BCSJ

Conversion of Methyl Lactate to Acrylates over Modified NaY Zeolite Catalysts

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Figure 1. K content dependence of product distribution of reaction of methyl lactate over K/NaY zeolites. ▲; AD, acetaldehyde, ■; AA, acrylic acid, ◆; MA, methyl acrylate, ★; MeOH, methanol, ▼; CO, ▶; CO_2. Open symbols indicate data for a sample prepared by ion exchange. Reaction conditions: temperature, 350 °C; methyl lactate concentration, 10 vol %; W/F, 1.0×10^{-2} g min cm^{-3}.

The catalytic activity of alkali metal- and alkaline earth metal-modified NaY zeolites for production of acrylic acid and methyl acrylate from methyl lactate was investigated. The reaction pathways and the role of the alkali metals in acrylate production are discussed.

Acrylic acid (AA) and acrylic acid esters are the primary building blocks of acrylate polymers and plastics. Currently, AA is manufactured mainly by two-step oxidation of propylene, a process that is totally dependent on a nonrenewable fossil resource. Therefore, the development of a novel process that is both sustainable and economically viable would be of great importance. One possible process is the formation of AA by dehydration of lactic acid (LA) or methyl lactate (ML). New fermentation-based technologies for producing LA from starch hydrolysates make LA a viable feedstock for chemical production.[1] Furthermore, a new chemical process for the conversion of cellulose to LA and its derivatives, mainly ML, has been developed.[2]

There have been numerous reports of the dehydration of LA to AA over catalysts such as sulfates,[3] phosphates,[3–6] mixtures of sulfates and phosphates,[7] NaY zeolites, and NaY zeolites modified with potassium (K).[8,9] In contrast, there have been only a few reports dealing with catalyst systems for ML dehydration. NaY modified with K by means of an ion-exchange method has been shown to catalyze the dehydration of ML to methyl acrylate (MA) in a relatively high yield (38%).[10] However, the reaction mechanism and the nature of the active sites for ML dehydration are not well understood.

In the present work, we carried out the dehydration of ML to MA and AA over NaY zeolite catalysts and studied how the catalyst activity was affected by modification with alkali and alkaline earth metals. The reaction pathways and the active sites for ML dehydration are discussed.

Na-form Y zeolites (NaY; JRC-Z-Y-5.3, SiO$_2$/Al$_2$O$_3$ = 5.3) were obtained from the Catalysis Society of Japan and used as
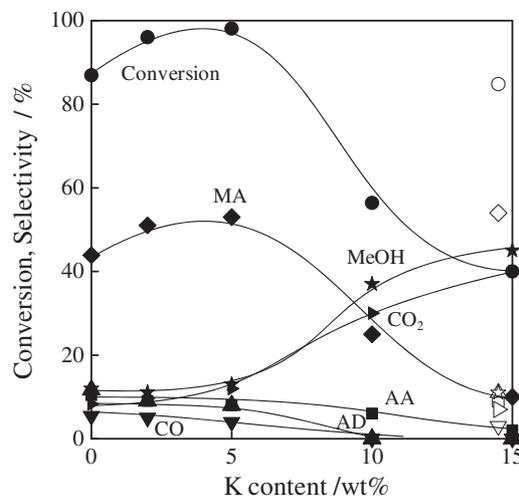
received. The zeolites were impregnated with hydroxide salts of alkali metals (LiOH·H$_2$O, NaOH, KOH, and CsOH·H$_2$O) and hydroxide or nitrate salts of alkaline earth metals (Mg(NO$_3$)$_2$· 6H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O, Sr(OH)$_2$, and Ba(OH)$_2$·H$_2$O) by means of the incipient wetness method. All catalysts were dried in air at 100 °C for 10 h prior to use.

Reactions of ML were carried out in a continuous-flow fixed-bed tubular reactor at atmospheric pressure. ML was vaporized with a heater, and the vapor was diluted with N$_2$ to a ML concentration of 10 vol %. The reaction temperature was 350 °C. The catalyst temperature was monitored with a thermocouple in the catalyst bed. Oxygenated reaction products were analyzed by means of an online gas chromatograph equipped with a hydrogen-flame ionization detector and a TC-FFAP column, and CO and CO$_2$ were analyzed with a thermal conductivity detector and a Shincarbon ST column (Shinwa Chemical Industries, Japan). Product yields were calculated on a carbon number basis.

We examined the effect of K content on the catalytic activity of K-modified NaY zeolites (K/NaY) (Figure 1). ML conversion over unmodified NaY zeolites was 86%, and the AA and MA selectivities were 43% and 10%, respectively. Both ML conversion and MA selectivity increased (reaching maxima of 98% and 53%, respectively) with increasing K content up to 5 wt %, whereas AA selectivity was unchanged. CO and CO$_2$ were produced as by-products of the reaction. We confirmed acetaldehyde and methanol as the counter-part chemicals of CO formation (decarbonylation) and CO$_2$ formation (decarboxylation) by GC measurements. The CO selectivity was 5% over unmodified NaY zeolites, and the selectivity decreased with increasing K content (no CO was produced at 10 wt % K); whereas CO$_2$ production increased with increasing K content. Decarbonylation of LA to form CO is reported to occur on acidic sites, whereas CO$_2$ is produced by decarboxylation of LA on basic sites.[11] Over NaY zeolites, the conversion of LA to

Table 1. Catalytic activity of zeolites for reaction of methyl lactate[a]

Catalyst	Conversion /%	Yield (Selectivity)/%							
		AD	AA	MA	PA	MeOH	2,3P	CO	CO_2
NaY	86.9	9.8 (11)	8.8 (10)	37.0 (43)	0 (0)	10.1 (12)	0 (0)	4.5 (5)	7.0 (8)
Li/NaY	89.8	5.0 (6)	0 (0)	0 (0)	0 (0)	45.6 (51)	0 (0)	0 (0)	39.1 (44)
K/NaY	98.1	7.8 (8)	8.1 (8)	51.8 (53)	0 (0)	13.0 (13)	0 (0)	3.8 (4)	11.6 (12)
Cs/NaY	93.3	5.2 (6)	10.8 (12)	55.0 (59)	0.7 (1)	10.2 (11)	0 (0)	1.6 (2)	7.1 (8)
Mg/NaY	61.4	25.1 (41)	0 (0)	0 (0)	0 (0)	31.8 (52)	0 (0)	0 (0)	4.4 (7)
Ca/NaY	70.3	27.4 (39)	5.6 (8)	0 (0)	0 (0)	28.8 (41)	0 (0)	0 (0)	8.4 (12)
Sr/NaY	74.0	24.4 (33)	2.2 (3)	3.7 (5)	0 (0)	28.1 (38)	0 (0)	0 (0)	15.5 (21)
Ba/NaY	70.2	21.8 (31)	1.4 (2)	0 (0)	0 (0)	31.6 (45)	0 (0)	2.8 (4)	12.6 (18)

a) Reaction temperature, 350 °C; methyl lactate concentration, 10 vol %; W/F, 1.0×10^{-2} g min cm^{-3}; loading of metal additive, 5 wt %. Abbreviations: AD, acetaldehyde; AA, acrylic acid; MA, methyl acrylate; PA, propanoic acid; MeOH, methanol; 2,3P, 2,3-pentanedione.

AA is suppressed by the presence of strongly acidic sites, on which decarbonylation to form CO occurs.[8] Our results suggest that K selectively interacted with the strongly acidic sites on NaY and neutralized them to inhibit decarbonylation to form CO. In addition, the added K provided basic sites after complete neutralization of the strongly acidic sites, and decarboxylation of ML to form CO_2 occurred on the basic sites. We have also measured the NH_3-TPD and CO_2-TPD in order to clarify the acidic and basic nature of the catalysts (Figure S1). NH_3-TPD results indicated that the intensity of the NH_3 desorption peaks at 200 and 270 °C were decreased with increasing K content, suggesting that the acidic sites over NaY decrease by addition of K. On the other hand, a CO_2 desorption peak was observed at 200 °C on NaY. This desorption peak area slightly increased by adding K (5 wt %). When more K was added, the peak at 200 °C disappeared and a new desorption peak appeared at 400 °C. That is, the distribution of products obtained from the reaction of ML over NaY zeolites changed as the acid–base properties of the zeolites were altered by the addition of K.

As mentioned above, K/NaY prepared by ion exchange has high activity for the production of acrylates from ML.[10] Therefore, we prepared 14.7 wt % K/NaY zeolites by means of ion exchange (all the Na ions were assumed to have been exchanged for K ions) and evaluated the activity of the resulting catalyst for ML conversion (Figure 1, open symbols). The activity of the catalyst prepared by ion exchange was almost the same as that of 5 wt % K/NaY prepared by impregnation, indicating that the impregnation method used in this study was more effective for neutralizing the strongly acidic sites on NaY than was the ion-exchange method.

Next, we investigated the effects of adding alkali metals other than K, as well as alkaline earth metals, on acrylate production over NaY zeolite catalysts with the goal of optimizing the acid–base properties of the zeolites (Table 1). When the zeolites were modified with Li, neither AA nor MA was produced. Over Cs/NaY zeolites, the selectivity for and yield of acrylates were 71% (AA + MA) and 66%, respectively. In contrast, NaY zeolites modified with Mg, an alkaline earth metal, showed lower ML conversion than did NaY, K/NaY, or Cs/NaY zeolites, and no AA or MA was produced. Like Mg, the other alkaline earth metals (Ca, Sr, and Ba) had deleterious effects on ML conversion to acrylates. Our results indicate that
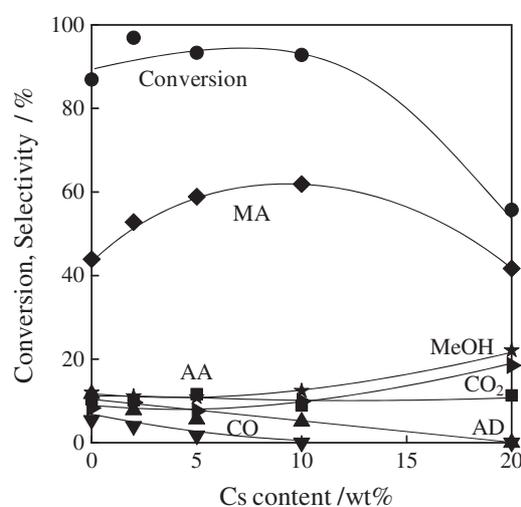
Figure 2. Cs content dependence of product distribution of reaction of methyl lactate over Cs/NaY zeolites. ▲; AD, acetaldehyde, ■; AA, acrylic acid, ◆; MA, methyl acrylate, ★; MeOH, methanol, ▼; CO, ▶; CO_2. Reaction conditions: temperature, 350 °C; methyl lactate concentration, 10 vol %; W/F, 1.0×10^{-2} g min cm^{-3}.

Cs/NaY zeolites were the most effective catalyst for ML conversion to acrylates. Compared to addition of K, addition of Cs suppressed CO and CO_2 production and promoted the production of MA. These results indicate that Cs addition was better for controlling the acid–base properties of the zeolites than was K addition.

To further optimize the acid–base properties of Cs/NaY zeolites, we investigated the influence of Cs content on the activity of the catalyst for production of acrylates (Figure 2). The selectivity for AA was independent of Cs content, whereas the MA selectivity increased with increasing Cs content up to 10 wt %, at which point the MA selectivity was 60%, and the selectivity and yield of acrylates were 73% and 68%, respectively. To our knowledge, none of the other reported zeolite catalysts demonstrate such remarkably high activity for acrylate production from ML. As the Cs content was increased above 10 wt %, ML conversion and MA selectivity decreased considerably, and CO_2 and methanol production increased, indicating that excess Cs in the NaY poisoned the acidic sites and
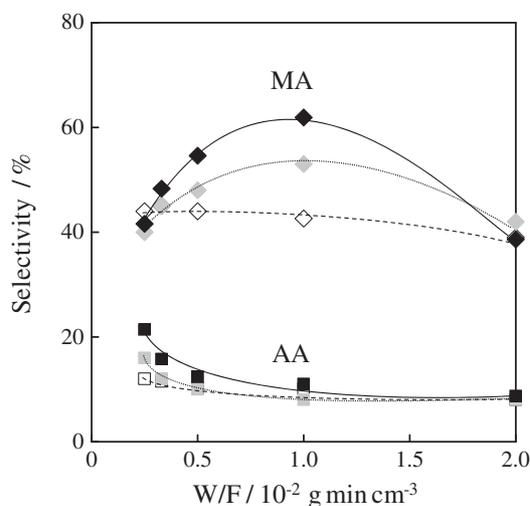
Figure 3. Effect of contact time on product selectivity of reaction of methyl lactate (10 vol %) over NaY zeolites at 350 °C. ■; AA, acrylic acid, ◆; MA, methyl acrylate. Open symbols and dashed lines, NaY; gray symbols and dotted lines, 5 wt % K/NaY; closed symbols and solid lines, 10 wt % Cs/NaY.

acted as a basic catalyst to promote decarboxylation, as was observed for K/NaY zeolites.

We found that the addition of Cs promoted MA production but not AA production. To determine why MA production but not AA production was promoted, we compared the dependence of the MA and AA selectivities on contact time (W/F, where W = weight of catalyst and F = feed gas flow rate) over NaY zeolites and K- and Cs-modified NaY zeolites (Figure 3). Over the NaY zeolites, the selectivities for both AA and MA decreased slightly with increasing contact time, and the AA/MA ratio was the same at all contact times. In contrast, over both of the alkali metal-modified NaY zeolites, the selectivity for MA increased with increasing contact time up to 1.0×10^{-2} g min cm^{-3} and then decreased with further increases in contact time; whereas the AA selectivity continued to decrease with increasing contact time.

On the basis of these results on the effects of contact time, we will now discuss the reaction pathways for ML conversion to AA and MA over NaY, as well as the role of the added alkali metals. As mentioned above, over unmodified NaY, the MA/AA ratio was the same at all contact times. Zhang et al. proposed that the main reaction pathway for ML conversion over silica-supported sodium phosphates involves dehydration of ML to form MA and de-esterification of ML to form AA (eqs 1 and 2, respectively).[12]

$$ML \rightarrow MA + H_2O \qquad (1)$$

$$ML \rightarrow AA + CH_3OH \qquad (2)$$
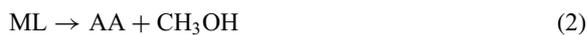
Our results (Figure 3) strongly suggest that MA and AA were produced in parallel from ML over NaY zeolites, which is in agreement with the results reported by Zhang et al. In contrast, over alkali metal-modified NaY zeolites, AA selectivity decreased and MA selectivity increased with increasing

contact time up to 1.0×10^{-2} g min cm^{-3}, which indicates that the reaction pathways for MA and AA formation were changed by modification of the catalyst. On the basis of a theoretical study of the mechanism of ML conversion over a NaH$_2$PO$_4$ catalyst, Zhang et al. suggested that the main route for the formation of MA from ML is esterification of AA with CH$_3$OH.[13] Therefore, we believe that the esterification of AA with CH$_3$OH (eq 3) occurred over alkali metal-modified NaY zeolites and was selectively promoted by the presence of Cs.

$$AA + CH_3OH \rightarrow MA + H_2O \qquad (3)$$

Another possibility is that promotion of MA production by alkali species was due to inhibition of MA decomposition by alkali modification. However, at longer contact times, MA decomposition predominated, resulting in a decrease in MA selectivity. We confirmed that the production of CO$_2$ increased at longer contact times (data not shown).

In summary, we investigated the catalytic activity of NaY zeolites modified with alkali and alkaline earth metals for the production of AA and MA from ML. We found that MA production was greatly promoted by the addition of an alkali metal to the zeolites. The yields of AA and MA reached 73% over 10 wt % Cs/NaY zeolites. We proposed reaction pathways for ML conversion into acrylates over Cs/NaY zeolites and determined that the added Cs not only promoted the esterification of AA to form MA but also inhibited MA decomposition.

Supporting Information

Temperature-programmed desorption spectra of NH$_3$ and CO$_2$ over NaY and Cs/NaY zeolites. This material is available electronically on J-STAGE.

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