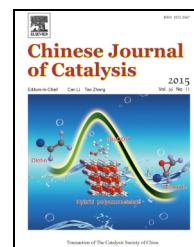


available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc

Article

Alkali-metal-modified ZSM-5 zeolites for improvement of catalytic dehydration of lactic acid to acrylic acid

Chuan Yuan^a, Huayan Liu^a, Zekai Zhang^a, Hanfeng Lu^a, Qiulian Zhu^a, Yinfei Chen^{a,b,*}^a College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, Zhejiang, China^b Zhejiang Province Key Laboratory of Green Chemistry and Technology, Zhejiang University of Technology, Hangzhou 310014, Zhejiang, China

ARTICLE INFO

Article history:

Received 3 June 2015

Accepted 6 September 2015

Published 20 November 2015

Keywords:

ZSM-5 zeolite

Alkali metal

Lactic acid

Acrylic acid

Dehydration

ABSTRACT

Various ZSM-5 zeolites modified with alkali metals (Li, Na, K, Rb, and Cs) were prepared using ion exchange. The catalysts were used to enhance the catalytic dehydration of lactic acid (LA) to acrylic acid (AA). The effects of cationic species on the structures and surface acid-base distributions of the ZSM-5 zeolites were investigated. The important factors that affect the catalytic performance were also identified. The modified ZSM-5 catalysts were characterized using X-ray diffraction, temperature-programmed desorptions of NH₃ and CO₂, pyridine adsorption spectroscopy, and N₂ adsorption to determine the crystal phase structures, surface acidities and basicities, nature of acid sites, specific surface areas, and pore volumes. The results show that the acid-base sites that are adjusted by alkali-metal species, particularly weak acid-base sites, are mainly responsible for the formation of AA. The KZSM-5 catalyst, in particular, significantly improved LA conversion and AA selectivity because of the synergistic effect of weak acid-base sites. The reaction was conducted at different reaction temperatures and liquid hourly space velocities (LHSV) to understand the catalyst selectivity for AA and trends in byproduct formation. Approximately 98% LA conversion and 77% AA selectivity were achieved using the KZSM-5 catalyst under the optimum conditions (40 wt% LA aqueous solution, 365 °C, and LHSV 2 h⁻¹).

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Biomass conversion has recently become a research hotspot because of environmental deterioration and shortages of non-renewable fossil fuel resources such as oil and coal [1,2]. Lactic acid (LA), a biomass with hydroxyl and carboxyl groups, can be converted to other chemicals [3,4] such as acetaldehyde (AD) [5], propionic acid (PA) [6], acrylic acid (AA) [7], and 2,3-pentanedione (2,3-P) [8]. AA is commonly used in the synthesis of functional materials, including superabsorbent resins [9], and is produced mainly by two-step oxidation of propylene derived from the petrochemical industry. The production of AA from propylene will be difficult to sustain because of potential

petroleum shortages in a few decades, therefore a sustainable route, namely one-step dehydration of LA (or LA derivatives) to AA, has attracted much attention [10]. Catalysts such as sulfates (BaSO₄) [11], phosphates (Ca₃(PO₄)₂-Ca₂(P₂O₇)) [12], and NaY and β zeolites [13–15] have been reported for LA dehydration; this suggests that moderate surface acid-base strength and density are crucial for efficient catalysis of LA dehydration to AA. However, sulfate and phosphate catalysts only work efficiently at high temperature (400 °C) because of the limited number of surface active sites. A high temperature promotes decarbonylation, decarboxylation, and coking of hydrocarbon compounds, resulting in feedstock waste [11,16]. Zeolite catalysts with high surface acidities and basicities can catalyze LA

* Corresponding author. Tel: +86-13606643528; E-mail: yinfei.chen@gmail.com

dehydration to unsaturated acids at low temperatures. KI/NaY gives a good catalytic performance in terms of LA conversion (97.6%) and AA selectivity (67.9%) at 325 °C and a liquid hourly space velocity (LHSV) of 2.25 h⁻¹. Yan et al. [15] used alkali-metal-modified β zeolites as catalysts and obtained an AA yield of 61 mol% using the best catalyst, i.e., K_{0.94}Na_{0.06} β . However, NaY zeolites have numerous strong acid surface sites and three-dimensional supercages, which facilitate carbon deposition, resulting in fast zeolite deactivation of zeolites [17].

ZSM-5 zeolites have been used in alcohol dehydration because of their adjustable surface acidities and basicities and the absence of supercages [18,19]. There has as yet been no report of the catalytic dehydration of LA using ZSM-5 zeolites. In this study, ZSM-5 zeolites modified with alkali metals using an ion-exchange method to adjust the strengths and densities of the surface acidity and basicity were used to catalyze LA dehydration to AA. Coking inhibition and improved catalytic selectivity were expected.

2. Experimental

2.1. Materials

LA (analytical grade) was purchased from the Hangzhou Shuanglin Chemical Reagent Co. Alkali metal (Li, Na, K, Rb, and Cs) nitrates, AA, AD, PA, 2,3-P, and isopropanol were obtained from the Aladdin Reagent Co.

2.2. Catalyst preparation

ZSM-5 zeolite (Si/Al molar ratio = 75; Shanghai Shentan Environmental New Materials Co., Ltd., China) was preheated at 550 °C for 6 h and treated with an aqueous solution of MnO₃ (1 mol/L; M = NH₄, Li, Na, K, Rb, or Cs; 14 g of ZSM-5 zeolite in 140 mL of MnO₃) at 80 °C for 6 h to obtain ion-exchanged ZSM-5. The treated ZSM-5 zeolites were filtered and washed at least three times with distilled water to remove excess MnO₃. The catalysts were dried at 110 °C for 12 h and calcined at 550 °C for 4 h to obtain the catalysts M_xNa_{1-x}ZSM-5 (x is the exchange degree of M⁺, i.e., the molar ratio of M⁺/(Na⁺+M⁺), determined using X-ray fluorescence), which are denoted by HZSM-5, LiZSM-5, NaZSM-5, KZSM-5, RbZSM-5, and CsZSM-5. All the modified ZSM-5 catalysts were prepared under identical conditions.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) was performed using an X'Pert PRO instrument operated at 40 kV and 30 mA, with Cu K α radiation; the patterns were recorded at $2\theta = 10^\circ$ to 60° at a rate of 5°/min. The surface acidity and basicity were investigated using NH₃/CO₂ temperature-programmed desorption (TPD; Chem-Adsorption Finesor-30102). The nature of the surface acid sites (Brønsted or Lewis acid) was determined using pyridine adsorption Fourier-transform infrared (Py-IR) spectroscopy in the range of 600–4000 cm⁻¹ (2 cm⁻¹ resolution; Vertex 70 spectrometer). Thermogravimetric analysis (TGA) was performed using a thermal analyzer (STA409PC, Netzsch) at 20–650 °C with a heating rate of 10 °C/min in air. The Brunauer-Emmett-Teller (BET) specific surface areas and pore volumes of the samples were determined by N₂ adsorption (3Flex, Micromeritics). Elemental analysis was performed using a Shimadzu XRF-1800 spectrometer.

2.4. Catalytic reaction

The catalytic dehydration of LA to AA was performed in a continuous-flow fixed-bed reactor (inner diameter 8 mm) at atmospheric pressure. The pelletized catalysts (0.8–1.2 g, 20–40 mesh) were placed in a quartz reactor and pretreated for 30 min under N₂ flow. The reactant (40 wt% LA aqueous solution) was pumped into a vaporizer using a micro-injection pump, and the vapor was carried through the catalyst bed by N₂ (30 mL/min, LHSV = 2–4 h⁻¹). The outlet products were condensed and then analyzed using a gas chromatography system (Agilent 6890) with an Innowax capillary column and flame ionization detector. Isopropanol was used as the internal standard for liquid product analysis.

3. Results and discussion

3.1. Catalyst performance

3.1.1. Catalytic reaction results

Alkali-metal-modified ZSM-5 zeolites were used to catalyze LA dehydration. The products and selectivity data are listed in Table 1. The main product was AA, with AD, 2,3-P, and PA as the main byproducts; other byproducts included pyruvic acid, acetic acid, and gaseous products. The modified zeolites gave

Table 1
Performance of different ion-exchanged ZSM-5 catalysts for LA dehydration.

Catalyst	LA conversion (%)	Selectivity (%)					AA formation rate (mmol g ⁻¹ cat min ⁻¹)	Carbon deposits ^b (mg g ⁻¹ cat h ⁻¹)
		AA	AD	2,3-P	PA	Others ^a		
HZSM-5	99.88	1.43	40.13	0.02	0.48	57.94	0.011	27.50
LiZSM-5	97.69	38.20	31.56	0.74	0.56	28.94	0.141	10.04
NaZSM-5	94.47	51.69	17.33	0.45	0.82	29.71	0.180	8.63
KZSM-5	91.24	70.29	15.17	0.66	0.64	13.24	0.231	8.75
RbZSM-5	91.86	56.22	15.40	3.42	1.92	23.04	0.175	11.25
CsZSM-5	85.33	62.01	15.15	0.45	0.82	21.57	0.189	7.78

Reaction conditions: RT, 350 °C; 40 wt% LA aqueous solution, 0.8 mL/h; carrier gas, 50 mL/min; catalyst, 2 mL (0.9 g); time on stream (TOS) = 8 h.

^aOthers: pyruvic acid, acetic acid, carbon deposit, gaseous products (CO/CO₂ and H₂). Selectivity for others = 100% – the total selectivity for each listed products. ^bAccumulated in 8 h reaction time.

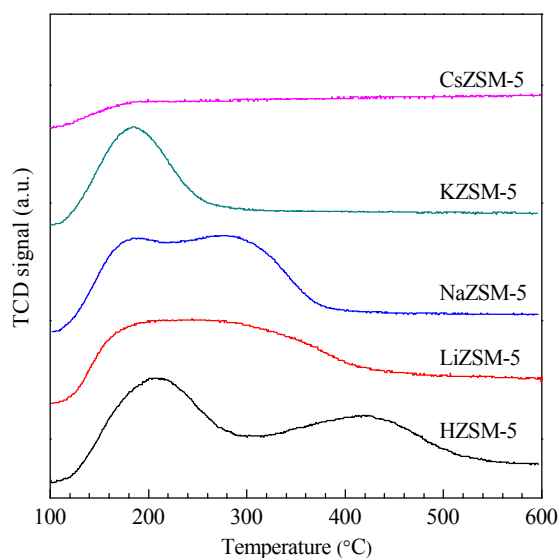


Fig. 1. NH_3 -TPD profiles of catalysts.

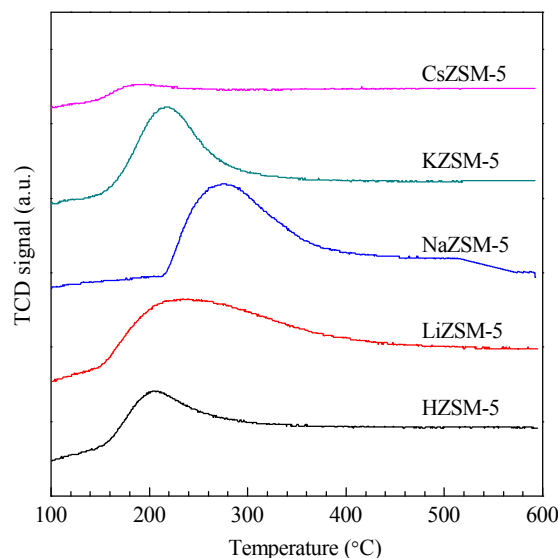


Fig. 2. CO_2 -TPD profiles of catalysts.

enhanced catalytic performance in LA dehydration to AA. LA conversion decreased in the following order $\text{H} > \text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ -modified ZSM-5; the AD selectivity decreased from HZSM-5 to CsZSM-5. The highest AA selectivity was obtained using the KZSM-5 catalyst ($\text{K}_{0.84}\text{Na}_{0.16}\text{ZSM-5}$). The same phenomenon was observed in the catalysis of LA dehydration to AA by a K^+ -modified NaY catalyst [17,20]. These results suggest that the introduction of an alkali metal efficiently inhibits decarbonylation and decarboxylation of LA to AD. Low selectivities for the other side products such as 2,3-P and PA were observed because the ZSM-5 micropores efficiently suppressed the formation of large molecules. The NH_3/CO_2 -TPD results (Figs. 1 and 2) suggest that the high AA selectivity and the low selectivity for side products over KZSM-5 are caused by surface synergistic effects between weak acid and base sites and the shape selectivity of ZSM-5. KZSM-5 was therefore selected as the catalyst for further studies because of its superior performance.

The influence of reaction temperature was investigated using KZSM-5. The results (Table 2) show that LA conversion increased with increasing temperature from 350 to 400 °C, and the highest AA selectivity was observed at 365 °C. The catalytic performance of the alkali-metal-modified ZSM-5 zeolites was better than those of sulfate and phosphate catalysts reported in the literature [11,16]. The byproduct selectivity also increased with increasing temperature, which indicates that more side

reactions occurred at high temperature. Zeolite-catalyzed reactions should therefore be performed at low temperature to suppress formation of side products.

The effect of the LHSV on LA dehydration was investigated at 2–4 h^{-1} using the KZSM-5 catalyst. LA conversion decreased from 98.49% to 90.59% with increasing LHSV (Table 3). However, the AA selectivity increased slightly to 78.88% and then decreased to 74.44%, which suggests that a higher LHSV gave high selectivity for AA but low LA conversion. High LA conversion and AA selectivity were achieved at an LHSV of 2 h^{-1} .

3.1.2. Catalyst stability

The catalytic effect of KZSM-5 with time on stream (TOS) at 365 °C is shown in Fig. 3. LA conversion decreased from 97.18% to 90.59%, whereas the AA selectivity increased from

Table 3
Effect of LHSV on LA dehydration using KZSM-5.

LHSV (h^{-1})	LA conversion (%)	Selectivity (%)				
		AA	AD	2,3-P	PA	Others
2.0	98.49	77.13	17.28	0.96	0.78	3.85
2.4	95.21	76.47	13.61	0.85	0.91	8.16
3.0	92.83	78.88	16.23	0.69	0.68	3.52
4.0	90.59	74.44	15.53	0.63	0.67	9.03

Reaction conditions: reaction temperature, 365 °C; 40 wt% lactic acid aqueous solution, 0.8 mL/h; carrier gas, 50 mL/min.

Table 2
Effect of reaction temperature on LA dehydration using KZSM-5.

$t/^\circ\text{C}$	LA conversion (%)	Selectivity (%)					AA formation rate ($\text{mmol g}^{-1}\text{cat min}^{-1}$)	Carbon deposits ($\text{mg g}^{-1}\text{cat h}^{-1}$)
		AA	AD	2,3-P	PA	Others		
350	91.24	70.29	15.17	0.66	0.64	13.24	0.23	8.75
365	95.21	76.47	13.61	0.85	0.91	8.16	0.36	9.38
375	97.70	68.74	15.16	1.07	0.57	14.46	0.33	10.52
400	98.82	61.29	16.12	1.77	2.00	18.82	0.29	11.25

Reaction conditions: 40 wt% LA aqueous solution, 0.8 mL/h; carrier gas, 50 mL/min; catalyst, 2 mL (0.9 g); TOS = 8 h.

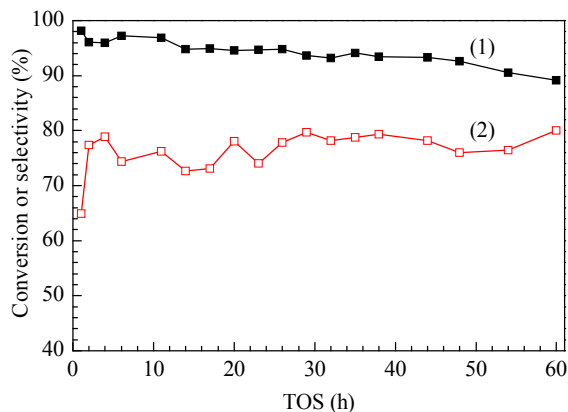


Fig. 3. Stability of KZSM-5 catalyst. (1) LA conversion; (2) AA selectivity. Reaction conditions: 365 °C; 40 wt% LA aqueous solution, 0.8 mL/min; carrier gas, 50 mL/min; catalyst, 2 mL (0.9 g).

64.92% to 79.37% for TOS = 60 h. TGA showed that mass loss of the used catalyst was 6%, which suggests that KZSM-5 gives an excellent anti-coking performance. It was reported in the literature that for modified NaY zeolites, the LA conversion decreased from 80% to 65% and the AA selectivity decreased from 74% to 55% for TOS = 5 h. This may be because NaY zeolites have strong surface acid sites and a three-dimensional supercage structure, which facilitates hydrocarbon coking and results in fast deactivation of the catalyst [21]. However, ZSM-5 zeolites give high anti-coking performance because of their moderate acid sites and the absence of supercages [22,23]. The modified ZSM-5 zeolites, in particular KZSM-5, only have weak acid and base sites (Figs. 1 and 2), which are favorable for high AA selectivity and restriction of hydrocarbon coking, therefore they are stable and their activities can be recovered by regeneration.

3.2. Catalyst characterization

3.2.1. Physicochemical properties of catalysts

The physicochemical properties of the catalysts are shown in Table 4. The modified ZSM-5 catalysts had high surface areas. The surface areas and pore volumes of these catalysts decreased after ion exchange. The reductions were high for HZSM-5 and LiZSM-5, but the introduction of other alkali-metal cations only slightly affected the ZSM-5 structure. The physical

Table 4
Physicochemical properties of catalysts.

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Amount (mmol/g)		Density (μmol/m ²)	
			Acid site	Base site	Acid site	Base site
ZSM-5	287	0.293	—	—	—	—
HZSM-5	231	0.133	0.144	0.278	0.625	1.204
LiZSM-5	170	0.105	0.074	0.668	0.439	3.933
NaZSM-5	275	0.241	0.094	0.454	0.345	1.656
KZSM-5	263	0.262	0.037	0.295	0.142	1.125
RbZSM-5	249	0.235	—	—	—	—
CsZSM-5	255	0.241	0.007	0.031	0.027	0.124

properties of KZSM-5, in particular, hardly changed. The surface acidities and densities decreased in the order H- > Li- > Na- > K- > Cs-modified ZSM-5. The same trend was observed for surface basicity and density. The introduction of alkali-metal cations decreased the total acid-base number, which improved AA selectivity.

3.2.2. XRD

XRD was performed to investigate the structures of the modified ZSM-5 zeolites; the patterns are shown in Fig. 4. The powder XRD profiles showed a pure MFI crystal phase, which implies that metal-ion exchange did not affect the crystal phases of the ZSM-5 zeolite. The same peaks were observed from HZSM-5 to KZSM-5, but the peak intensity of the Cs-modified ZSM-5 was slightly lower. This result indicates that the introduction of Cs⁺ destroyed the crystal phase; this explains why the LA conversion achieved using CsZSM-5 was lower than those achieved with the other catalysts.

3.2.3. Surface acidity and basicity

In Figs. 1 and 2, the temperature ranges of regions I (100–200 °C), II (200–400 °C), and III (400–600 °C) represent weak, medium, and strong acid/bases, respectively. Previous studies have shown that the surface acidities and basicities of catalysts play key roles in LA dehydration [12]. Table 3 and Fig. 1 show that the strengths and amounts of the acid sites in the metal-modified zeolites decreased in the order H- > Li- > Na- > K- > Cs-ZSM-5. Strong acid sites were eliminated from the surfaces of Li-, Na-, K-, and Cs-ZSM-5, whereas medium acid sites were eliminated by introduction of K⁺ and Cs⁺. These results suggest that the introduction of alkali metals reduced the surface acidity of the ZSM-5 zeolites to varying degrees. The surface basicities are shown in Fig. 2. Only one peak was observed for all the modified ZSM-5 zeolites. The peak for the KZSM-5 and CsZSM-5 catalysts appeared at around 200 °C and repre-

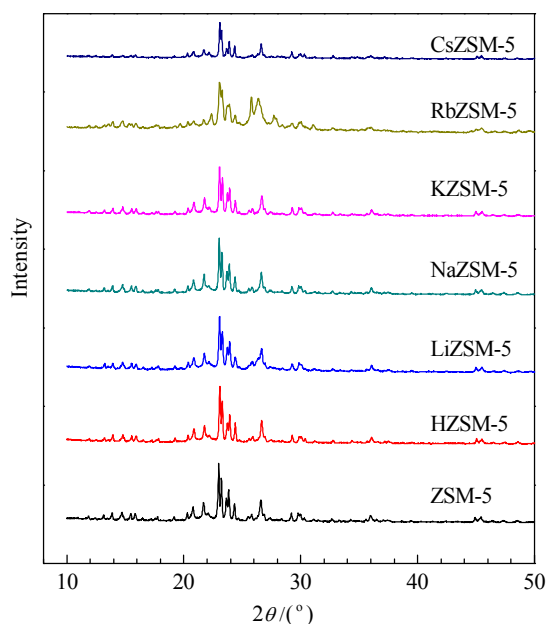


Fig. 4. XRD patterns of ion-exchanged ZSM-5.

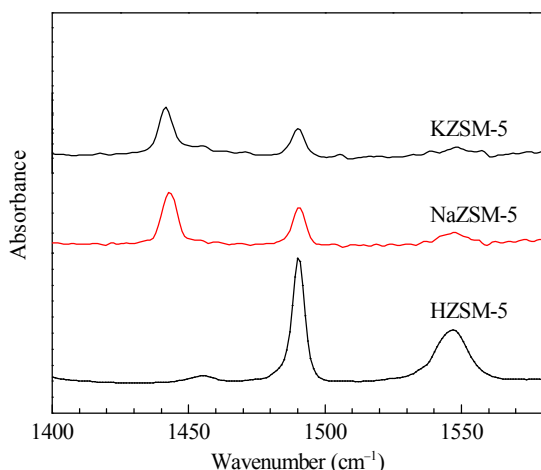


Fig. 5. FTIR spectra of pyridine adsorbed on catalysts.

sented weak base sites. The acid and base sites of KZSM-5 and CsZSM-5 were weak. The NH_3/CO_2 -TPD results show that the strengths of the weak acid-base sites matched each other well, which could enhance the acid-base synergistic effect. Previous studies have also shown that moderate acid and base sites favor LA dehydration to AA [24,25]. The highest AA selectivity was obtained over the KZSM-5 and CsZSM-5 catalysts.

Py-IR was used to study the nature of the acid sites; the results are shown in Fig. 5. The peaks at 1450 and 1549 cm^{-1} are ascribed to pyridine adsorbed on Lewis acid and Brønsted sites, respectively. The results show that the Brønsted acid peak intensity decreased significantly from HZSM-5 to KZSM-5. In particular, the Brønsted acid peak was almost absent from the KZSM-5 spectrum. However, the Lewis acid peak intensity increased with the introduction of metal cations; this is consistent with a previous report that cations in alkali-metal-exchanged zeolites behave as Lewis acid centers, whereas the framework oxygens behave as Lewis base centers [26]. Decreases in the number of Brønsted acid sites and increases in the number of Lewis acid sites on NaZSM-5 and KZSM-5 were confirmed by NH_3 -TPD, which showed elimination of strong acid sites and an increase in weak acid sites. Although there was no direct experimental evidence, it can be inferred that the

Lewis acid centers are mainly weak acid sites in the modified ZSM-5 zeolites. An increase in the number of Lewis acid centers can increase the number of weak acid sites, thereby promoting LA dehydration to AA.

4. Conclusions

Alkali-metal-cation-modified ZSM-5 zeolites were used to catalyze the dehydration of LA to AA under various reaction conditions. The modified ZSM-5 zeolites showed excellent catalytic activity and high AA selectivity. Among the studied catalysts, the KZSM-5 catalyst gave the best catalytic performance because of the synergistic effect of weak acid-base sites. An increase in the number of Lewis acid sites, which was caused by metal-cation modification of ZSM-5, was beneficial to LA dehydration to AA. The KZSM-5 zeolite had excellent stability in catalytic LA dehydration because of its shape selectivity and the absence of strong acidity and three-dimensional supercages. The KZSM-5 catalyst gave 98% LA conversion and 77% AA selectivity under the optimum conditions (i.e., 40 wt% LA aqueous solution, 365 °C, and LHSV 2 h^{-1}).

References

- [1] Corma A, Iborra S, Velty A. *Chem Rev*, 2007, 107: 2411
- [2] Alonso D M, Bond J Q, Dumesic J A. *Green Chem*, 2010, 12: 1493
- [3] Martinez F A C, Balciunas E M, Salgado J M, Gonzalez J M D, Converti A, Pinheira de Souza K. *Trends Food Sci Technol*, 2013, 30: 70
- [4] Dusselier M, Van Wouwe P, Dewaele A, Makshina E, Sels B F. *Energy Environ Sci*, 2013, 6: 1415
- [5] Katryniok B, Paul S, Dumeignil F. *Green Chem*, 2010, 12: 1910
- [6] Korstanje T J, Kleijn H, Jastrzebski J T B H, Klein Gebbink R J M. *Green Chem*, 2013, 15: 982
- [7] Beerthuis R, Granollers M, Brown D R, Salavagione H J, Rothenberg G, Shiju N R. *RSC Adv*, 2015, 5: 4103
- [8] Zhang J F, Feng X Z, Zhao Y L, Ji W J, Au C T. *J Ind Eng Chem*, 2014, 20: 1353
- [9] Lunt J. *Polym, Degrad Stab*, 1998, 59: 145
- [10] Xu X B, Lin J P, Cen P L. *Chin J Chem Eng*, 2006, 14: 419
- [11] Peng J S, Li X L, Tang C M, Bai W. *Green Chem*, 2014, 16: 108
- [12] Hong J H, Lee J M, Kim H, Hwang Y K, Chang J S, Vallgudi S B, Han Y H. *Appl Catal A*, 2011, 396: 194

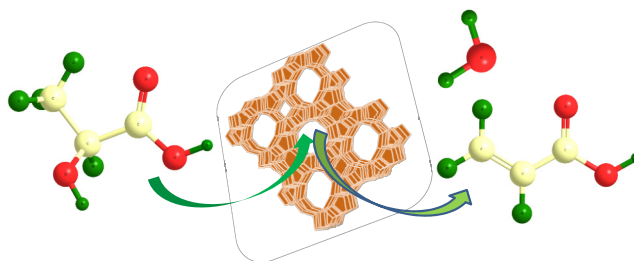
Graphical Abstract

Chin. J. Catal., 2015, 36: 1861–1866 doi: 10.1016/S1872-2067(15)60970-6

Alkali-metal-modified ZSM-5 zeolites for improvement of catalytic dehydration of lactic acid to acrylic acid

Chuan Yuan, Huayan Liu, Zekai Zhang, Hanfeng Lu, Qiulian Zhu, Yinfei Chen*
Zhejiang University of Technology

Lactic acid (LA) conversion of 98% and 77% acrylic acid (AA) selectivity were achieved under the operating conditions 40 wt% LA aqueous solution, 365 °C, and 2 h^{-1} , using a KZSM-5 catalyst, in LA dehydration to AA, because of the synergistic effect of weak acid-base sites.



- [13] Wang H J, Yu D H, Sun P, Yan J, Wang Y, Huang H. *Catal Commun*, 2008, 9: 1799
- [14] Zhang J F, Zhao Y L, Feng X Z, Pan M, Zhao J, Ji W J, Au C T. *Catal Sci Technol*, 2014, 4: 1376
- [15] Yan B, Tao L Z, Liang Y, Xu B Q. *ChemSusChem*, 2014, 7: 1568
- [16] Lee J M, Hwang D W, Hwang Y K, Halligudi S B, Chang J S, Han Y H. *Catal Commun*, 2010, 11: 1176
- [17] Sun P, Yu D H, Tang Z C, Li H, Huang H. *Ind Eng Chem Res*, 2010, 49: 9082
- [18] Xia W, Takahashi A, Nakamura I, Shimada H, Fujitani T. *J Mol Catal A*, 2010, 328: 114
- [19] Vishwanathan V, Jun K W, Kim J W, Roh H S. *Appl Catal A*, 2004, 276: 251
- [20] Sun P, Yu D H, Fu K M, Gu M Y, Wang Y, Huang H, Ying H J. *Catal Commun*, 2009, 10: 1345
- [21] Zhang J F, Zhao Y L, Pan M, Feng X Z, Ji W J, Au C T. *ACS Catal*, 2010, 1: 32
- [22] Satterfield C N. *Heterogeneous Catalysis and Industrial Practice*. 2nd Ed. New York: McGraw-Hill, 1991. Chapter 7
- [23] Jun K W, Lee H S, Roh H S, Park S E. *Bull Korean Chem Soc*, 2003, 24: 106
- [24] Yan J, Yu D H, Li H, Sun P, Huang H. *J Rare Earths*, 2010, 28: 803
- [25] Yan J, Yu D H, Sun P, Huang H. *Chin J Catal*, 2011, 32: 405
- [26] Deka R C, Hirao K. *J Mol Catal A*, 2002, 181: 275