Short communication

Effect of zeolite solid acids on the *in situ* hydrogenation of bio-derived phenol

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A B S T R A C T

The effect of zeolite solid acids on the *in situ* hydrogenation of bio-derived phenol over Raney Ni was investigated, which indicated that the conversion of phenol increased with the addition of zeolite solid acids and Hbeta (Si/Al = 60) showed the best performance of high phenol conversion and selectivity towards the desired products and low carbon loss. In addition, the quantity of Hbeta (Si/Al = 60) and Raney Ni had marked impact on the carbon loss, but little effect on both the conversion and the products distribution. And the mixed catalysts of Raney Ni and Hbeta (Si/Al = 60) exhibited excellent stability.

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1. Introduction

Lately, the method of the *in situ* hydrogenation has been proposed to upgrade the quality of bio-oil. In this method, liquid hydrogen donor solvents were used to generate hydrogen instead of external source of hydrogen. Ton and Fisk used acids as hydrogen donors to hydrogenate model compounds of bio-oil and raw bio-oil over Pd and Nickel based catalysts [1,2]. Xu investigated the methanol's aqueous phase reforming and the coupling on the *in situ* hydrogenation of bio oil model compounds phenol and acetone over Raney Ni catalyst [3]. Wang reported liquid phase *in situ* hydrodeoxygenation of bio-derived phenol to cyclohexene and cyclohexane over Raney Ni and Nafion/SiO$_2$ with methanol as hydrogenation donor [4]. Zeolite solid acids, including Y-type zeolite, ZSM-5 and Beta-type zeolite, were regarded to be one of the most promising catalysts in the application of bio-oil upgrading and have been widely used in acid catalyzed reaction such as dehydration, isomerization, cracking, alkylation, as well as promoting esterification between alcohols and acids in raw bio-oil [5–7]. However, the effect of zeolite solid acids on the *in situ* hydrogenation of bio-oil has not been reported.

In this paper, we firstly systematically investigated the effect of zeolite solid acids on the *in situ* hydrogenation of bio-oil. Phenol was chosen as a model compound of phenols in bio-oil and was upgraded using the *in situ* hydrogenation over Ni catalyst and zeolite solid acids including

Hbeta and HZSM-5 with different Si/Al ratio. And the effect of the quantity of catalysts and the stability of the catalysts were also studied.

2. Experimental section

2.1. Materials

Phenol (≥99.0%, AR), methanol (≥99.9%, GC) were purchased from Aladdin Reagent Co. Ltd. Ethanol (≥99.8%, HPLC), benzaldehyde (≥99.0%, GCS), cyclohexanol (99.0%), cyclohexanone (≥99.8%, GR) were purchased from Tianjin Yuanli Chemical Co. Ltd.

The Raney Ni (20–40 meshes) was obtained from Aladdin Reagent Co. Ltd. The Hbeta (Si/Al = 25, 40, and 60) and HZSM-5(Si/Al = 25, 50) were supplied by Tianjin Nanhua catalyst Co. Ltd. All materials were used without any further purification treatment.

2.2. In situ hydrogenation process

All experiments were carried out in a sealed 100 mL stainless steel batch reactor with methanol (10 mL), deionized water (30 mL), Raney Ni, zeolite solid acid and phenol (3.0 g). Prior to the reaction, the reactor was purged for 10 times with N$_2$ to remove air from the reactor and charged with 1 MPa N$_2$. Then the reactor was heated to the reaction temperature (220 °C) and the reaction proceeded for 4 h with the stirring speed of 500 rpm. After reaction, the reactor was cooled down to room temperature and then sampled gas and liquid products for analysis.

Table 1
The results of the in situ hydrogenation of phenol over Raney Ni and zeolite solid acids.

Catalysts	Phenol			Methanol			Carbon loss (%)
	C(%)	S(%)(Cyclohexanol)	S(%)(Cyclohexanone)	C(%)	S(%) (H₂)	S(%)(CH)	
Raney Ni + Hbeta(25)	93.0	2.8	5.3	62.5	55.3	30.4	85.4
Raney Ni + Hbeta(40)	94.0	5.3	5.5	65.7	56.6	32.2	83.8
Raney Ni + Hbeta(60)	96.0	65.1	24.5	73.0	60.0	31.9	9.0
Raney Ni + HZSM-5(25)	99.3	4.6	1.2	78.7	59.5	29.3	93.5
Raney Ni + HZSM-5(50)	92.9	5.4	4.3	70.6	56.0	30.2	83.9
Raney Ni [a]	71.0	59.8	28.3	79.1	58.6	28.9	8.6
Raney Ni [b]	-	-	-	56.0	41.8	57.0	-

C: Conversion; S: Selectivity; CH: hydrocarbons. Reaction conditions: 1.0 g Raney Ni, 0.3 g zeolite solid acid, $T = 220\,°C$, $t = 4$ h, $P = 1$ MPa (N₂).

[a] APR of methanol with phenol.
[b] APR of methanol without phenol.

2.3. Product analysis

The liquid products were analyzed by GC-FID (GC1100, Beijing Purkinje General Co. Ltd. China) and the gas products were analyzed by GC-BID (SHIMADZU GC-2010). The amounts of liquid products were determined based on GC data using benzaldehyde as the internal standard compound and the amounts of gas products were determined using the external standard method. And the liquid products were identified by Agilent GC6890N/5975MS while the retention time of respective standard was compared with that in GC. The conversion of phenol and the selectivity of main products, H₂ and alkane were calculated based on the Ref. [3]. And the carbon loss was calculated as follows:

$$Carbon\ Loss = \left(1 - \frac{Moles\ of\ reactants + Moles\ of\ all\ liquid\ products}{Moles\ of\ reactants\ loaded\ initially}\right) \times 100\%$$

2.4. Characterization of catalysts

The acidity of the zeolite solid acids was characterized by FTIR spectroscopy of adsorbed pyridine in a Bruke VERTEX 70 spectrometer. A self-supporting wafer made of the sample was placed in the IR cell and degassed at 400 °C for 2 h under dynamic vacuum (10^{-6} mbar). After cooling to 60 °C, the samples were saturated with pyridine vapor and then evacuated at 150 °C. Spectra were recorded at evacuation temperature in the 4000–1300 cm⁻¹ range. The amounts of Brønsted and Lewis acid sites in samples were calculated from the integrated intensities of characteristic bands at ca. 1450 and 1545 cm⁻¹, respectively, using the molar extinction coefficients reported by Emeis [8].

TG (Netzsch, 209-F3) analyses of the fresh and used zeolite catalysts were carried out under a N₂ flow of 30 mL/min by increasing the temperature from 35 to 900 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Effect of zeolite solid acids on the in situ hydrogenation of phenol

The in situ hydrogenation of phenol over Raney Ni and combined catalysts of Raney Ni and zeolite solid acids were studied. The zeolite

Table 2
Py-IR acid properties of zeolite solid acids.

Zeolites	Acid amount/(mmol g⁻¹)	
	Lewis acid	Brønsted acid
Hbeta (25)	0.220	0.170
Hbeta (40)	0.243	0.076
Hbeta (60)	0.235	0.020
HZSM-5 (25)	0.045	0.305
HZSM-5 (50)	0.055	0.210

solid acids included Hbeta and HZSM-5 with different Si/Al ratio (Hbeta with the Si/Al ratio of 25, 40, 60, HZSM-5 with the Si/Al ratio of 25, 50). The experiment results were presented in Table 1.

From Table 1, it could be seen that the conversions of phenol using a mixture of Raney Ni and zeolite solid acid were higher than that using pure Raney Ni, which indicated that zeolite solid acid facilitate the phenol conversion. This might owed to the fact that zeolite solid acids provided a larger catalytic specific surface area and more contact sites to the reactant than Raney Ni [9]. It also could be seen that the Si/Al ratio of Hbeta had little effect on the conversion of phenol while had significant effect on the selectivity of the desired products. The conversion of phenol increased slightly and the selectivity of the desired products improved significantly with the Si/Al ratio of Hbeta increasing from 40 to 60. But the Si/Al ratio of HZSM-5 had no notable effect on both the conversion of phenol and the selectivity of the desired products. The conversion of phenol decreased slightly with the increase of Si/Al ratio and the selectivity of the desired products were particularly little. It occurred severe carbon loss by adding the Hbeta or HZSM-5 except Hbeta (Si/Al = 60). In order to explain these facts, FTIR spectroscopy of adsorbed pyridine and TG analysis were performed. In addition, the hydrogenation of the substrate could promote the APR of methanol, improve the selectivity of hydrogen and suppressed the selectivity of CH. And adding the zeolite solid acids to the Raney Ni had no significant effect on the APR of methanol.

The IR spectra of pyridine absorbed on the Hbeta (Si/Al = 25, 40 and 60) and HZSM-5 (Si/Al = 25, 50) were shown in Table 2 and Fig. 1. Hbeta and HZSM-5 with different Si/Al ratio both had Lewis and Brønsted acid sites. The concentrations of Lewis acid sites were
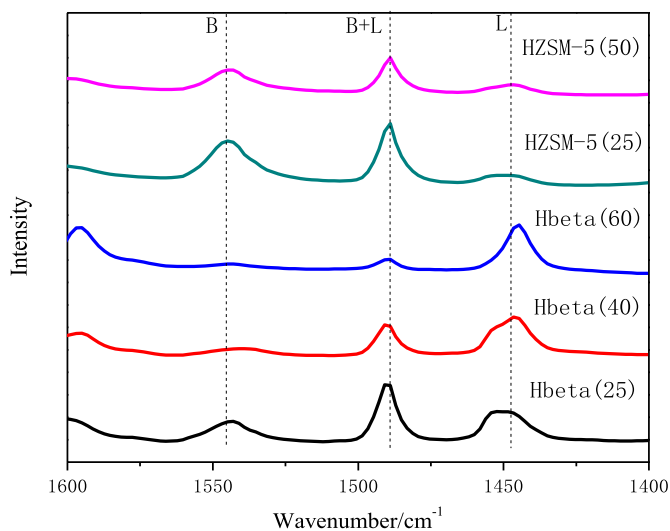
Fig. 1. FTIR spectra of Hbeta and HZSM-5 after pyridine adsorption and evacuation at 423 K. B: Brønsted acid sites; L: Lewis acid sites.
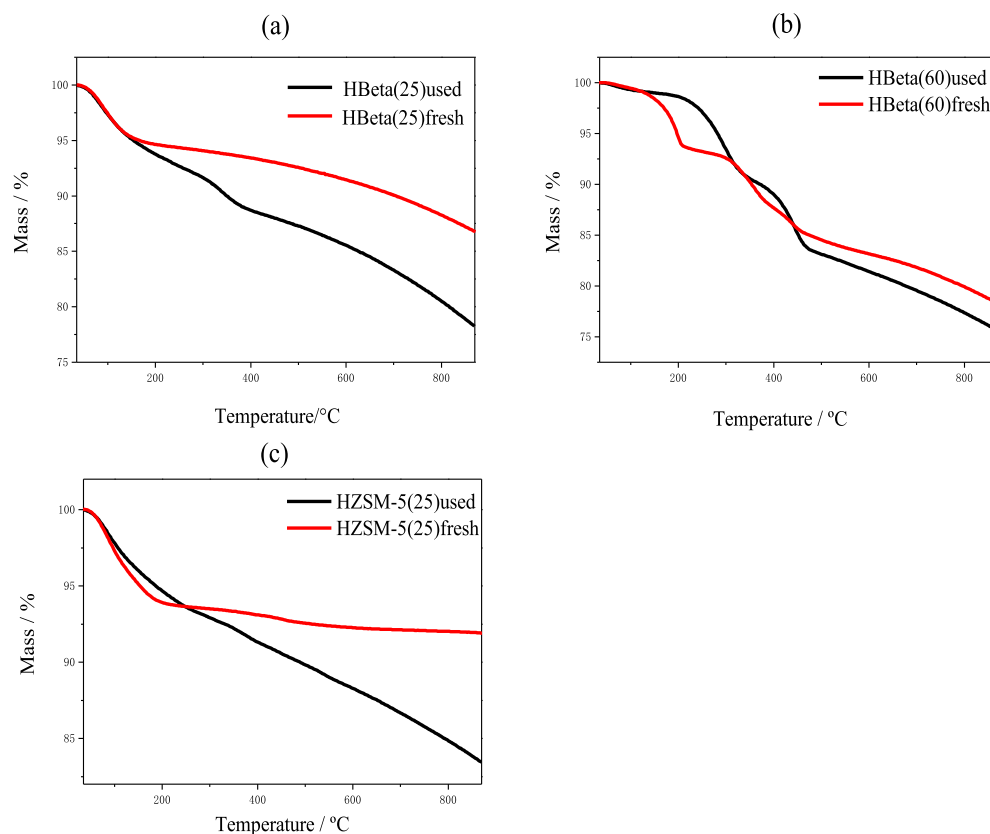
Fig. 2. TG curves of the used and fresh zeolite solid acids under a N_2 flows. (a): Hbeta (Si/Al = 25), (b): Hbeta (Si/Al = 60), (c): HZSM-5 (Si/Al = 25).

dramatically higher than that of Brønsted acid sites on Hbeta. Lewis acid sites changed little while Brønsted acid sites decreased significantly with the increase of Si/Al ratio. In contrast, the concentrations of Brønsted acid sites were markedly higher than that of Lewis acid sites on HZSM-5 and the former decreased while the latter enhanced with the increase of Si/Al ratio. So Hbeta contained more Lewis acid sites and HZSM-5 contained more Brønsted acid sites. Especially, Brønsted acid sites on Hbeta (Si/Al = 60) were very little. It was proved in reports that phenol selectively reacted with the *in situ* generated cyclohexanol or cyclohexene on Brønsted acid sites and two cyclohexanone molecules condensed to produce dimer-cyclohexanone on both Lewis acid and Brønsted acid sites [10,11]. In addition, pore size of the zeolite solid acids was also one of the important factors for these side reactions. Therefore, it was the combined effect of both the strength of acid and the pore size that result in these side reactions. The micropore of zeolite HZSM-5 contained more Brønsted acid sites which led to the alkylation reactions between phenol and cyclohexanol and self-condensation of cyclohexanone as a result of the products selectivity decreasing. The macroporous of zeolite Hbeta contained strong Lewis acid sites and weak Brønsted acid sites while owned larger pore, which provided much wider space for occurring the side reactions and led to the products selectivity decrease. The tendency of these side reactions went down with the increase of Si/Al ratio of Hbeta and HZSM-5 due to the

decline of the strength of acid on zeolite solid acids. In particular, these side reactions hardly occurred over combined catalysts of Raney Ni and the macroporous of zeolite Hbeta (60). The possible reason was that the Brønsted acid sites on Hbeta (60) were so lower that could not promote the alkylation and condension reactions.

TG analysis was conducted to explain the side reactions as mentioned above. The thermal behavior under N_2 flows of 35 to 900 °C of Hbeta (Si/Al = 25, 60), HZSM-5 (Si/Al = 25) were showed in Fig. 2a, b, c, respectively and the mass losses were listed in Table 3. For the three figures, the first mass loss all took place between 100 and 150 °C and corresponded to the removal of H_2O from the zeolite solid acids. The curves after 150 °C, which might relate to the decomposition of oligomers stuck inside the zeolite solid acid, were very different. Fig. 2a showed the comparisons of the used and fresh Hbeta (Si/Al = 25) TG curves. The mass change in the curve of used Hbeta (Si/Al = 25) from 150 to 400 °C was much greater than the fresh Hbeta (Si/Al = 25), which demonstrated the oligomers production. The mass change in the both curves after 400 °C possibly related to the impurities in the zeolite solid acid. The TG curves of used and fresh Hbeta (Si/Al = 60) were compared and shown in Fig. 2b. The mass loss in both curve were almost similar that indicated there were only little oligomers produced by alkylation and condension reactions. Fig. 2c showed the TG curves of the used and fresh HZSM-5 (Si/Al = 25). The mass decreased greatly in the used HZSM-5 (Si/Al = 25) TG curve with the increase of temperature which related to the decomposition of oligomers attached to zeolite surface and pore, while the mass almost unchanged after 150 °C in the fresh HZSM-5 (Si/Al = 25) TG curve. Therefore, the TG analysis could confirm partial oligomers in zeolite solid acids which were produced by alkylation and condension reactions.

Reaction pathway of phenol *in situ* hydrogenation on mixed catalysts of Raney Ni and zeolite solid acid was depicted in Fig. 3. Hydrogen used in all the catalytic hydrogenation reactions was produced from the APR of methanol. The detected products contained cyclohexanone,

Table 3
The mass loss in TG analysis of fresh and used zeolite solid acids.

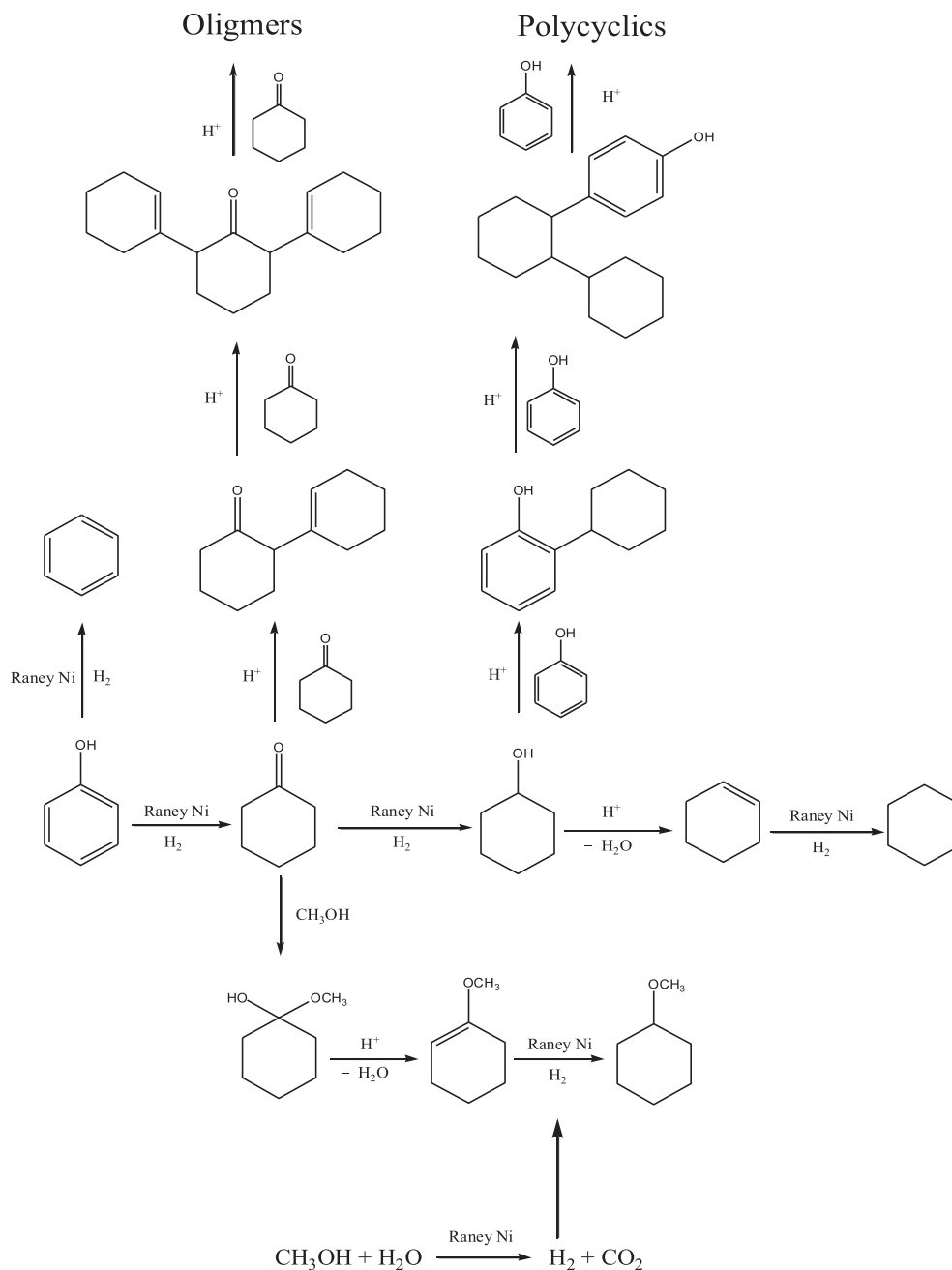| Zeolites	Mass loss (%)
Fresh Hbeta (25)	13.87
Used Hbeta (25)	21.75
Fresh Hbeta (60)	21.70
Used Hbeta (60)	24.40
Fresh HZSM-5 (25)	8.10
Used HZSM-5 (25)	16.56

Fig. 3. Reaction pathway of phenol *in situ* hydrogenation over Raney Ni and zeolite solid acids.

cyclohexanol, cyclohexene, cyclohexane, cyclohexyl methyl ether and benzene. But the hydrogenation for benzene ring of phenol was the main reaction pathway in producing cyclohexanone and cyclohexanol.

The addition of zeolite solid acids to Raney Ni in the *in situ* hydrogenation process hardly led to dehydration of cyclohexanol to cyclohexene and further hydrogenation to cyclohexane owing to the low selectivity

Table 4
The results of the *in situ* hydrogenation of phenol with different quantities of catalysts.

Raney Ni	Hbeta (60)	Phenol			Methanol			Carbon loss
		C (%)	S (%) (Cyclohexanol)	S (%) (Cyclohexanone)	C (%)	S (%) (H₂)	S (%) (CH)	
1.0 g	0.5 g	88.9	63.6	20.4	72.1	57.0	36.4	12.6
1.0 g	0.3 g	96.0	65.1	24.5	73.0	60.0	31.9	9.0
1.0 g	0.1 g	100	71.7	24.5	76.7	62.8	27.6	3.0
1.2 g	0.3 g	98.1	67.8	26.8	79.6	64.9	26.2	4.2
0.8 g	0.3 g	95.8	64.2	17.3	73.5	56.2	32.2	17.0
–	0.3 g	2.6	–	–	9.9	–	86.3	–
1.0 g	–	71.0	59.8	28.3	79.1	58.6	28.9	8.6

C: Conversion; S: Selectivity; CH: hydrocarbons. Reaction conditions: $T = 220$ °C, $t = 4$ h, $P = 1$ MPa (N₂).
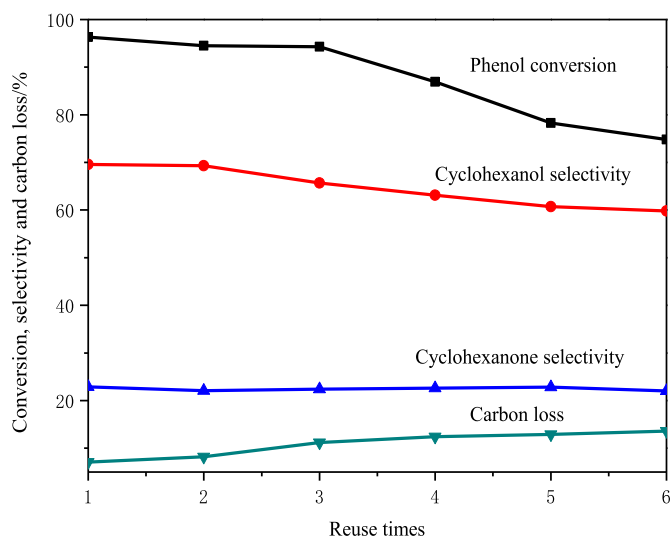
Fig. 4. The recyclability of the mixed catalysts of Raney Ni and Hbeta (60). Reaction conditions: 1.0 g Raney Ni, 0.3 g Hbeta (60), $T = 220$ °C, $t = 4$ h, $P = 1$ MPa (N_2).

of them, which was different from the previous reports using external hydrogen [7,12]. The reasons could be summarized as follows: (1) the cyclohexanol dehydration and acid–catalyzed alkylation of phenol with cyclohexanol were parallel reactions [10]. Plenty of water existing in reaction suppressed the cyclohexanol dehydration and alkylation of phenol was facilitated to produce heavier products. (2) The hydrogen produced from methanol aqueous-phase reforming was not enough. And the low hydrogen pressure of 1.075 MPa/h obtained from APR of methanol stabilized the production of cyclohexanone intermediate, which was in accordance with the previous reports [7,13]. So the formation of cyclohexane decreased and the oligomers produced by self-condensation of cyclohexanone increased. (3) The micropore of zeolite HZSM-5 contained strong Brønsted acid sites which catalyzed dehydration, but they were ineffective for dehydration in the presence of water because water competed effectively catalytic active sites to block the access of reacting molecules. (4) The macroporous of zeolite Hbeta contained strong Lewis acid sites and weak Brønsted acid sites which were not effective for phenol hydrodeoxygenation in water. In addition, cyclohexyl methyl ether formed from the acetal reactions between the cyclohexanone and methanol. The reaction pathway was as follows: methoxycyclohexanol formed from cyclohexanone and methanol *via* the acetal reaction, then further dehydrated by zeolite solid acids and hydrogenation over Raney Ni to cyclohexyl methyl ether [14]. And the benzene production was perhaps by hydrodeoxygenation of phenol.

3.2. Effect of the quantity of catalysts

Further experiments were carried out at different quantities of Raney Ni and Hbeta (Si/Al = 60) to investigate the effect of the quantity of catalysts on the *in situ* hydrogenation of phenol. The relevant results were shown in Table 4. With the increase of the quantity of Hbeta (Si/ Al = 60), the conversion of phenol, selectivity of cyclohexanol and cyclohexanone all decreased slightly, but the carbon loss increased. It showed that excessive Hbeta (Si/Al = 60) would result in more side reactions. With the increase of quantity of Raney Ni, more phenol was transformed owing to more hydrogen producing from the APR of methanol. And more cyclohexanol and cyclohexanone produced, less carbon loss occurred, indicating that more Raney Ni suppressed the side reactions of cyclohexanol and cyclohexanone. In addition, it was because the coplanarly absorbed on the Raney Ni that favored the production of more cyclohexanol [15].

Comparing with entry 2, 6, 7 in Table 4, there were no hydrogen produced from the APR of methanol and no phenol converted with Hbeta

(60) as catalyst, while the conversion of phenol and the selectivity of H_2 were both high with Raney Ni as catalyst, but the conversions of phenol and the selectivity of H_2 with a mixture of Raney Ni and Hbeta (60) as catalysts were higher than that with pure Raney Ni as catalyst, which demonstrated that Raney Ni was indispensable to the APR of methanol to produce H_2 and hydrogenation of benzene ring while the zeolite solid acid was responsible for providing a larger catalytic specific surface area and more contact sites to the reactant.

3.3. The recyclability of the mixed catalysts

The recyclability of the catalyst was an important parameter for the heterogeneous catalysis. Therefore, the mixed catalysts of Raney Ni and Hbeta (60) were collected after the reaction and washed with methanol; after that, the catalysts were directly used for the next run and the experimental results were shown in Fig. 4. The catalysts were used six times and they maintained good activity, with no notable decrease in conversion or selectivity and increase in carbon loss, which indicated that Raney Ni and Hbeta (60) exhibited excellent stability.

4. Conclusion

In this work, the *in situ* hydrogenation of phenol to stable oxygenated organics was conducted over Raney Ni and zeolite solid acids. The effect of zeolite solid acids was discussed and the catalytic activities were compared. The conversion of phenol increased with the addition of zeolite solid acids, which indicated that zeolite solid acids could enhance the catalytic activity. And in these tested zeolite solid acids, Hbeta (Si/ Al = 60) was much better than others for *in situ* hydrogenation of phenol with lower carbon loss and higher conversion and selectivity to the desired products. The main reaction pathway was hydrogenated for benzene ring of phenol to produce cyclohexanone and cyclohexanol. In addition, the quantity of Hbeta (Si/Al = 60) and Raney Ni had marked impact on the carbon loss, but little effect on both the conversion and the products distribution. And the mixed catalysts of Raney Ni and Hbeta (60) exhibited excellent stability after cyclic uses.

Acknowledgments

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