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In-situ Hydrogenation of Furfural with Additives over Raney Ni Catalyst

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The hydrogenation of furfural was studied over Raney Ni catalyst (RN) under N_2 atmosphere in water. Methanol, as hydrogen donor, was used for hydrogenation by reforming reaction. Additive, including acetone, acetic acid and phenol was deliberately added in the in-situ hydrogenation process of furfural to investigate the effect and interaction between two kinds of compounds. The results showed that the conversion of furfural decreased to some extent and the product distribution changed a lot because of second additives. Furfuryl alcohol (FA) was detected in the product in presence of additives which was not detected in single reactant of furfural. The selectivity of FA reached its highest degree of 19.01% with the acetic acid addition. Addition of acetone increased the decarboxylation reaction of furfural, and the selectivity of tetrahydrofurfuryl alcohol increased from 24.53% to 38.07%. The addition of phenol enhanced the rearrangement reaction of furfural and the selectivity of five-membered ring increased from 47.99% to 88.76%. Compared with the in-situ hydrogenation of single reactant, the conversion of acetone increased and the conversion of acetic acid and phenol decreased in presence of furfural. The reaction pathway of the hydrogenation of furfural was also discussed in this paper.

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Introduction

Fast pyrolysis is a kind of promising technology for the conversion of biomass into liquid fuels due to its low capital and operating cost advantages.[1, 2] But the properties of bio-oil, the liquid product of biomass by fast pyrolysis, result in multiple significant problems during its utilization and storage for its chemically and thermally unstable.[3] Therefore, the transformations of bio-oil into useful chemicals or stable compounds have attracted much attention[4]. Hydrotreatment in aqueous phased is one of potential methods to upgrade bio-oil[5, 6]. Acetone[7], acetic acid[6, 8], furfural[9, 10], phenol[11] and its derivative have been chosen as model compounds to investigate the activity of different catalysts and the mechanism for upgrading bio-oil. But the mechanism of model compounds can not totally explain the path way of compounds conversion and the catalysts are less active in raw bio-oil. The investigation on these reasons is still scarce.

Furfural, as key platform molecule in biomass conversion, is one of the main compositions in bio-oil[12, 13]. The products of furfural are complexed in nature during the hydrogenation process. Zhou[14] investigated the transformation of furfural to cyclopentanol over Ni/CNTs catalysts. Over 30 wt% Ni/CNTs, the conversion of furfural was up to 96.5% with a yield of 83.6% toward cyclopentanol. Guo[15] has developed a new catalytic system of CuZnAl for selective conversion of furfural to cyclopentanone. The CuZnAl-500-0.5 was recycled five times and maintained good activity and stability. Villaverde[16] studied the liquid-phase transfer hydrogenation of furfural on Cu-based catalysts. With Cu-Mg-Al after 6h at 150° C, furfural could convert to furfuryl alcohol completely. Yang[9] pointed out that in the conversion of furfural into cyclopentanone over Ni-Cu bimetallic catalysts, furfuryl alcohol, 4-hydroxy-2-cyclopentenone and 2-cyclopentenone were verified as three key intermediates. The rearrangement of furan ring was closely related to the attack of a H_2O molecule on the 5-position of furfural alcohol. In view of high-pressure H_2 using in furfural hydrogenolysis, Paraskevi used alcohol as hydrogen donor on methyl furan production through catalytic transfer hydrogenation of furfural in the liquid phase[17]. From the reports on the hydrogenation of furfural, most of researches performed catalytic hydrogenation to yield different products, but few studies are focussed on the effect additives on the product distribution during the upgrading process in raw bio-oil[18-21].

The present work highlights the furfural in-situ hydrogenation of furfural over RN. In addition the effect on the product distribution by different kinds of compounds in bio-oil is also presented. This study is motivated in part by our recent work[22]. The additives were including acetone, acetic acid and phenol. The comparison of hydrogenation vs in-situ hydrogenation and the hydrogenation pathway of furfural were also discussed in this paper.

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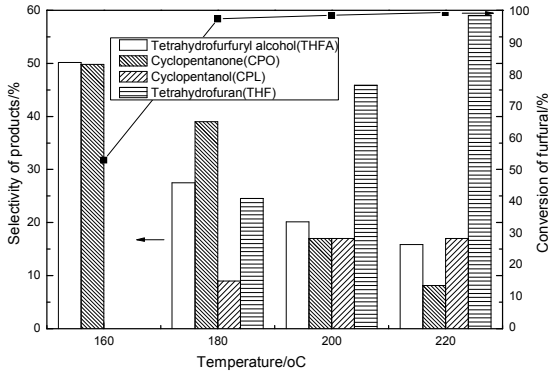
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Results and discussion

Effect of reaction conditions on the conversion of furfural and product distributions

Effects of temperature

Temperature is one of key factors for hydrogenation. As inferred from Fig. 1, the furfural could convert without H_2 over RN in water and methanol, which meant that the hydrogenation of furfural could couple with the aqueous-phase reforming(APR) of methanol as acetone and phenol did[22]. The furfural conversion significantly increased with the increasing of reaction temperatures and the product distributions also displayed noticeable temperature dependence.



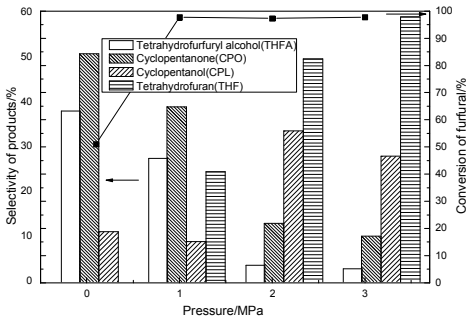
Reaction conditions: 0.5g of RN, 30 mL of water, 0.2 mol of methanol, 0.04 mol of furfural, N_2 pressure of 1MPa, and batch reaction time of 4h

Fig.1 Conversion of furfural and the product distributions at different temperatures

When the reaction temperature was 160° C, the furfural conversion degree was only 53.11%. But after the temperature reached to 180° C, the conversion of furfural increased to above 90%. With the temperature increasing, the selectivity of tetrahydrofurfuryl alcohol(THFA) and cyclopentanone(CPO) decreased gradually. Correspondingly, the cyclopentanol(CPL) and tetrahydrofuran(THF) formation commenced around 180 ° C and the selectivities increased rapidly to 16.96% and 59.03% at 220° C. More aldehyde group was cut from furfural when the reaction temperature increased. The falling off of side chain accounted for the decreasing selectivity of CPO and CPL. On the basis of Fig. 1, it was concluded that the in-situ hydrogenation of furfural was favored at 180° C, leading to high furfural conversion and less carbon loss. In summary, low temperature favored for the hydrogeantion of C=C and C=O, leading to higher THFA and 5-membered carbon ring compounds selectivity. While high temperatures favored for the cutting of aldehyde group from furan ring, resulting in higher selectivity of THF.

Effects of N_2 initial pressure

In view of the hydrogen was from the reforming of methanol in the in-situ hydrogenation process and the yield of hydrogen generated from the reforming of methanol in the in-situ hydrogenation process depends on the initial pressure of N_2[22]. So it's necessary to investigate the influence on the conversion of furfural and the product distribution by N_2 initial pressure in the in-situ hydrogenation process. Pressure-tuning studies were conducted over RN at 180° C for 4h duration. As expected, the furfural conversion increased with N_2 pressure and the product distribution changed a lot. (Fig. 2)



Reaction conditions: 0.5g of RN, 30 mL of water, 0.2 mol of methanol, 0.04 mol of furfural, temperature of 180°C, and batch reaction time of 4h

Fig.2 Conversion of furfural and the product distributions at different initial pressures of N_2

The furfural conversion increased from 51.04 to 97.79% when the N_2 initial pressure increased from 0.1 MPa to 1 MPa. With the initial pressure increased from 1MPa to 3MPa, the conversion of furfural changed little. The product distribution profiles indicated that the THFA and CPO selectivity decreased with the increasing of N_2 initial pressure. In contrast, the CPL selectivity remained low when the initial pressure was below 1 Mpa and increased significantly after the pressure increased to 2 Mpa. The formation of THF commenced at 1 Mpa initial pressure and the selectivity increased significantly with the initial pressure increased. The obvious changes might be ascribed to the APR of methanol. From our previous research[22], the conversion of methanol and the selectivity of H_2 were affected by the initial pressure. With the initial pressure increasing, the conversion of methanol and the yield of H_2 increased. The solubility of H_2 in the solvent also increased meanwhile, which could promote the hydrogenation reaction happened.

The coupling of APR of methanol and in-situ hydrogenation of furfural

In view of the hydrogen was from the APR of methanol, the coupling of APR of methanol and in-situ hydrogenation of furfural was investigated. The conversions of methanol and the product distributions at the optimum condition with and without furfural were shown in Table 1. From Table 1, the hydrogenation of substrate could promote the APR of methanol and the conversion of methanol increased from 18.18% to 25.38. In the gas product of furfural in-situ hydrogenation at optimum condition, 2.90% H_2 was left over.

Table 1 Conversion of methabol APR and the product distribution with and without furfural over Raney Ni catalyst

C(%)	Content(%)				
	H_2	C_nH_m	CO_2	CO	N_2
18.18[a]	42.05	5.81	21.78	-	30.36
25.38[b]	2.90	9.44	29.40	0.11	58.15

a- APR of methanol without furfural; b-APR of methanol with furfural

Reaction conditions: 0.5g of RNs, 30 mL of water, 0.2 mol of methanol, 0.04 mol of furfural, temperature of 180° C, N_2 pressure of 1MPa, and batch reaction time of 4h

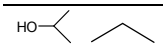
Hydrogenation of the mixed feed of furfural and second additive

Experiments were performed over RN at 180° C and 1MPa to investigate the in-situ hydrogenation of mixed feed of furfural and acetone, furfural and acetic acid, furfural and phenol respectively. For comparision, the reactions with single reactant of furfural, acetone, acetic acid and phenol were conducted under the same identical reaction conditions.

Conversion of second additive and product distributions

The conversion of second additives and the product distributions were different from that as single reactant(Table 2). As single reactant, the acetone conversion was 42.50%. While the conversion degree increased to 72.68% when hydrogenated with furfural. Isopropanol was the main product whose selectivity was above 96% in both of in-situ hydrogenation processes. The improvement on the conversion of acetone might be combined with the addition of furfural. In our previous work[22], acetone was not found and isopropanol was detected in the upgraded bio-oil by in-situ hydrogenation. Acetic acid, as single reactant or as second additive with furfural, was reacted with methanol via esterification and than hydrogenated to ethanol over RN. The ester product was only methyl acetate which was different from the results of one-step hydrogenation-esterification of furfural and acetic acid[23]. Because of abundant of methanol as solvent and hydrogen donor at the beginning of the reaction, the esterification between acetic acid and methanol was dominated reaction. As second additive, the conversion of acetic acid and phenol were 40.84% and 36.50%, which as sole reactant, the conversion was 52.35% and 46.01%. The conversion of acetic acid and phenol were suppressed by the presence of furfural in the mixed feed[24]. There was no reaction happened between second additives and furfural in in-situ hydrogenation system.

Table 2 Conversion of second additives and the product distributions with and without furfural

Reactant	Con. (%)	Selectivity(%)					
							
acetone[a]	42.50	98.23	1.77	-	-	-	-
acetone[b]	72.68	96.75	3.25	-	-	-	-
acetic acid[a]	52.35	-	-	-	-	83.01	16.99
acetic acid[b]	40.84	-	-	-	-	89.11	10.89
phenol[a]	46.01	-	-	46.67	53.33	-	-
phenol[b]	36.50	-	-	82.65	17.35	-	-

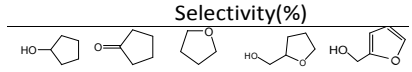
a-single reactant; b-as second additive adding to furfural

Reaction conditions: 0.5g of RNs, 30 mL of water, 0.2 mol of methanol, 0.04 mol of furfural, 0.02mol of second additive, temperature of 180° C, N_2 pressure of 1MPa, and batch reaction time of 4h

Conversion of furfural and product distributions with second additive

As single reactant, the furfural conversion was as high as 97.79%, while in the mixed feed sysytems, the furfural conversion all decreased in some extent(Table 3).

Table 3 Conversion of furfural and the product distributions within second additives

Additive	Con.(%)	Selectivity(%)				
						
-	97.79	8.98	39.01	24.53	27.48	-
acetone	87.63	19.66	14.96	38.07	18.88	8.43
acetic acid	86.94	16.73	21.19	27.29	15.78	19.01
phenol	94.40	79.75	9.21	0	5.63	5.41

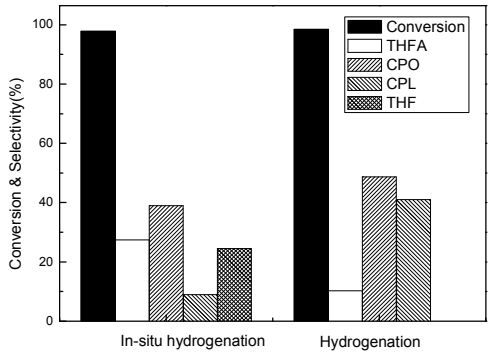
Reaction conditions: 0.5g of RNs, 0.04 mol of furfural, 0.02mol of second additive, 30 mL of water, 0.2 mol of methanol, temperature of 180°C, N_2 pressure of 1MPa, and batch reaction time of 4h

It is interesting to note that, with acetone, acetic acid and phenol addition to furfural, the product distributions changed a lot. Compared with single reactant of furfural, FA could be detected in the products, whose selectivity reached the highest point(19.01%) with acetic acid as coreactant. The CPL selectivity increased to some extent in presence of acetone and acetic acid. Meanwhile, the rearrangement for five-membered carbon ring from furfural was significantly improved in the presence of phenol. The total selectivity of CPO and CPL increased from 47.99% to 88.96% and the selectivity of CPL increased from 8.98% to 79.75%. The THF selectivity decreased from 27.48% to 18.88% and 15.78% in

presence of acetone and acetic acid, which could barely be detected when the coreactant was phenol.

Comparison of furfural in-situ hydrogenation with hydrogenation in hydrogen atmosphere

The comparison between in-situ hydrogenation and hydrogenation in H_2 atmosphere was conducted under identical reaction conditions.(Fig. 3)



In-situ hydrogenation:0.5g of RN, 0.04 mol of furfural, 30 mL of water, 0.2 mol of methanol, temperature of 180°C, N_2 pressure of 1MPa, and batch reaction time of 4h

Hydrogenation:0.5g of RN, 0.04 mol of furfural, 30 mL of water, temperature of 180°C, H_2 pressure of 3MPa, and batch reaction time of 4h

Fig.3 Conversion of furfural and the product distributions in in-situ hydrogenation and hydrogenation

In in-situ hydrogenation, the conversion of furfural was 97.79%, while in water under H_2 atmosphere, nearly total conversion (98.51%) was also observed. In water and methanol, the products of in-situ hydrogenation of furfural included CPO, CPL, THFA and THF and there was no THF detected in H_2 atmosphere. Meanwhile, the selective of THFA and CPO in hydrogenation were higher than the one in in-situ hydrogenation. The selectivity of THFA decreased from 27.48% to 10.26%. The total selectivity of CPL and CPO in hydrogenation increased from 47.99% to 89.74% compared with in in-situ hydrogenation, which means that in absence of methanol, the main reaction pathway is the rearrangement of furfural and furfuryl alcohol to cyclopentanone in water solvent under H_2 atmosphere.[25] The effect on the rearrangement of furan ring in existent of methanol needs for further investigation.

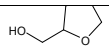
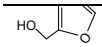
In-situ hydrogenation of furfural with recycled Raney Ni catalyst

The comparison between in-situ hydrogenation and hydrogenation in H_2 atmosphere was conducted under identical reaction conditions. The Raney Ni catalyst can be recycled by fliteration and washed by methanol. 70%-80% catalyst could be recycled for next use, but the activity of catalyst is a little lower than the fresh one.

Reaction pathway of the in-situ hydrogenation of furfural

For better understanding the reaction pathway, the in-situ hydrogenation of FA and THFA were conducted under identical reaction conditions.(Table 4)

Table 4 In-situ hydrogenation of FA and THFA

Reactant	Con. (%)	Selectivity (%)		
				
	64.18	27.07	25.57	47.36-
	0	-	-	-

0.5g of RN, 0.04 mol of FA, 30 mL of water, 0.2 mol of methanol, temperature of 180°C, N_2 pressure of 1MPa, and batch reaction time of 4h

As shown in Table 4, when FA was reactant, CPO, CPL and THFA were detected in product except THF. When THFA was chosen as reactant, there was no reaction happened over THFA. This suggested that CPO, CPL and THFA were all from FA. When the five-membered carbon ring was formed from furfural and FA, a rearrangement reaction was inevitable during the in-situ hydrogenation process. That means FA was one of the key intermediates to form five-membered carbon ring products[10]. And also, once the hydrogenation of C=O happened for C-O, furan was not easy to form, which concluded that the formation of FA and furan were parallel reactions. In summary, in the in-situ hydrogenation system, there were several parallel and cascade reactions, including decarboxylation, hydrogenation of C=O/C=C bonds and ring opening/closure(Fig. 4).

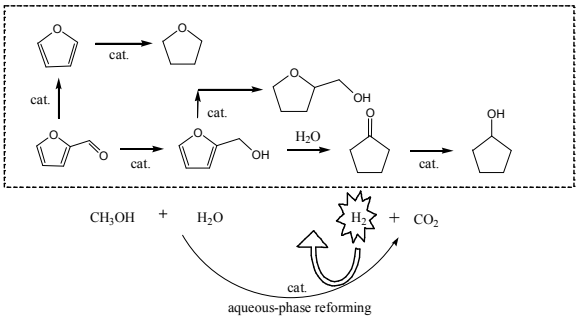


Fig. 4 The reaction pathway during in-situ hydrogenation of furfural

Experimental

Materials

Methanol (≥99.5%, analytical reagent), furfural (≥99.5%, analytical reagent) and furfuryl alcohol (≥99.5%, analytical reagent) were purchased from Beijing Hengzhang Chemical Co Ltd. Acetone (≥99.5%, analytical reagent), acetic acid (≥99.5%, analytical reagent), phenol (≥99.5%, analytical reagent) and tetrahydrofurfuryl alcohol (≥99.5%, analytical reagent) were purchased from Tianjin Fuchen Chemical Reagents Factory.

Preparation of catalysts[22]

Ni-Al alloy powder, a commercial product supplied by Dalian Toyounger Chemical Co., Ltd. was slowly added to a 20% aqueous solution of NaOH at 50(±2) ° C. The solution was precipitated after 1.5h of magnetic stirring at the temperature of 50 ° C. Actually, Al is oxidized and removed from the alloy; then almost pure Ni is obtained. The solid phase was washed by distilled water until the pH reaching 8-9 and then by ethanol for 6 times. The prepared RN was stored in ethanol.

In-situ hydrogenation process

The in-situ hydrogenation of furfural was performed in a 100mL stainless autoclave in the present of 0.5 g RN. The experimental apparatus is similar to the previously reported[22]. In a typical experiment, water(30mL), methanol(0.2mol) and furfural(0.04mol) were loaded into the reactor, which was sealed and purged with N_2 for 3 times to exclude air. An automatic controller was used to control the temperature and the revolution of stirrer. The pressure was raised to 0.1-3MPa and the reaction temperature was set from 160-220° C for 4h. After reaction, the autoclave was cooled down to the room temperature and then sampled liquid products for GC analysis. The second additive(0.02mol), including acetone, acetic acid and phenol, was added in the in-situ hydrogeantion process seperately.

Products analysis

The liquid phase samples were analyzed by a Shimadzu model GC-2014 using HP-INNOWAX column(30m*0.25mm*0.25um) and a flame ionization detector(FID). The conversion of reactants(mol%) and the selectivity(mol%) of main products were calculated according to eqs.(1) and (2) through the moles of reactants and the products before and after in-situ hydrogenation by GC results.

$$Conversion = (1-\frac{Moles\ \ of\ \ reactants}{Moles\ \ of\ \ ractants\ \ loaded\ \ initially})\times 100\% \quad (1)$$

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

Conclusions

The conclusions are drawn as follows:(1)Over RN, the hydrogenation of furfural could couple with the APR of methanol. (2)Acetone, acetic acid and phenol had a significant effect on the product distributions of furfural. In presence of additives, FA was found in product which was not detected in single reactant of furfural. In presence of phenol, the main reaction pathway was the rearrangement of furfural to CPL&CPO and the selectivity of five-membered carbon ring was 88.96%. (3)In the in-situ hydrogenation of furfural process, there were several parallel and cascade reactions, decarboxylation, hydrogenation of C=O/C=C bonds and ring opening/closure. (4)In view of high content of oxygen and water, converting raw bio-oil into stable oxygenated fuel might be one of potential methods to replace petroleum in the production of fuels for the transportation sector.

Acknowledgements

This project was supported by Science and Technology Plan Key Project in Guangdong Province of China(Project No.2014A010106019), Chinese Academy of Sciences (Project No.KGZD-EW-304-3), Science and Technology Plan Key Project in Dongguan City of China(Project No.201208101005) and Foundation of Guangzhou Insititute of Energy Conversion, Chinese Academy of Sciences (Project No.y307r91001)

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