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Alkali-metal-ions promoted Zr-Al-Beta zeolite with high selectivity and resistance to coking in the conversion of furfural toward furfural alcohol

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Abstract: Zirconium-substituted zeolites prepared by post-synthetic procedure have demonstrated excellent performance in the upgrading process of biomass platform compounds owing to the unique Lewis acid character. However, many pressing questions still surround these materials, especially relating to specific conversion, catalyst stability and substrate scalability. In the present study, a simple alkaline treatment to the Zr-Al-Beta zeolite in alcoholic solution of alkali metal hydroxide was conducted. The modification of alkali-metal ions on both Lewis acid sites and Brønsted acid sites in Zr-Al-Beta was evidenced by XPS and FT-IR spectroscopy (CO and pyridine). The untreated materials displayed poor product selectivity and high coke deposit in the Meerwein-Ponndorf-Verley reduction of furfural and isopropanol; however, the treatment of alkali-metal ions promoted their catalytic performance with improved recalcitrance to deactivation and coking significantly. Both the type of alkali-metal ions and the concentration of alkaline solution influenced the catalytic performance, which were found to correlate to the acidity and textual properties. The optimum reaction result (97.3% yield of furfuryl alcohol at 99.6% conversion of furfural) can be obtained on 0.025M-Na⁺-Zr-Al-Beta with high tolerance to the furfural concentration.

Keywords: Zirconium-substituted zeolites, alkaline treatment, acid sites, deactivation, Meerwein-Ponndorf-Verleyreduction,furfural.

1. Introduction

Since the discovery and extensive use of TS-1, heterogeneous metallosilicates catalysts, e.g. Sn-, Ti-, Zr-, Hf-substituted zeolites, have created an abundance of opportunities for the sustainable upgrading of biomass platform compounds due to their unique Lewis acid activities [1-3]. Zirconium-substituted zeolite Beta (Zr-Beta), for example, has been widely applied to upgrading of biomass platform chemicals, by driving cross aldol condensation [4], ring-opening aminolysis of epoxides [5], Meerwein–Ponndorf– Verley (MPV) reduction [6, 7], Diels-Alder reaction [8, 9] and so on. Generally, Zr-Beta zeolite possesses two distinct types of Lewis acid sites: 4-fold coordinated Zr atoms in framework positions (closed site) and 4-fold coordinated Zr centers with one Zr-OH hydroxyl group (open site) [10-12]. Recently, Ivanova et al. have proved that the open Zr (IV) sites have stronger Lewis acidic properties than the closed sites through FT-IR spectroscopy [13]. The heteroatom zeolites can be prepared by both direct hydrothermal method and post-synthetic method. Compared to direct hydrothermal crystallization, post-synthetic method possesses a more universe application range, and is demonstrated to be preferential to form open sites [14, 15]. Our previous work has reported a simple post-synthetic strategy to prepare a Zr-Al-Beta zeolite with both plentiful Lewis acid open Zr (IV) sites and Brønsted acid sites, which has shown a superior catalytic activity, water-tolerance ability and reusability in the cascade conversion of cinnamaldehyde toward 1-cinnamyl 2-propyl ether [16]. Although a beneficial combination of double acid sites can promote some of the chemical transformations [16, 17], this simple combination can also cause the possibility of other undesired reaction pathways except for the aimed reaction route, such as dehydration, polymerization and isomerization [18-20]. Therefore, controllable tuning for the acid properties with various active sites is greatly required.

Furfural (FUR) has been regarded as a promising platform molecule, which can be converted to a

variety of valuable products by aldol condensation, reduction, arylation etc [21]. In particular, MPV reduction using alcohol as hydrogen donor provides an alternative for selective reduction of furfural to furfuryl alcohol (FAL). Efficient and specific conversion of FUR to FAL through MPV reduction catalyzed by Lewis acid zeolite, however, is still an urgent need and a challenging target. On the one hand, deactivation of catalysts is caused easily by the polymerization of reactants and products that are retained in the zeolite pores and block access to active sites. Jungho Jae et al. reported that great deactivation of Sn-Beta was observed in the transfer hydrogenation (TH) and etherification of 5-hydroxymethylfurfural (HMF) and the selectivity toward unidentified species increased significantly with the increase of HMF concentration [22]. Maura Koehle et al. compared the catalyst half-life of Sn-, Zr-, Hf-Beta in the MPV reduction of furfural and Hf-Beta had the longest half-life of only 6.6 h, followed by Zr-Beta (4.9 h) and Sn-Beta (3.5h) [23]. This fast deactivation of catalysts has been assigned to the active chemical properties of furfural derivatives. On the other hand, the selectivity of product is still not under control well and a lot of undesired byproducts can be obtained, especially when aluminium exists in the Beta zeolite. For instance, except for the undesired polymeric species, furfural alcohol ether, etherification product of alcohols, can be detected in the presence of either Brønsted acid Al sites or Lewis acid M (M = Sn, Zr, Hf) sites. Jennifer D. Lewis et al. have developed a continuous flow strategy for the coupled TH/etherification of HMF to produce a monoether derivative [24]. Despite fascinating cascade reaction in biomass chemistry, high selectivity towards desired products can be hindered by more complex composition of products [25, 26]. Hence, heteroatom zeolite with high product selectivity and resistance to coking during TH process is still desired, particularly for those active substrates and products.

Recently, great attention has been paid to alkaline treatment towards to various kinds of zeolites. Pérez-

Ramírez and co-workers has developed an effective alkaline-assisted metalation method to prepare Lewis acid zeolites, which shows a remarkable performance in biomass conversion [27]. Toshiyuki Yokoi et al. reported that the ion-exchange with a small amount of alkali-metal-ions or NH_4^+ to Sn-Beta could suppress side-reactions and improve the yield of caprolactone from cyclohexanone during Baeyer-Villiger oxidation [28]. Very recently, Davis et al. found that increasing extents of Na⁺ exchange onto Sn-Beta would shift the reaction pathway toward glucose-mannose epimerization from glucose-fructose isomerization [29]. Vlachos and co-workers suggested by calculation using density functional theory that Na⁺ exchange on Sn-Beta influenced the reaction pathway by electrostatic stabilization [30]. Furthermore, the post-synthetic grafting of alkali cations on the zeolite in alcoholic solution has been even used to prepare base catalysts. For example, alkali-metal-ion modified high-silica USY zeolites gained a remarkable catalytic performance in the self-condensation of propanal [31]. Besides, alkali-exchanged process has also been used to transfer Brøsnted acid sites in Al-containing zeolite into Lewis acid sites [32, 33] Therefore, it can be expected that appropriate alkaline treatment to heteroatom zeolites, particularly for the Al-containing heteroatom zeolite, may promote the catalytic performance and reduce the catalyst deactivation in the conversion of FUR toward FAL.

This work tackles the alkaline treatment to the Zr-Al-Beta zeolite in alcoholic solution of alkali metal hydroxide. The characterization of textural and acid properties of the processed samples demonstrated that a proper alkaline treatment process could not change the texture properties of Zr-Al-Beta zeolite but greatly change their acidities on not only Brøsnted acid but also Lewis acid. Its catalytic result in MPV reduction of FUR toward FAL showed that the alkaline treatment greatly promoted selectivity of FAL and significantly decreased the formation of humins during the reaction.

2. Experimental

2.1 Catalyst Preparation

Zr-Al-Beta was prepared based on a one-step strategy as we have reported earlier [16]. Typically, the commercial Al-Beta with a n_{Si}/n_{A1} =12.5 (Nankai University Catalyst Co. Ltd.), used as the starting material, was activated at 170 °C overnight to remove physically adsorbed water before the incorporation of zirconium. Afterwards, the as-received zeolite (1.0 g) was introduced into an ethanol solution (100 mL) containing dissolved Zr (NO₃)₄·5H₂O (0.0715 g), and refluxed under stirring for 5 h. Finally, the abovementioned mixture was filtered, washed with ethanol, dried at 60 °C, and calcined (1 °C min⁻¹, 200 °C, 6 h and 550 °C, 6 h) to obtain Zr-Al-Beta.

Zr-DeAl-Beta was prepared via the post-synthetic reflux method reported by Dijkmans et al [34], in particular, tin chloride pentahydrate (SnCl₄·5H₂O) was replaced by Zr (NO₃)₄·5H₂O. Briefly, Al-Beta was dealuminated by 65 wt% HNO₃ aqueous solution (20 mL g⁻¹ zeolite) at 100 °C for 20 h and then filtered, washed with deionized water, dried at 170 °C overnight. The subsequent zirconium grafting procedure was identical to that of Zr-Al-Beta.

MCM-41 was synthesized according to a procedure published by Kumar et al [35]. Typically, Ethanol (12.5 g), aqueous ammonia (25 wt.%, 10 mL) and CTAB (2.39 g) were dissolved in water (100 mL) in a 250 mL polypropylene reactor under continuous stirring. Subsequently, tetraethyl orthosilicate (10 g) was added drop-wise to the above stirred solution. Afterward, the reaction mixture was stirred at room temperature for 2 h at 500 rpm. The white precipitate was filtered off, washed with ethanol until the filtrate was ammonia free (neutral pH-value). The obtained colorless powder was dried at 60 °C in air for 16 h. The template was removed via calcination in air, using the same ramping profile as before (1 °C min⁻¹, 200 °C, 6 h and 550 °C, 6 h). Finally, the zirconium was incorporated to obtain Zr-MCM-41 using above mentioned procedure.

The alkaline treatment was carried out according to the procedure reported by Pérez-Ramírez [31]. The zeolite (0.5 g) was introduced into methanol solution (15 mL) with the desired concentration (0.00625-0.1 M) of alkali metal hydroxide at room temperature, stirred at 600 rpm for 10 min, washed thoroughly with methanol (3 times with ca.25 mL), and dried at 60 °C. The zeolite treated by 0.025M of alkali solution was denoted with M⁺-zeolite (M = Li, Na, K), and the zeolites treated by different concentration of MOH were denoted by x M-M⁺-zeolite, in which x represents the molarity of MOH solution used in the alkaline treatment.

2.2 Catalyst Characterization

The X-ray powder diffraction (XRD) patterns were obtained with the Bruker D8 ADVANCE diffractometer (Cu-K α radiation, 40 kV and 40 mA). N₂ sorption-desorption isotherms were measured using a Quantachome Autosorb instrument at 77 K after the samples were activated at 573 K for 6 h under vacuum condition. The elemental analysis was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using the Perkin Elmer Optima 8000 instrument. Prior to analysis, the samples were dissolved in a mixture of HF, followed by neutralization with B(OH)₃. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5300 ESCA System with Mg K α source at 14.0 kV and 250 W. All binding energies were calibrated using carbonaceous C1s line at 284.6 eV. Scanning transmission electron micrographs (STEM) in high-angle annular dark-field (HAADF) modes, as well as energy dispersive X-ray spectroscopy (EDS) element maps were acquired on a JEM-2100F operated at 200 kV. Temperature-programmed desorption of ammonia (NH₃-TPD) was carried out in a Micrometrics AutoChem 2920 instrument. The FT-IR studies of pyridine and carbon monoxide adsorption were conducted via the Bruker Tensor 27 spectrometer equipped with an analysis platform (a CRCP-7070 supplied by Tianjin Xianquan Industry and Trade Development Co., Ltd, China.)

designed for in situ FTIR spectroscopy. A self-supporting wafer of about 10 mg was placed into the cell and then activated at 450 °C for 2 h under vacuum (both in pyridine adsorption and CO adsorption). Subsequently, the spectrum of the dehydrated samples was recorded. For pyridine adsorption, when the activation procedure was finished, reference spectrums at different temperatures (150 °C, 300 °C, 450 °C) were recorded (128 scans at a 4 cm⁻¹ resolution). After cooling to room temperature, the samples were subjected to pyridine vapor for enough time and IR spectra were recorded repeatedly until the evolution of adsorbed species indicated that pyridine saturation of the surface was reached. Afterwards, the samples were evacuated under vacuum at 150 °C, 300 °C, 450 °C for 30 min and spectra were collected. For carbon monoxide adsorption, when the activation procedure was finished, the cell was cooled with liquid nitrogen until the temperature was stable and the background spectra were recorded. Carbon monoxide was then gradually introduced into the cell controlled by pressure, and spectra were subsequently recorded. Difference spectra were obtained by subtraction of the reference spectra with the spectra of the samples with adsorbate. Thermogravimetric analysis (TGA) was conducted on a PE TGA8000 thermal analysis instrument with a heating rate of 10 °C min⁻¹ under the condition of air from 30 °C to 800 °C.

2.3 Catalytic Evaluation

The catalytic tests were performed in a 30 mL vial under microwave irradiation provided by a singlemode microwave instrument. (Nova-2S, Preekem Scientific Instruments Co., Ltd, China). Typically, the vial was charged with a mixture of furfural (2.5-10 mmol), isopropanol (50 mmol), and 100 mg of the catalyst, and mixed using a magnetic stirrer. A known quantity of 1,3,5-trimethylbenzene was used as the internal standard for chromatographic analysis and quantification. The catalytic reactions were conducted at 120 °C under the stirring of 600 rpm. After a certain interval, aliquots of the reaction mixture were taken through a pipette and were quantitatively analyzed by the Shimadzu GC-2010 plus gas chromatograph equipped with a DM-FFAP capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$) and a flame ionization detector (FID). Identification of these products was based on retention time analysis and confirmed by GC-MS. The quantification analysis of products mixture was based on calibration curves obtained by analyzing standard solutions.

Experiments on the selective poisoning of Brønsted acid sites using 2,6-ditertbutylpyridine (DTB-Py) were performed by the addition of certain amounts of DTB-Py into the reaction mixture.

To verify the recyclability of the catalysts, recycling tests were performed. After each reaction completion, the spent catalyst was recovered by centrifugation and washed three times with 6 mL of isopropanol. After drying at 60 °C overnight, the solid catalyst was directly used for the next cycles.

3. Results and discussion

3.1 Structure and composition of catalyst

Zr-Al-Beta and Zr-De-Al-Beta as well as their corresponding alkaline treatment samples were prepared by using the commercial Al-Beta as parent material, respectively. Herein, Zr-MCM-41 and Na⁺-Zr-MCM-41 were also prepared as control samples. To study the influence of alkaline treatment in their structures, XRD patterns and N₂ sorption isotherms of all samples were collected. XRD patterns in Figure S1 demonstrate that all samples display single characteristics of zeolite beta containing random intergrowth of BEA and BEB polytypes [36], indicating that the crystalline structures of beta zeolite are well preserved during post-treatment processes. The textural properties and compositions of all the samples were summarized in Table 1. It is found that the microporosities, BET surface areas and external surface areas of Zr-Al-Beta and Al-Beta change slightly after alkaline treatment (Table 1 and Figure S2). However, the microporous pore volume and BET surface areas of Zr-DeAl-Beta and Zr-MCM-41 decrease apparently after alkaline treatment (Table 1 and Figure S2). This can be assigned to their

frameworks with more defects which is sensitive to the alkaline treatment process in methanol media [31]. Complementary investigation by HAADF-STEM coupled with EDX analysis, indicates that the zirconium and sodium species are homogeneously distributed over the whole crystals, suggesting high dispersibilities of zirconium and alkali metal (Figure S3).

Sample	$V_{\text{micro}}{}^{a}$	$\mathbf{S}_{\text{BET}}^{b}$	S_{ext}^{a}	Si/Al ^c	Si/Zr ^c	M/Al ^c
	(cm ³ g ⁻¹)	(m ² g ⁻¹)	$(m^2 g^{-1})$	(mol mol ⁻¹)	(mol mol ⁻¹)	(mol mol ⁻¹)
Al-Beta	0.19	602	132	14.2		-
Na ⁺ -Al-Beta	0.18	577	143	-		-
Zr-Al-Beta	0.18	573	129	14.3	73.7	-
Na ⁺ -Zr-Al-Beta	0.18	579	136	16.1	80.4	0.89
Li+-Zr-Al-Beta	0.16	545	141	14.4	76.0	0.74
K ⁺ -Zr-Al-Beta	0.16	533	113	16.8	85.0	0.84
Zr-DeAl-Beta	0.20	625	132	trace	93.0	-
Na ⁺ -Zr-DeAl-Beta	0.16	510	113	trace	87.5	-
Zr-MCM-41	0	1354	1244	-	81.1	-
Na ⁺ -Zr-MCM-41	0	1100	1099	-	77.2	-

Table 1. Textural properties and chemical composition of the prepared samples.

^a t-plot method. ^b BET method. ^c ICP-AES.

3.2 Chemical state and location of active sites

The FTIR spectroscopy in the hydroxyl stretching region of the parent Al-Beta, Zr-Al-Beta and other post-treated samples were shown in Figure 1. In accordance with previous studies [12], the band at approximately 3610 cm⁻¹, 3745 cm⁻¹ and 3782 cm⁻¹ in the parent Al-Beta are unequivocally attributed to bridging hydroxyl Si (OH)Al groups, isolated terminal Si–OH groups and extra-framework Al–OH groups, respectively. It is clear that the incorporation of Zr species leads to an obvious decrease of the

3745 cm⁻¹ band as compared to Al-Beta owing to the preferential grafting of the Zr species with isolated terminal silanols. After alkaline treatment, the M⁺-Zr-Al-Beta zeolites (M = Li, Na, K) show the absences of the bands at 3610 cm⁻¹ and 3782 cm⁻¹, proving that alkali-metal cations preferentially interact with Al species. Notably, the signals of M⁺-Zr-Al-Beta zeolites at 3745 cm⁻¹ partly shift to 3735 cm⁻¹ with respect to Zr-Al-Beta. This implies that the alkali-metal cations can exchange with the silanol proton, which is consistent with previous report [29]. Similarly, after dealumination by HNO₃ aqueous solution, the bands at 3610 cm⁻¹ and 3782 cm⁻¹ disappear completely, evidencing the complete removing of Al from Al-Beta. However, compared to aluminium-containing zeolites, the signal at 3745 cm⁻¹ in the Zr-DeAl-Beta increases significantly (Figure S4), indicating that there is partial destruction of zeolite framework and much more terminal Si-OH groups are generated during dealumination step.



Figure 1. FTIR spectra of the hydroxyl stretching vibration regions of Al-Beta and Zr-Al-Beta before

and after alkaline treatment.

The local environments of Zr species in Zr-Al-Beta zeolites before and after alkaline treatment were studied by XPS analysis (Figure 2). The binding energy values of 182.2 eV and 184.6 eV in ZrO_2 reference are corresponding to Zr $3d_{5/2}$ and Zr $3d_{3/2}$, respectively. The significant shift toward to higher

values for Zr-Al-Beta can be interpreted in terms of the formation of framework Zr species [5, 11, 37]. The lower electronegativity of Zr (1.33, Pauling scale) than that of Si (1.98) leads to a higher positive charge on the Zr atom in beta zeolite framework, and so shows a higher binding energy. In the case of M^+ -Zr-Al-Beta (M = Li, Na, K), a clear decrease in the binding energy with respect to Zr-Al-Beta is observed in the sequence of Li < Na < K, which is in good agreement with the electronegativity order of Li (0.98) > Na (0.93) > K (0.82). This demonstrates that the alkali-metal cations introduced into the Zr-Al-Beta samples decrease partly electropositivity of Zr atom, and result in a decrease of its Lewis acidity.



Figure 2. Zr 3d XPS spectra of Zr-Al-Beta, Li⁺-Zr-Al-Beta, Na⁺-Zr-Al-Beta, K⁺-Zr-Al-Beta and ZrO₂. To unravel the detailed information about the Zr active sites as well as the influence of alkali-metal cations on Zr-Al-Beta zeolite, the FTIR spectroscopy of CO adsorbed on them at low temperature (~100 K) was investigated (Figure 3). With the increasing CO pressure from 3×10⁻⁴ bar to 3×10⁻³ bar, Zr-Al-Beta sample exhibits two major bands at 2190 cm⁻¹ and 2174 cm⁻¹ successively, which are attributed to CO adsorbed over the open Zr Lewis sites and Brønsted acid sites Si-O(H)-Al (Figure 3a), respectively [13]. Moreover, the preferential adsorption of CO on the Zr sites (Figure 3a) demonstrates that the open

Zr Lewis sites had a strong interaction with CO, that is to say, stronger acidity. After alkaline treatment, the disappearance of adsorption band at 2174 cm⁻¹ on M⁺-Zr-Al-Beta (M = Li, Na, K) zeolites indicates the elimination or transformation of Brønsted acid sites by the ion exchange. Meanwhile, new signals at 2185 cm⁻¹, 2179 cm⁻¹, 2168 cm⁻¹ appeared quickly and became the main adsorption bands (Figure 3b-d). According to previous studies, these bands could be ascribed to the C-O stretching vibration of CO molecules C-end coordinated to isolated single Li⁺, Na⁺, K⁺ ions (Figure 3d) [38, 39]. Note that the intensity of the bands representing Zr Lewis sites in alkali treated samples decreases dramatically. This means that alkali-metal cations could effectively weaken the acidic properties of the open Zr Lewis sites. Interestingly, the bands at 2195 cm⁻¹ (open Zr Lewis sites) in Li⁺-Zr-Al-Beta sample showed higher wavenumbers than Zr-Al-Beta sample. Ugliengo et al. have investigated the vibrational features of CO adsorbed on H⁺, Li⁺, Na⁺ and K⁺-exchanged chabazite and found that the sequence of hypsochromic CO frequency shift was Δv (Li) > Δv (H) > Δv (Na) > Δv (K) [40]. They described this phenomenon as coexistence of electrostatic interaction and covalent bond for CO adsorbed on Li-exchanged chabazite. In addition, for the M⁺-Zr-Al-Beta samples, a signal at 2118 cm⁻¹ is observed with the increasing CO dose, which is assigned to M^+ -OC adducts, i.e. that the CO molecules coordinate on the M^+ ion through the oxygen end [41]. So far, we can conclude that M⁺ ions modify not only the Al sites but the Zr sites as well, which is expected to promote their catalytic performances.



Figure 3. FTIR spectra of CO adsorbed over Zr-Al-Beta (a), Li⁺-Zr-Al-Beta (b), Na⁺-Zr-Al-Beta (c)

and K⁺-Zr-Al-Beta (d) with the increasing CO pressure.

3.3 Catalytic performance

Different heterogeneous catalysts were applied to the MPV reduction of furfural (FUR) with isopropanol, in which furfuryl alcohol (FAL) could be obtained as main product (Table 2). Herein, the etherification product of FAL, furfuryl isopropyl ether (FPE), as well as other undesired oligomers could be formed as byproducts in the presence of Brønsted and Lewis acids. As shown in Table 2, when using Al-Beta as catalyst, FUR conversion reaches only 18.8% after reaction at 120 °C for 3 h and no FAL can be acquired (Table 2, entry 1). Meanwhile, FPE and other undesired byproducts are obtained, including acetal products, some oligomers and even humins which are difficult to be detected by gas chromatography. After the incorporation of Zr atom in Al-Beta, FUR conversion on it improves greatly at the same reaction time, but the FPE still is the main product in these reactions (Table 2, entry 3). This demonstrates that the Zr Lewis sites possess high activity and can catalyze both the MPV reduction of FUR and subsequent etherification of FAL [24].

It is clearly observed that catalytic performance is enhanced drastically after alkali treatment, which occurs in both Al-Beta and Zr-Al-Beta (Table 2, entries 2, 4-6). Typically, the FUR conversion for Na⁺-Al-Beta increases to 46.0% from 18.8% of Al-Beta within reaction time of 3 h. Moreover, FAL rather than FPE becomes the primary product; this implies that the Brønsted acid sites in Al-Beta are successfully transformed into weak Lewis acid sites, which can perform the MPV reduction of FUR toward FAL but not further etherification of FAL. Furthermore, all the M⁺-Zr-Al-Beta catalysts display higher FUR conversion and FAL selectivity than those without alkaline treatment. Na⁺-Zr-Al-Beta shows the highest conversion of FUR (99.6%), and follows by Li⁺-Zr-Al-Beta (96.2%) and K⁺-Zr-Al-Beta (91.9%) at the reaction time of 3h. Specifically, the conversion rate of FUR in the initial reaction period in three catalytic systems follows an order of Li⁺-Zr-Al-Beta > Na⁺-Zr-Al-Beta > K⁺-Zr-Al-Beta (Table 2, entry 4-6), which is consistent with the order of Lewis acidities of Zr species in M⁺-Zr-Al-Beta zeolites (Figure 2 and 3b-d). Furthermore, it is found that the selectivity of FAL in all the three catalysts is quite high in the early stage of reaction, however, with the increase of reaction time, it gradually decreases with their increasing Lewis acidities among the three catalysts (Table 2, entry 4-6). Instead, their FPE yield shows an opposite trend with the increasing reaction time. Moreover, when K⁺-Zr-Al-Beta with lowest Lewis acidity is used as catalyst, only FAL is observed during the reaction (Table 2, entry 6), which suggests that the activity of all the Lewis acid sites in it is not enough for the efficient etherification of FAL with isopropanol. These not only

 Table 2. Schematic showing the MPV reduction of furfural (FUR) and isopropanol and

 subcequent etherification process as well as the catalytic performance of various zeolites.

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Entry	Catalyst	Time (h)	FUR conv. (%)	FAL yield (%)	FAL sel.	FPE yield (%)	Carbon Balance (%)
1	Al-Beta	3	18.8	0.0	0.0	10.0	90.6
2	Na ⁺ -Al-Beta	3	46.0	39.4	85.7	3.2	95.5
3	Zr-Al-Beta	3	32.7	1.3	4.0	29.5	94.3
4	Li ⁺ -Zr-Al-Beta	0.5	82.7	82.1	99.3	0.6	>99
		1	92.0	90.1	97.9	1.9	>99
		2	94.5	85.3	90.3	9.2	>99
		3	96.2	82.8	86.1	13.4	>99
5	Na ⁺ -Zr-Al-Beta	0.5	72.5	72.5	100	0.0	>99
		1	87.9	87.9	100	0.0	>99
		2	95.5	95.3	99.8	0.2	>99
		3	99.6	97.3	97.7	2.3	>99
6	K ⁺ -Zr-Al-Beta	0.5	53.1	53.1	100	0.0	>99
		1	71.2	71.2	100	0.0	>99
		2	86.2	86.2	100	0.0	>99
		3	91.9	91.9	100	0.0	>99
7	Zr-De-Al-Beta	3	50.1	6.3	12.6	40.7	93.8
8	Na ⁺ -Zr-De-Al-Beta	3	12.7	12.7	100	0.0	>99
9	Zr-MCM-41	3	43.5	21.4	49.2	19.8	94.8
10	DTB-Py-Zr-Al-Beta	3	87.0	9.5	10.9	70.2	91.6

Reaction conditions: FUR, 5 mmol; isopropanol, 50 mmol; catalyst, 100 mg; 120 °C.

demonstrate their different strengths of Lewis acids but also imply, as shown in Table 2, that FPE is obtained through the etherification of FAL and isopropanol. Taking the above characterization results of active sites into account, it is confirmed that alkaline treatment not only transfers Brønsted acid sites of Zr-Al-Beta zeolite into Lewis acid sites but suppresses its Lewis acidity as well. Moreover, the Lewis acidities change with different alkaline ions, and so leads to their different catalytic activities and product selectivity in FUR conversion.

Besides, the catalytic performance of Zr-DeAl-Beta and Zr-MCM-41 without Al species also were studied to clarify the roles of Lewis acid and Brønsted acid of Zr-Al-Beta in FUR conversion process. It is found that the absence of Al species slightly promotes the conversion of FUR on Zr-DeAl-Beta and Zr-MCM-41 compared to Zr-Al-Beta, but appreciable amount of FPE is still obtained (entries 7 and 9). It suggested that Zr Lewis acid sites of Zr-DeAl-Beta and Zr-MCM-41 can carry out not only MPV reduction of FUR but etherification of FAL with isopropanol. This fact can be further confirmed by the result of FUR conversion on Zr-Al-Beta poisoned with 2,6-ditertbutylpyridine (DTB-Py). DTB-Py has been known as a specific poison of Brønsted acid sites because of steric obstruction [42, 43]. Herein, DTB-Py with the same stoichiometric ratio of total acid amount in Zr-Al-Beta was used to prepare DTB-Py-Zr-Al-Beta, and the total acid amount of Zr-Al-Beta was quantitated according to its NH₃-TPD data (Table S2). As shown in Table 2, the conversion of FUR on DTB-Py-Zr-Al-Beta has been also improved dramatically with respect to the parent Zr-Al-Beta (87.0% to 32.7%), and FPE is the main product (Table 2, entry 10). Interestingly, among three catalysts only with Zr Lewis acid sites (DTB-Py-Zr-Al-Beta, Zr-DeAl-Beta and Zr-MCM-41), DTB-Py-Zr-Al-Beta zeolite shows the highest conversion (87.0%) of FUR, following by Zr-DeAl-Beta (50.1%) and then Zr-MCM-41 (43.5%), indicating that as-prepared Zr-Al-Beta zeolite possesses more open Zr Lewis acid sites and so displays the highest catalytic activity.

Furthermore, when the same alkaline treatment is performed on Zr-DeAl-Beta, Na⁺-Zr-DeAl-Beta shows a significant decreasing MPV reduction activity and even etherification activity is inhibited completely (Table 2, entry 8); this further demonstrates that alkaline treatment can decrease the Lewis acidity of Zr species in zeolite.

Additionally, we further investigated the influence of the concentration of alkali metal hydroxides on catalytic performance. As shown in Figure 4, for three kinds of M⁺-Zr-Al-Beta, similar volcanic curves of FUR conversion with the MOH concentration are obtained. When the concentration of MOH is lower than 0.025 M, conversion of FUR and the yield of FAL increase but FPE is still the main product. Obviously, alkaline treatment at such concentration is not enough to modify all the Brønsted acid and Lewis acid. Thus, the strong acidity of the resulting M⁺-Zr-Al-Beta accounts for its considerable etherification activity and its low FUR conversion due to fast deactivation caused by coking. This can be further confirmed by their chemical composition (low M/Al molar ratio) in Table S1. When MOH concentration is higher than 0.025 M, however, FUR conversion on them begins to decrease with the increasing MOH concentration. Meanwhile, the resultant M/Al molar ratio in M⁺-Zr-Al-Beta is over 1.0. This indicates that the excessive metal ions are introduced by grafting to deprotonated silanol groups [31], which will further decrease the Lewis acidities of M⁺-Zr-Al-Beta zeolite, even convert them into alkali ones. This can be demonstrated by the appearance of the product of base-catalytic Aldol condensation in the catalytic system of 0.1M-K⁺-Zr-Al-Beta (Figure 4c). Only when MOH concentration is just at 0.025 M, all the 0.025M-M⁺-Zr-Al-Beta catalysts show the highest FUR conversion and FAL become main even sole product. At this point, their M/Al molar ratios are just nearly 1.0 (Table S1), which just reaches an appropriate modification of alkaline ions toward the active sites.

Additionally, to further clarify the relation between catalytic activity and framework

structure/composition, the structures and acidities of samples treated with different concentrations of NaOH solution were characterized. The XRD results evidence that the framework structures of Beta zeolites after alkaline treatment can be preserved (Figure S5), but the relative crystallinity of 0.1M-Na⁺-Zr-Al-Beta (79%) is significantly lower than 0.025M-Na⁺-Zr-Al-Beta (93%). The N₂ sorption results (Table S2) show that the microporosity, BET surface area and external surface area of 0.025M-Na⁺-Zr-Al-Beta are close to those of Zr-Al-Beta, but those of 0.1M-Na⁺-Zr-Al-Beta are clearly lower than Zr-Al-Beta. These imply the partial destruction of zeolite framework in the presence of 0.1M NaOH solution, which are responsible for their decreasing catalytic activity.



Figure 4. The catalytic performance of MPV reduction of furfural (FUR) and isopropanol over Zr-Al-

Beta treated with different concentrations of MOH.

Acidic properties of several samples were further investigated by NH₃-TPD (Figure S6) and FTIR adsorbed pyridine (Figure S7). The NH₃-TPD profiles detected over Zr-Al-Beta reveals a broad peak in the range of 100-300 °C and a shoulder peak in 300-400 °C, corresponding to weak and strong acid sites, respectively. The strong acid in the profile is significantly weakened and the shoulder peak nearly disappears after alkaline treatment. Note that there is a small increase of weak acid site in 0.025M-Na⁺-Zr-Al-Beta and 0.1M-Na⁺-Zr-Al-Beta with respect to Zr-Al-Beta. Meanwhile, their FTIR spectra adsorbed pyridine show that a new band at 1443 cm⁻¹ appears, which could be attributed to the interaction of pyridine with new Lewis acid sites, namely Na⁺ ions whose acidity is significantly lower than Zr

species and tri-coordinated aluminium species [44, 45]. At the same time, their Brønsted acidic sites decrease with the increasing concentration of Na⁺. Taking their similar total acid amounts into account (Table S2), this result not only confirms the transformation between Brønsted acid sites and Lewis acid sites by the exchange of Na⁺ but also explains the reason of the lower activity of 0.1M-Na⁺-Zr-Al-Beta than 0.025M-Na⁺-Zr-Al-Beta. Therefore, we attribute the decreased activity of 0.1M-Na⁺-Zr-Al-Beta to both the partial destruction of the zeolite framework and the lower acidity.

As above mentioned, both furfural and furfuryl alcohol are easy to oligomerize and finally form humins to block the active sites, especially in the presence of strong acid. Therefore, the coking resistance of the catalysts were studied. As we predicted, all the reaction solution in the presence of catalysts without alkaline treatment become black and opaque after the reaction of 3 h. But only the reaction solution performed by M⁺-Zr-Al-Beta displays a relative light and transparent colour (Figure S8a). Obviously, the alkaline treatment process can reduce carbon deposition, which can be assigned to modification effect of alkali metal ions on the Brønsted/Lewis acid sites of the Zr-Al-Beta zeolite. Thermo-gravimetric analysis (TGA) results of the spent catalysts (Fig. S8b) further confirms this, that is, the weight loss in the Zr-Al-Beta and Zr-DeAl-Beta is approximately the same (about 21%), but the Na⁺-Zr-Al-Beta displays a low total weight loss (15%). Moreover, the weight loss of Na⁺-Zr-Al-Beta occurs at lower temperature compared to those of Zr-Al-Beta and Zr-DeAl-Beta, indicating that the deposited species on it is easy to be removed. Furthermore, the N₂ sorption/desorption curves of the spent samples also demonstrate that the retention of carbon species within the micropores of the catalysts which results in the dramatic decrease of microporosity, BET surface area of the spent Zr-Al-Beta (Figure S8c).



Figure 5. Recyclability of 0.025M-Na⁺-Zr-Al-Beta, Zr-Al-Beta and Zr-DeAl-Beta for the MPV reduction of furfural. The blue bars and orange bars represent FUR conversion and FAL yield, respectively. For 0.025M- Na⁺-Zr-Al-Beta, calcination and secondary alkaline treatment to the catalyst was performed after the 5th run.

This apparent different coking resistance of M⁺-Zr-Al-Beta catalyst is also conducive to its recyclability in the upgrading transformation of furfural. The recycling abilities of Zr-Al-Beta catalyst before and after alkaline treatment were further examined (Figure 5). After each run, the catalysts were separated from reaction mixture, washed with IPA for three times, dried overnight at 80 °C and used for next run directly. For Zr-Al-Beta, significant catalytic deactivation occurs after only one cycle. Even if Zr-DeAl-Beta is used, there is a dramatic deactivation after one cycle. Their very fast deactivation can be derived from of their fast coking within the micropores (Figure S8). Na⁺-Zr-Al-Beta, however, exhibits a relative superior reusability. Conversion of FUR is still higher than 60% and the selectivity of FAL only declines slightly even after five runs. The gradual loss in FUR conversion is probably due to slight sorption of some undesired species (Figure S8b). According to the element analysis results of the used catalyst and the reaction mixture after the fifth run, it is found that the Zr species is completely retained, but the Na/Al ratio decreases from 0.89 to 0.65, implying the slowly leaching of Na⁺ ions during

the reaction [28]. The decrease of Na⁺ ions in Na⁺-Zr-Al-Beta will bring about the increase of its acidity, which results in the formation of undesired species on it and the decrease of its catalytic performance in the recycles. Therefore, after 5 run numbers, we removed the undesired species (e.g. humins) deposited on the catalyst by calcination, and then a secondary alkaline treatment was done. It is found that the activity of Na⁺-Zr-Al-Beta after calcination and alkaline treatment can partially recovered, that is, the FUR conversion can reach 72.5% with 6 h and the selectivity of FAL is higher than 95%. The loss activity of Na⁺-Zr-Al-Beta is probably related to distortion of Lewis acid sites, which is consistent with the previous reports [16, 22, 24].

IPA / FUR (molar	FUR	FUR conv.	FAL yield	FAL sel.	FPE yield
ratio)	(mmol)	(%)	(%)	(%)	(%)
20	2.5	97.2	95.0	97.7	2.2
10	5	98.6	95.8	97.1	2.9
6.7	7.5	91.4	84.2	92.1	7.2
5	10	91.0	84.7	93.1	6.3

Table 3. Effect of FUR concentration with the fixed catalyst/FUR ratio^a.

a Reaction condition: isopropanol, 50 mmol; catalyst: Na⁺-Zr-Al-Beta, catalyst/FUR = 20 mg/1mmol;
120 °C, 3h.

Finally, it is expected that high coking resistance ability of M⁺-Zr-Al-Beta gives it not only a superior reusability but also the possibility of applying to a high FUR concentration system. This is very important for its further practical application. Therefore, the catalytic performances of Na⁺-Zr-Al-Beta in the different IPA/FUR molar ratios with the fixed catalyst/FUR ratio were studied to prove the scalability of Na⁺-Zr-Al-Beta (Table 3). It is clear that the FUR conversion and the selectivity of FAL

can still reach to 91.0% and 93.1% respectively after 3 h even though the IPA/FUR molar ratio decreases to 5, which is much higher than the previous reported work [46, 47]. Obviously, the M⁺-Zr-Al-Beta zeolites is better for the high concentration reaction system than the many times reaction.

4. Conclusions

In summary, a mild alkaline treatment process was applied to Zr-Al-Beta zeolites to regulate their active sites. The series characterization results showed that through the simple alkaline treatment, the Brønsted acidic sites and Lewis acidic sites of Zr-Al-Beta were transformed and weakened significantly by alkalimetal cations, which greatly promoted its catalytic performance and coking resistance ability in MPV reduction of FUR and IPA. Furthermore, among three alkaline ions, the Lewis acidities of M⁺-Zr-Al-Beta zeolites decreased with their alkalinity orders of LiOH < NaOH < KOH, and so led to their different catalytic activities and product selectivity in FUR conversion. Besides, an appropriate treatment concentration of alkaline ions was required, and the optimum reaction result was obtained on 0.025M-Na⁺-Zr-Al-Beta, on which the yield of FAL is 97.3% at furfural conversion of 99.6% after reaction at 120 °C for 3 h. Moreover, the 0.025M-Na⁺-Zr-Al-Beta displayed a high tolerance to the FUR concentration due to its opportune acidity and high coking resistance. This work offers a simple strategy to promote the catalytic performance including activity, product selectivity and carbon deposition in a particular reaction by tuning and normalizing the various acidic sites of zeolites.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found in the online version.

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Highlights

- Zr-Al-Beta zeolites promoted by alkali-metal ions possess good stability and tolerance to carbon deposits in Meerwein-Ponndorf-Verley reduction of furfural and isopropanol.
- 2. Detailed characterizations demonstrated the modification of alkalimetal ions on Lewis and Brønsted acid sites.
- 3. Alkaline ion modified Zr-Al-Beta zeolite can high-selectively convert furfural into furfural alcohol under a high furfural concentration.
- 4. Simple alkaline treatment to zeolites was proved possibility of potential application.



A mild alkaline modification treatment to both Lewis and Brønsted acid sites of Zr-Al-Beta zeolite, leading to its superior catalytic performance and resistance to coking in MPV reduction of furfural.

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