Comparison of Acrylic Acid Production from Lactic Acid and Alkyl Lactates over K^+-exchanged Beta and ZSM-5 Zeolites

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Abstract: This work compares the conversion of lactic acid (LA), methyl lactate (ML) and ethyl lactate (EL) for acrylic acid (AA) production over K^+-exchanged zeolite beta and ZSM-5 catalysts. The data demonstrate that the use of EL and ML for AA production is advantageous in offering a higher AA yield. Particularly, the use of the ZSM-5 based catalyst for EL and ML conversion resulted in much cleaner products and offered an AA selectivity as high as 90%. Discussion on the nature of active sites and mechanisms of the reactions will be made based on measurements of the reaction kinetics of LA and EL under different conditions, including co-feeding acidic and basic molecules for the reactions.

Keywords: Biomass conversion, Acid-base catalysis, Acrylic acid, Sustainable chemistry, Zeolites

1. Introduction

Recent studies from our and other laboratories have shown that alkali-ion exchanged zeolites like beta and ZSM-5 can be highly efficient catalysts for the selective dehydration of lactic acid (LA) to form acrylic acid (AA),[1-4] a versatile monomer for many kinds of polymers being widely used in super absorbents, detergents, dispersants, thickeners, textiles and etc. As high purity LA is usually manufactured with industrial-grade raw LA from biomass fermentation through esterification with methanol or ethanol, followed by distillation and hydrolysis of the lactate.[5] It would be economically more attractive if the alkyl lactate, i.e., methyl lactate (ML) or methyl lactate (EL), could be directly converted to AA or acrylate by catalytic dehydration of ML[6] or EL,[7] not mention that ML or EL could also be obtained by selective oxidation of glycerol, the co-product of biodiesel manufacture, in methanol or ethanol.[8] Presented herein is our comparative study of AA production in the gas-phase dehydration reaction of LA, ML and EL over K^+-exchanged Beta (β) and ZSM-5 zeolites.

2. Experimental

K^+-exchanged β ($K_xNa_{1-x}\beta$) and ZSM-5 (K_xNa_{1-x}ZSM-5) zeolites were prepared by ion exchange of Naβ_y and NaZSM-5_y zeolites (***y*** denotes the molar SiO_2/Al_2O_3 ratio of the zeolite) with an aqueous solution of KBr, as reported previously;[1-3] the ion exchange degree of K^+ was controlled higher than 93% ($x \geq 0.93$). The gas-phase dehydration reaction was conducted at 360 °C under atmospheric pressure in a vertical fixed bed quartz reactor, using an aqueous solution of LA, ML or EL (the reactant concentration in water was 10 mol%) as the feed and N_2 as the reaction carrier gas. Unless otherwise specified, the feeding gas mixture contained 7.4 kPa LA, 66.9 kPa H_2O and 25.7 N_2. The effluents from the reactor were condensed with an ice-water trap and collected hourly for analysis by GC.[9]

3. Results and discussion

The time courses of ML and EL conversion over the $K_xNa_{1-x}\beta$ and K_xNa_{1-x}ZSM-5 catalysts appeared similar to those of LA conversion;[1-3] the reactant conversion and product selectivity became stabilized when the reaction time-on-stream (TOS) was no shorter than 3~4 h. Table 1 compares the stable catalytic reaction data for the three reactants (LA, ML and EL) over $K_{0.97}Na_{0.03}\beta$_42 and $K_{0.95}Na_{0.05}$ZSM-5_27 catalysts, which were obtained during TOS = 7~8 h. Apparently, LA shows the highest reactivity over both catalysts, and among the two lactates ML is more reactive than EL. In addition to the production of AA, ethyl acrylate (MA) and ethyl acrylate (EA) were also produced, respectively, in the conversion of ML and EL. However, the combined selectivity of AA and MA in ML conversion or AA and EA in EL conversion was similar to the AA selectivity in LA conversion over $K_{0.97}Na_{0.03}\beta$_42 but only lightly higher over $K_{0.95}Na_{0.05}$ZSM-5_27.

The much lower selectivity for MA in ML conversion and EA in EL conversion over $K_{0.95}Na_{0.05}$ZSM-5_27 catalyst than over $K_{0.97}Na_{0.03}\beta$_42 would suggest that the acrylate products were probably produced after the formation of AA by bimolecular esterification reactions. The data in Table 1 also disclose a distinct advantage of $K_{0.95}Na_{0.05}$ZSM-5_27 to $K_{0.97}Na_{0.03}\beta$_42, i.e., the 10-ring pore system of the former zeolite is efficient in preventing the formation of 2,3-pentanedione (2,3-PD) and many other minor products, enabling remarkably higher selectivity (ca. 80%) for AA production.

Table 1. Performance of $K_{0.97}Na_{0.03}\beta$_42 and $K_{0.95}Na_{0.05}$ZSM-5_27 catalysts for gas-phase dehydration of LA, ML and EL[a]

Catalyst	Reactant	Conv. (%)	Product selectivity (C%)[b]					AA + MA/EA Yield (C%)
			AA	MA/EA	AD	2,3-PD	Others[c]	
$K_{0.97}Na_{0.03}\beta$_42	LA	98	49	-	22	4	25	48
	ML	54	27	24	15	3	33	28
	EL	33	41	10	13	2	34	14
$K_{0.95}Na_{0.05}$ZSM-5_27	LA	93	80	-	17	1	2	74
	ML	31	78	4	15	0	3	24
	EL	22	82	1	16	0	1	18

[a] Catalyst loading: 500 mg; temperature: 360 °C; $GHSV_{total}$: 7000 h^{-1}.
[b] AA: acrylic acid; AD: acetaldehyde; MA: methyl acrylate; EA: ethyl acrylate; 2,3-PD: 2,3-pentanedione.
[c] Selectivity for "others" (C%) = 100 - ∑(selectivity for each listed product).

We further investigated the effect of ***y*** on the catalytic performance of $K_{0.90+m}Na_{0.10-m}$ZSM-5_***y*** ($m < 0.1$, ***y*** = 18 ~ 75) for the conversion of EL as the selectivity for AA was the highest over the $K_{0.95}Na_{0.05}$ZSM-5_27 catalyst. The results identified that the sample of ***y*** = 27 provided the highest selectivity and yield for AA production from EL; the same catalyst (***y*** = 27) was found most efficient for AA production from LA in our earlier work.[3] Long-term reaction test of this $K_{0.95}Na_{0.05}$ZSM-5_27 catalyst for EL conversion was also conducted, which detected little deactivation of the catalyst in 160 h.

The $K_{0.95}Na_{0.05}$ZSM-5_27 catalyst was then used to establish the reaction kinetics of LA and EL, by investigating the effects of space velocity and temperature, as well as partial pressure effects of the reactant (LA and EL) and H_2O. Under certain conditions, the selectivity of AA reached as high as 90%. Effects of the co-feeding trifluoroacetic acid, CO_2, and NH_3 on the catalyst performance are being studied, respectively, for gaining an insight into the nature of the active sites on the catalyst surface. The results will be presented at the conference to discuss the possible mechanisms of LA and lactate conversion at the catalyst surface.

4. Conclusions

This work demonstrated that the use of EL or ML instead of LA as the reaction feed for AA production is advantageous in offering a higher yield for AA and acrylate. In particular, the use of $K_{0.95}Na_{0.05}$ZSM-5_27 catalyst for EL and ML conversion can make the product much cleaner and offer a very high selectivity (ca. 90%), with AD being the major byproduct. Our investigations on the kinetics of LA and EL conversion over the $K_{0.95}Na_{0.05}$ZSM-5_27 catalyst under different conditions, including those in the presence of acidic and basic additives, will enable us to discuss the nature of active sites and mechanisms of the reactions.

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