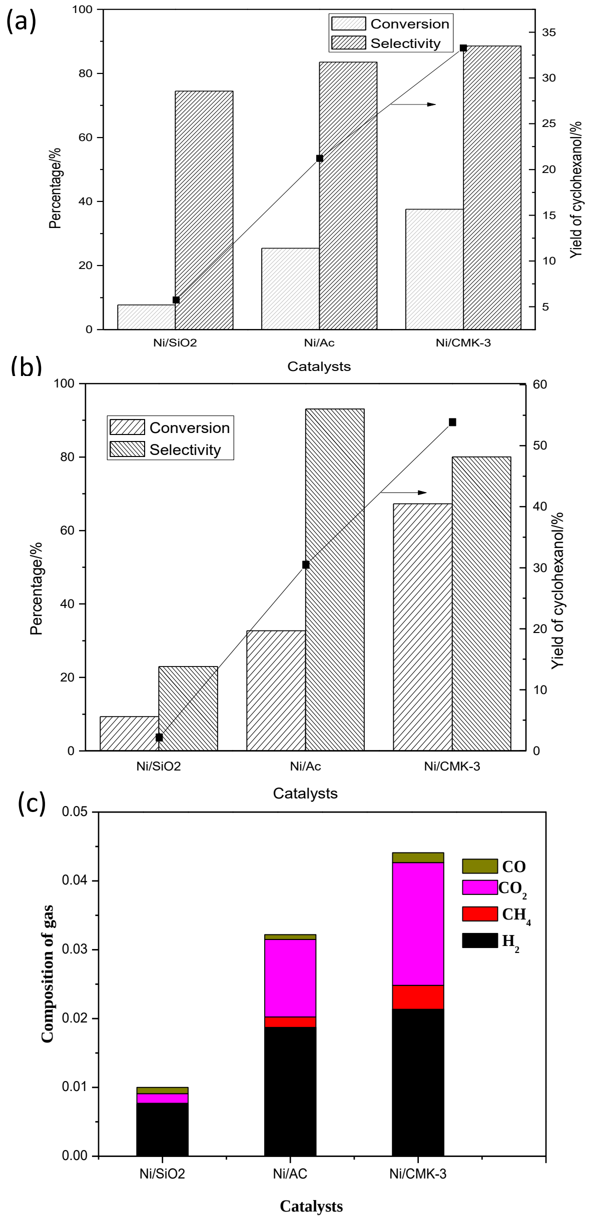
Ni/AC. It followed the sequence of Ni/SiO$_2$ < Ni/AC < Ni/CMK-3. For phenol, there were two products including cyclohexanol and cyclohexanone, the selectivity of cyclohexanol was all above 75% over the three kinds of catalysts. As for guaiacol, the selectivity of cyclohexanol was the highest of 93.11% over Ni/AC, meanwhile the conversion was up to 67.26% over Ni/CMK-3. For phenol and guaiacol, cyclohexanol reached the maximum yield under the action of catalyst Ni/CMK-3. The BET and XRD results of Ni/CMK-3 catalyst were the most optimistic among the three-characterization analysis of catalysts. The higher specific surface area and smallest particle size might lead to a higher adsorption capacity and a better catalytic activity [37].



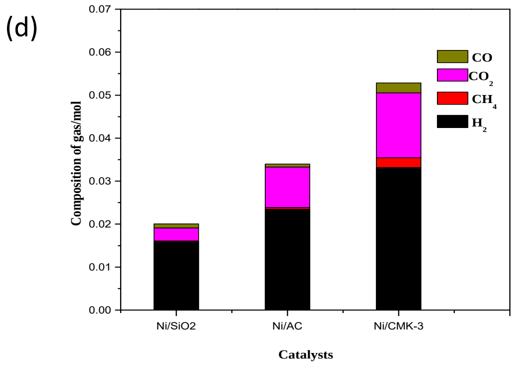


Fig.5 The in-situ hydrogenation results of phenol(a,c) and guaiacol(b,d) over Ni/SO2, Ni/Ac and Ni/CMK-3 (1MPa (N2), 240 °C, 4 h; 1.5g catalyst, 36g water, 16g methanol and 0.08mol model compounds)

The gas products after the in-situ hydrogenation of model compounds were also quite different. Compared with the gas products after the APR of methanol (Fig. 1), the yield of H$_2$ was 0.03mol over Ni/SiO$_2$. After the process of the in in-situ hydrogenation of phenol, this amount deceased from 0.03 mol to 0.0076mol, dropping more than 0.02mol. But from the conversion of phenol (7.7%) and the selectivity of cyclohexanol (74.5%), the consumption was only 0.014mol. Therefore, the addition of phenol might inhibit the Ni/SiO$_2$ catalytic activity of APR. Meanwhile, for the catalysts of Ni/AC and Ni/CMK-3, the consumption of H$_2$ for the hydrogenation of phenol was comparable to the difference of the H$_2$ yield between Fig. 1 and Fig. 5. For the hydrogenation of guaiacol, the yield of H$_2$ in the in-situ hydrogenation was higher than that in the APR of methanol, which might because the detached methoxy group may further happen APR reaction on the surface of Ni/CMK-3, providing more hydrogen for the reaction system. The catalytic capacity of the catalyst to produce hydrogen after the addition of phenolic compounds might be another factor affecting the activity of in-situ hydrogenation of phenolic compounds.

The gas product after in-situ hydrogenation of phenol under Ni/CMK-3 catalysts was shown in Fig. 6. From Fig. 6, the yields of the gas products were quite different and all increased compared with the catalyst of Ni/CMK-3 after the addition of Co, Cu and La, except for adding Fe in Ni/CMK-3. The conversion of phenol and the selectivity of cyclohexanol over Ni/CMK-3 catalysts were shown in Fig. 7.

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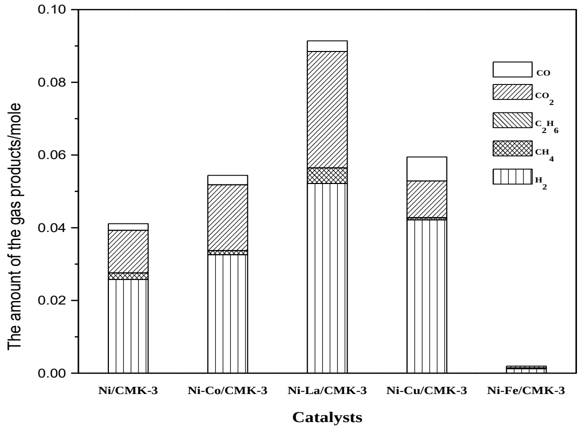

Fig.6 Gas product after in-situ hydrogenation of phenol under Ni/CMK-3 catalysts

Compared with Ni/CMK-3, the addition of Co and La enhanced the catalysts' in-situ hydrogenation performance both on the conversion of phenol and the selectivity of cyclohexanol. Especially over La-Ni/CMK-3, the conversion of phenol increased from 37.56% to 80.88% and the selectivity of cyclohexanol increased from 88.59% to 94.76%. From the gas products, we might foresee this result for the highest H_2 yield. Over Cu-Ni/CMK-3 and Fe-Ni/CMK-3 catalyst, the conversion of phenol decreased. The selectivity of cyclohexanol was nearly 100% over Ni-Fe/CMK-3 but the conversion of phenol was only 1.40%, which might be for the lower yield of H_2.

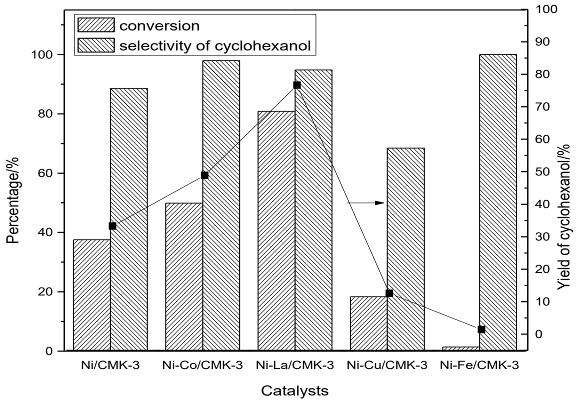

Fig.7 The conversion of phenol and the selectivity of cyclohexanol over Ni/CMK-3 with different promoters (1MPa (N_2), 240 °C, 4 h; 1.5g catalyst, 36g water, 16g methanol and 0.08mol phenol)

We observed that in general, the catalysts active order of the yield of cyclohexanol followed the sequence of Ni-La/CMK-3 > Ni-Co/CMK-3 > Ni/CMK-3 > Ni-Cu/CMK-3 > Ni-Fe/CMK-3 and from Table 2, the Ni particle size order of the catalysts followed the sequence of Ni-La/CMK-3 < Ni-Co/CMK-3 < Ni/CMK-3 < Ni-Cu/CMK-3 < Ni-Fe/CMK-3. The change in activity might be related with the size of Ni particles. Furthermore, the reason why the activity of Ni-Fe/CMK-3 decreased might be that the hydrogen production during the in-situ hydrogenation process does not provide enough H_2 for the hydrogenation of phenol. Abdullah[38] found Ni-La-co-impregnated Al_2O_3 catalyst had excellent activity for the production of hydrogen. Feed conversion of 88.53% was achieved over 10% Ni/Al_2O_3 catalyst which increased to 95.83% in the case of 10% Ni-5% La/Al_2O_3 catalysts with a H_2 selectivity of 70.44%. As shown in Fig, 6, the catalytic capacity of the Ni-La/CMK-3 catalyst to produce hydrogen in the in-situ hydrogenation process was the best among all the catalysts with the amount of H_2 product was more than 0.05 mol. While enough hydrogen was one of the important factors in the hydrogenation of phenol. Bahari[39] also found that after adding La in Ni/Al_2O_3, Ni particles were finely dispersed on the catalyst surface. Meanwhile, the particle size was not only importance on the activity, but also on the stability and the production distributions [40, 41].

The in-situ hydrogenation of raw lignin depolymerization products over Ni-La/CMK-3

The GC-MS spectra of the lignin depolymerization product before and after in-situ hydrogenation over Ni-La/CMK-3 were shown in Fig.8 and the main composition of liquefaction products were shown in Table 3.

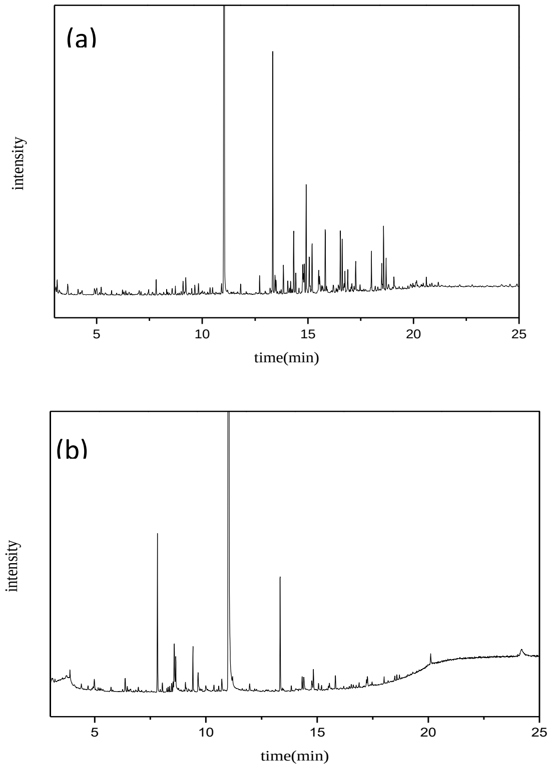

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Fig.8 GC-MS spectra of the lignin depolymerization products before(a) and after(b) in-situ hydrogenation over Ni-La/CMK-3

From Fig. 8 we could observe that the two spectrograms were quite different before and after the in-situ hydrogenation. The retention time (R.T.) of the most depolymerization products from lignin was between 13.30 min and 20.00 min, and after the in-situ hydrogenation reaction, the retention time of the products mainly concentrated from 7.80 min to 15.00 min.

From Table 3, the type of compounds, whose contents were above 0.8 %, was more than 20. After the in-situ hydrogenation reaction, the type of compounds, whose retention time concentrated from 13.30 min to 20.00 min, was nearly 10.

Table 3 Main Composition of liquefaction products before and after in-situ hydrogenation

		Content (%)		Possibility from GC-MS (%)
R.T. (min)	Compound	Raw oil	Ni-La/CMK-3	
3.04	1-Propanol	1.34	-	80
4.99	Cyclopentanone,2-methyl-	1.74	2.07	62
6.37	Cyclohexanone	-	2.84	72
7.82	Cyclohexanol	-	25.08	90
8.05	Cyclohexanol,2-methyl-, cis-	-	0.96	83
8.31	Cyclohexanol,4-methyl-, cis-	-	0.87	43
8.46	Cyclohexanol, 3-methyl-	-	0.79	40
8.53	Cyclohexanol, 4-methyl-	-	1.41	62
8.57	Acetic acid	1.91	9.84	50
9.65	Propanoic acid	-	3.79	67
10.72	Butanoic acid	-	2.56	48
11.02	Acetophenone		-	80
13.34	Phenol, 2-methoxy-	32.42	15.59	97
13.84	Phenol, 2,6-dimethyl-	0.92		91
14.33	Phenol,2-methoxy-4-methyl-	3.18	2.06	95
14.41	cis-1,2-Cyclohexanediol	-	2.79	94
14.76	Phenol, 2,4,6-trimethyl-	0.99	-	68
14.79	Phenol, 2-methyl-	0.97	-	97
14.83	Phenol	5.44	3.28	94
14.92	Diphenyl ether	12.22	-	78
15.20	Phenol, 2,4,6-trimethyl-	1.40	-	68
15.52	Phenol, 2,5-dimethyl-	0.80	-	82
15.55	Phenol, 2,4-dimethyl-	1.04	-	80
15.83	Phenol,2-methoxy-4-propyl-	7.02	2.62	64
16.54	Phenol,2,3,5,6-tetramethyl-	1.44	-	58
16.89	Phenol, 2,3,5-trimethyl-	0.89	-	68
17.27	Phenol, 2,6-dimethoxy-	1.68	1.83	90
18.01	Phenol,2-methoxy-4-(1-propenyl)-, (E)-	3.10	-	76
18.71	Phenol,2,3,5,6-tetramethyl-	0.85	-	82
19.86	Vanillin	0.89	-	96
	others	19.76	21.62	

Several high chromatographic peaks appeared between 7.80min and 8.60 min, most of which were ascribed to saturated alcohols. The depolymerization products of lignin were mainly phenolic compounds with little acids and alcohols. The content of methoxyphenol (such as guaiacol) was 32.42%, while that of other substituted phenols was about 30%. After in-situ hydrogenation reaction, the content of phenolic compounds decreased significantly, and the structure of phenolic compounds was simplified. The saturated alcohols’ contents increased obviously, which mainly concluded cyclohexanol and methyl cyclohexanol. According to the quantitative analysis of the internal standard method, the content of phenolic compounds decreased from 75.25% to 25.38%, meanwhile the content of saturated alcohol increased from1.34% to 31.19% over Ni-La/CMK-3.

Conclusions

In this paper, a series of Ni-based catalysts were prepared to use in the in-situ hydrogenation of lignin derived compounds and lignin depolymerization products. Among these catalysts of Ni/SiO_2-ZrO_2, Ni/HZSM-5, Ni/Al_2O_3, Ni/SiO_2, Ni/AC and Ni/CMK-3, the relative higher hydrogen yield was obtained in the APR of methanolover the catalyst of Ni/SiO_2, Ni/AC and Ni/CMK-3, which were used in the in-situ hydrogenation of phenol and guaiacol. For phenol and guaiacol, cyclohexanol reached the maximum yield under the action of catalyst Ni/CMK-3. The catalyst of Ni/CMK-3 and Ni/CMK-3 modified by Co, La, Cu and Fe were studied in the in-situ hydrogenation of phenol to investigate the in-situ hydrogenation activity. The results showed that the activity of catalysts might be related with the size of Ni particles in the catalysts and including the yield of H_2 production during the reaction. After adding La to Ni/CMK-3, the conversion of phenol increased from 37.56% to 80.88% and the selectivity of cyclohexanol increased from 88.59% to 94.76%, meanwhile the Ni partial size decreased from 46.15 nm to 36.26 nm. After upgrading the lignin depolymerization product over La-Ni/CMK-3, the content of phenolic compounds decreased from 75.25% to 25.38%,

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while the content of saturated alcohol increased from 1.34% to 31.19%.

Conflicts of interest

There are no conflicts to declare.

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