Catalytic dehydration of glucose into 5-hydroxymethyfural on Fe/β zeolites with extra-framework isolated Fe species in a biphasic reaction system

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Abstract: A series of Fe/β zeolite catalysts with various Fe/Al ratios were prepared by liquid ion-exchanged method. The catalysts were used to catalyze the transformation of glucose into 5-hydorxymethyfural (HMF) in a biphasic reaction system. The Fe/β catalysts can effectively improve the HMF yield compared to H-β zeolite, which is ascribed to the enhanced isomerization activity of glucose-to-fructose by Lewis acidic Fe species. Under optimal reaction conditions, Fe/β-0.06 catalyst afforded 61% HMF yield at 120 ^{o}C for 90 min. Furthermore, extra-framework isolated Fe species are most likely the active sites for the isomerization of glucose-to-fructose in the conversion of glucose.

Keywords: HMF, Fe/β zeolite, Glucose.

1. Introduction (11-point boldface)

Effective utilization of biomass resources into valuable chemicals and fuels has gained significant interest as a potential alternative to crude oil [1-5]. Among these platform compounds, 5-hydorxymethyfural (HMF) can be used for the generation of fine chemicals, plastics, pharmaceuticals, and liquid fuel and is also considered the most promising high-value renewable energy substitute [1,2].

Glucose is an ideal raw material for the production of HMF because it is the most abundant and the cheapest hexose [1]. In comparison with the fructose feedstock, a challenging issue using glucose as the reactant is that the HMF yield is very low owing to the occurrence of side reactions especially the use of high concentration glucose, and environmentally unfriendly mineral acids are used [1,2]. Recently, a tandem reaction system combining solid Lewis and Brønsted acidic catalysts has exhibited excellent activity in the conversion of biomass into HMF [1,2]. Takagaki et al. reported that a combination of hydrotalcite and Amberlyst-15 in N, N-dimethylformamide system gives HMF selectivity of 76% at 60% of glucose conversion [4]. Zeolite and metal-doped zeolite catalysts, which have Lewis and Brønsted acid sites, are envisioned to be a desired catalyst for the transformation of glucose into HMF.

In this contribution, we synthesized Fe/β zeolite catalysts with extra-framework isolated Fe species by "post-synthesized" method and used these catalysts for the conversion of glucose to HMF. The possible Lewis acidic Fe sites responsible for the isomerization of glucose to fructose were proposed.

2. Experimental (or Theoretical)

Fe/β zeolites were prepared by liquid ion-exchange method from H-β zeolite with $FeSO_4$. Samples with different Fe/Al mole ratios (0.06, 0.10, 0.14, 0.18) are denoted as Fe/β-0.06 zeolite, Fe/β-0.10 zeolite, Fe/β-0.14 zeolite and Fe/β-0.18 zeolite. The conversion of glucose to HMF was conducted a 100 mL high-pressure autoclave. The liquid products were analyzed by high performance liquid chromatography (HPLC, Agilent 1200) using a column (Zorbax SB-C18) with a UV detector.

3. Results and discussion

The as-prepared catalysts were characterized by N_2 adsorption, XRD, UV-Vis DRS, EPR, NH_3-TPD, and FTIR of pyridine adsorption techniques. The results show that Fe/β catalysts have new Lewis acid sites derived from extra-framework Fe species and Brønsted acid sites. In addition, the spectroscopic results clearly demonstrate that the Fe species are mainly extra-framework isolated Fe species, and the bulk Fe oxide is almost negligible for all Fe/β catalysts. The effect of reaction time, reaction temperature, catalyst dosage, and Fe/Al ratio on the HMF conversion and HMF yield was investigated. Table 1 presents the reaction results of glucose conversion into HMF. A blank experiment was firstly conducted without the addition of catalyst, a low yield of HMF (14%) was obtained (Table 1, entry 1). It is obvious that Fe/β zeolite promoted the formation of HMF as compared to H-β in the conversion of glucose under identical reaction conditions. Moreover, as the Fe/Al ratio is 0.06, a high HMF yield up to 61% was achieved. The possible interpretation is that excessive Fe species is unfavorable for the production of HMF [5].

Table 1 the reaction results of glucose conversion into HMF. [a]

Entry	Catalyst	Amount of catalyst/g	Conversion/%	HMF yield/%
1	/	0	89	14
2	Fe/β-0.06	0.10	95	61
3	H-β	0.10	97	36
4	Fe/β-0.10	0.10	97	58
5	Fe/β-0.14	0.10	99	40
6	Fe/β-0.18	0.10	98	37

[a] Reaction condition: Glucose (1.0 g), NaCl (3.5 g), H_2O (10 cm^3) and THF (30 cm^3), 120 ℃, 90 min.

We also investigated the correlation of the L/B ratio with the HMF yield, and the corresponding results are shown in Fig. 1. Interestingly, the HMF yield and the L/B ratio are shown to exhibit a “volcano relationship” with the Fe/Al ratio. The maximum HMF yield, 61%, was obtained when catalyst L/B ratios was 1.20. The possible explanation is the fact that at low L/B ratios, isomerization rate of glucose is slow, whereas fructose dehydration rate is fast in the presence of excess Brønsted acid sites, thereby leading to more side reaction such as the formation of humins. The catalyst with low L/B ratios cannot effectively catalyze the isomerization of glucose to fructose, thereby affording a low yield of HMF, whereas the catalysts with high L/B ratios lead to faster rates of fructose dehydration to HMF and degradation to humins [1-4]. Therefore, the synergetic effect of Brønsted and Lewis acid sites may be critical in the conversion of glucose, which requires an optimal ratio between the isomerization rate of glucose-to-fructose and the dehydration rate of fructose. As the L/B ratio is 1.20, there could be an optimal balance between the isomerization rates of glucose-to-fructose and fructose dehydration to HMF.

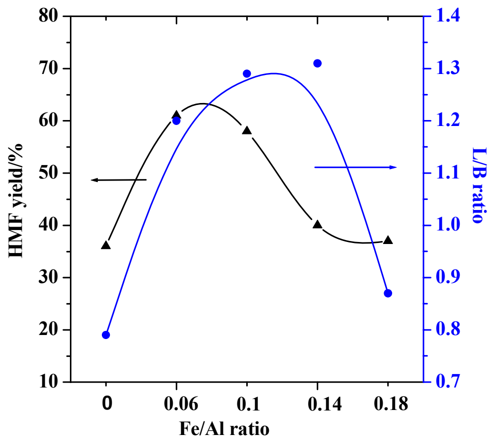

Fig. 1 The HMF yield and the L/B ratio as a function of the Fe/Al ratio for H-β and Fe/β zeolite catalysts. Reaction condition: Glucose (1.0 g), catalyst (0.1 g), NaCl (3.5 g), H_2O (10 cm^3), THF (30 cm^3), 120 ℃, 90 min.

4. Conclusions

A series of Fe/β zeolite catalysts with various Fe/Al ratios were prepared by liquid ion-exchange method. Under optimal reaction conditions, a HMF yield up to 61% was achieved at glucose conversion of 95% using high concentration of glucose as the reactant after the reaction of 90 min at 120 ^{o}C. The extra-framework isolated Fe species are shown to be the active sites for the isomerization of glucose into fructose in the conversion of glucose. An optimal match between the isomerization rate of glucose-fructose and the dehydration rate of fructose into HMF is very critical to achieving a high yield of HMF in the conversion of glucose.

References

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