Catalysis Communications 10 (2009) 1345–1349

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Potassium modified NaY: A selective and durable catalyst for dehydration of lactic acid to acrylic acid

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ARTICLE INFO

Article history:
Received 15 December 2008
Received in revised form 18 February 2009
Accepted 27 February 2009
Available online 10 March 2009

Keywords:
Potassium
NaY
Selectivity
Durability
Lactic acid
Dehydration

ABSTRACT

Potassium modification significantly improved the selectivity and durability of NaY zeolites during lactic acid dehydration reaction. The selectivity of 2.8K/NaY zeolites improved from 14.8% to 50.0% over NaY catalyst. Adding potassium also prolonged catalyst life. After 22 h the acrylic acid selectivity of NaY zeolites reduced to less than 10.0% while that of 3.5K/NaY retained 35.6%. Characterizations with NH_3-TPD, CO_2-TPD, N_2 adsorption and thermal analysis techniques revealed that the enhancement of catalytic performances could be attributed to the tuned acidity/basicity and the potassium electronic promoter effect.

1. Introduction

In order to reduce the dependence on fossil fuel, especially petroleum, much research on biorenewable feedstocks transformation has been reported. Dumesic et al. [1,2] have demonstrated that catalysis is a key to the transformation of many biorenewable resources to hydrogen, liquid fuel, and precursors for plastics. Therefore, catalysis technique would be a promising process to harness effectively many biomass feedstocks [3]. However, the excessive active functional groups of biorenewable molecules lead, in turn, to other side-reactions and fast deactivation of catalyst. The research and development on selective and durable catalysts for bio-based molecules transformation would be significant to biorefinery industry [4].

Lactic acid, the most prevalent product of fermentation, has been dehydrated to acrylic acid over $CaSO_4/Na_2SO_4$, Na_2HPO_4, $AlPO_4$ etc. [5–7]. These studies focused on improving the yield of acrylic acid and a possible reaction mechanism with Na_3PO_4 catalyst. We recently reported lactate or lactic acid dehydrated to acrylic acid over a NaY catalyst [8,9]. During the dehydration reaction, deactivation induced by coke deposit can hinder the catalyst life in industrial applications. However, to our knowledge, the reports on improvement of the durability of catalyst for lactic acid dehydration are scarce.

The main objective of this work is to elucidate the effects of the potassium on pore structure, acidity/basicity and catalytic performances of NaY zeolites for lactic acid dehydration.

2. Experimental

2.1. Catalyst preparation

NaY zeolites (BASF, Si/Al = 2.5) were treated with 1 N $NaNO_3$ aqueous solution to obtain the 100% Na ion-exchanged forms. Potassium was introduced into NaY zeolites by an impregnation method [10]. NaY after calcination was immersed into an aqueous solution of KNO_3 of a given concentration and stirred for 12 h at room temperature. The slurry was dried at 343 K for 4 h with continuous stirring. The solid sample was further dried in a vacuum at 313 K for 12 h. Then it was calcined in air by heating from ambient temperature to 823 K at a rate of 1 K min^{-1} and maintained at 823 K for 6 h to obtain the catalysts denoted as *n*K/NaY, where n represents the mass percentage of potassium.

2.2. Catalytic reaction

The catalytic reactions were carried out using a fixed-bed reactor with 8 mm as internal diameter operated at atmospheric pressure. Before the reaction, the catalyst of 1.5 g was pretreated at

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doi:10.1016/j.catcom.2009.02.019

598 K for 0.5 h under N_2 (30 mL min^{-1}). Then the feedstock (29 wt% lactic acid aqueous solution) was pumped into the preheating zone (LHSV = 3 h^{-1}) and the vapor was carried through the catalyst bed by nitrogen. The products were condensed and analyzed by GC (Agilent 6890 N) equipped with a FFAP (free fatty acid phase) capillary column and FID detector. Lactic acid conversion and product selectivity were calculated similar to our previous study [9].

2.3. Characterization

NH_3 temperature-programmed desorption (NH_3-TPD), and CO_2-TPD were performed by the BEL-CAT-B-82 instrument connected to a thermal conductivity detector. On the basis of N_2 adsorption isotherms obtained at 77 K with a Micromeritics ASAP 2020 apparatus, the specific surface area and micropore volume were calculated by BET and *t*-plot methods, respectively. The thermal analysis was recorded by the NETZSCH STA 409 PC equipment. The samples dried under N_2 flow at 598 K, ca. 5 mg, were placed in a Al_2O_3 cell and heated from room temperature to 1073 K at a heating rate of 10 K min^{-1} with a gas feed (air) of 50 mL min^{-1}.

3. Results and discussion

3.1. Catalytic performance

Table 1 shows the lactic acid conversion and products distribution over NaY and potassium modified NaY zeolites. NaY zeolites could catalyze lactic acid to acrylic acid and acetaldehyde, indicating the co-existence of dehydration and decarboxylation/decarbonylation reactions. As shown in Table 1, the acrylic acid selectivity increased and the acetaldehyde selectivity decreased with increasing potassium content, strongly suggesting that potassium modification was responsible for inhibiting acetaldehyde formation. NaY zeolites with potassium content of 2.8 wt% exhibited the best performance for acrylic acid selectivity, that was 50.0%, moreover, acetaldehyde selectivity decreased from 10.8% to 1.4%. The catalytic results indicated that potassium modification could improve acrylic acid selectivity and reduce acetaldehyde selectivity.

During the process of bio-based molecules catalytic transformation, catalyst deactivation is a common and serious problem due to the poor thermal stability of reactants. The catalytic performances with time on stream have been investigated to compare the durability of NaY zeolites with and without potassium modification. As shown in Fig. 1, potassium modified catalysts had better durability than NaY parent catalysts. The acrylic acid selectivity over NaY parent catalysts decreased less than 15% after 5 h. Meanwhile, lactic acid conversion decreased from 100% to 90.2% after 22 h. In contrast, lactic acid conversion and acrylic acid selectivity remained at 96.8% and 35.6%, respectively, over potassium modified NaY zeolites after 22 h. These results showed that potassium modification could improve catalysts durability. The higher durability with TOS over K/NaY could be ascribed to the acidity/basicity adjustment and potassium electronic promoter effect. This speculation will be elucidated combined with characterization results in discussion section.

Table 1
Catalytic performances of lactic acid over NaY zeolites and potassium modified NaY zeolites.

Catalyst	Conversion (mol%)	Selectivity [*]/(mol%)			
		AA	AD	PA	2,3-pen
NaY	96.1	14.8	10.8	–	–
0.35K/NaY	95.9	20.6	10.2	–	3.5
0.7K/NaY	96.4	31.2	8.3	2.1	4.8
1.4K/NaY	97.5	39.8	6.6	4.1	9.4
2.1K/NaY	98.2	40.2	4.7	4.0	10.1
2.8K/NaY	98.8	50.0	2.8	3.8	10.0
3.5K/NaY	98.8	41.3	1.4	3.5	10.6

[*] AA – acrylic acid; AD – acetaldehyde; PA – propanoic acid; 2,3-pen – 2,3-pentanedione. Reaction conditions: lactic acid feedstock: 29 wt%, lactic acid flow rate: 4.5 mL h^{-1}, N_2 flow rate: 30 mL min^{-1}, catalysts: 1.5 g, TOS: 360 min, temperature: 598 K.

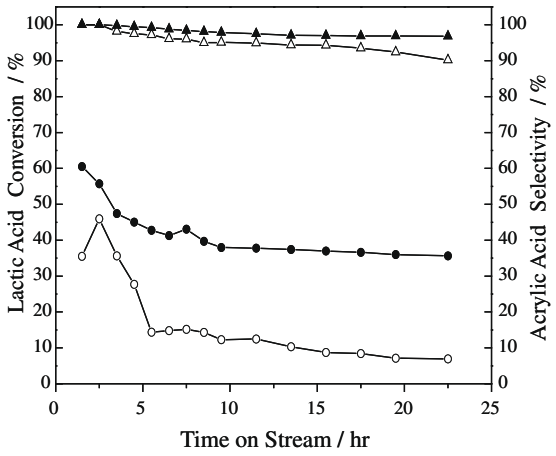

Fig. 1. Lactic acid conversion and acrylic acid selectivity with time on stream over the NaY zeolites with and without potassium modification. Conversion of (▲) 3.5K/NaY, (△) NaY, selectivity of (●) 3.5K/NaY, (○) NaY.

3.2. Characterization

3.2.1. Acidity and basicity

Potassium, selected as the modifier, could be expected to affect the acidic and basic properties of catalysts [11,12]. Here, the influence of the presence of potassium on the acidity of NaY zeolites has been investigated by NH_3-TPD measurements. NH_3-TPD profiles obtained over the NaY zeolites and potassium modified NaY zeolites are shown in Fig. 2.

NaY zeolites had NH_3 desorption peak at 476 K, consistent with the fact that NaY zeolites possessed acidic sites. After potassium modification, the peak intensity and the quantitative acidity

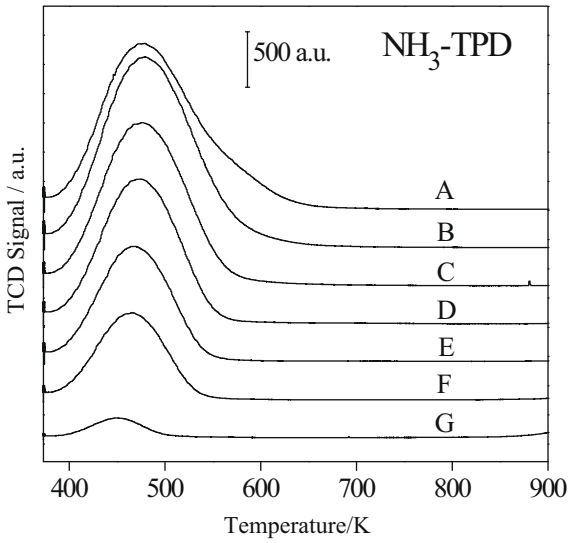

Fig. 2. NH_3-TPD profiles. A. NaY, B. 0.35KNaY, C. 0.7KNaY, D. 1.4KNaY, E. 2.1KNaY, F. 2.8KNaY and G. 3.5KNaY.