# Supporting Information

## Potassium-Ion Exchanged Zeolites for Sustainable Production of Acrylic Acid by Gas-Phase Dehydration of Lactic Acid

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**Table S1**. Comparison of the catalytic performance of $K_{0.97}Na_{0.03}$ZSM-5_27 and various other catalysts for the gas-phase LTA reaction

| Catalyst | $S_{BET}$ ($m^2$ $g^{-1}$) | Catalsyt Loading | LA aqueous solution[a] | | Rxn temp. (°C) | Space velocity[b] ($h^{-1}$) | Carrier gas[c] (ml/min) | TOS (h) | LA conv. (%) | AA sel. (%) | Rxn rate (μmol·$h^{-1}$·$m^{-2}$) | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | LA conc. (wt%) | Flow (ml $h^{-1}$) | | | | | | | $SA_{LA}$[d] | $SA_{AA}$[e] | |
| $Ca_3(PO_4)_2/Ca_2P_2O_7$ | 12 | 4 g, 6 ml | 50 | 2.1 | 390 | 0.3 (0.4) | $N_2$, 15 | 0-27 | 100 | 54 | 243 | 131 | 6 |
| $Ba_2P_2O_7$ | 2 | 0.57 g, 0.36 ml | 20 | 1.0 | 400 | 0.4 (1.8) | $N_2$, 1 | 1-2 (23-25) | 100 (93) | 76 (55) | 1949 (1813) | 1481 (997) | 9 |
| $Ba_2P_2O_7$ | 2 | 0.57 g, 0.36 ml | 20 | 3.0 | 400 | 1.0 (8.1) | $N_2$, 1 | 1-2 | 95 | 75 | 5731 | 4470 | 9 |
| 0.1wt%$H_3PO_4/Sr_2P_2O_7$ | 3 | 0.59 g, 0.4 ml | 20 | 1.0 | 400 | 0.4 (2.5) | $N_2$, 1 | 1-2 (20-24) | 97 (70) | 72 (39) | 1431 (1037) | 1033 (404) | 10 |
| Ca-HAP(Ca/P =1.67) | 61 | 1 g, - | 38 | 1.2 | 350 | 0.5 (-) | Ar, 40 | 5-6 | 76 | 50 | 63 | 34 | 12 |
| Ca-HAP(Ca/P =1.67) | 61 | 0.05 g, - | 38 | 1.2 | 350 | 9.7 (-) | Ar, 40 | 5-6 | 12 | 11 | 196 | 23 | 12 |
| Sr-HAP (Ca/P =1.67) | 46 | 1 g, - | 38 | 1.2 | 350 | 0.5 (-) | Ar, 40 | 5-6 | 72 | 63 | 79 | 54 | 12 |
| Sr-HAP (Ca/P =1.67) | 46 | 0.05 g, - | 38 | 1.2 | 350 | 9.7 (-) | Ar, 40 | 5-6 | 7 | 38 | 159 | 64 | 12 |
| $HAP_{1.62}$-360 | 143 | 0.5 g, 0.5 ml | 36 | 1.0 | 360 | 0.7 (2.0) | $N_2$, 15.5 | 1-2 (6-8) | 97 (97) | 57 (58) | 54 (54) | 31 (31) | 14 |
| $HAP_{1.62}$-360 | 143 | 0.5 g, 0.5 ml | 36 | 2.9 | 360 | 2.1 (5.8) | $N_2$, 15.5 | 1-2 (6-8) | 77 (70) | 70 (71) | 128 (118) | 89 (84) | 14 |
| $Na_2SO_4/CaSO_4$ | - | - | 10 | - | 400 | - | - | - | - | 68 (yield) | - | - | 15 |
| $KH_2PO_4/Na_2HPO_4/$ $CuSO_4/CaSO_4$ | - | 20 g, - | 26 | 6.0 | 330 | 0.1 (-) | $CO_2$, 20 | - | - | 64 (yield) | - | - | 16 |
| $BaSO_4$-700 | 3 | 0.57 g, - | 20 | 1.0 | 400 | 0.4 (-) | $N_2$, 1 | 1 (76-80) | 100 (90) | 74 (50) | 1481 (1333) | 1096 (667) | 17 |
| $BaSO_4$-700 | 3 | 0.57 g, - | 40 | 1.0 | 400 | 0.7 (-) | $N_2$, 1 | 0-1 | 82 | 57 | 2430 | 1384 | 17 |
| $MgSO_4$-500 | 10 | 0.57 g, - | 20 | 1.0 | 400 | 0.4 (2.0) | $N_2$, 1 | 0-1 | 85 | 62 | 378 | 234 | 17 |
| $CaSO_4$-500 | 6 | 0.57 g, - | 20 | 1.0 | 400 | 0.4 (2.0) | $N_2$, 1 | 0-1 (3-5) | 100 (75) | 69 (70) | 741 (556) | 511 (389) | 17 |
| 2wt%La/NaY_9 | 537 | 1.5 g, 1.5 ml | 38 | 4.5 | 350 | 1.1 (3.0) | $N_2$, 30 | 0-1 | 99 | 56 | 23 | 13 | 18 |
| 9.2wt%KI/NaY_5 | 548 | 1.5 g, - | 29 | 4.5 | 325 | 0.9 (-) | $N_2$, 30 | 1-2 (5-6) | 98 (96) | 68 (41) | 14 (14) | 13 (10) | 20 |
| 12wt%$Na_2HPO_4$/NaY_5 | 379 | 1.5 g, 2.2 ml | 34 | 6 | 340 | 1.4 (2.7) | $N_2$, 30 | 1-2 (26-28) | 80 (62) | 72 (38) | 32 (25) | 23 (10) | 21 |
| $Na_2HPO_4$/NaY_3 | 405 | 1.5 g, - | 34 | 6 | 340 | 1.4 (-) | $N_2$, 30 | 0-2 (26-28) | 95 (83) | 74 (39) | 35 (31) | 27 (13) | 22 |
| $K_{0.94}Na_{0.06}\beta$_43 | 420 | 0.5 g, 0.85 ml | 36 | 2.9 | 360 | 2.1 (3.4) | $N_2$, 15.5 | 1-2 (7-8) | 100 (91) | 62 (59) | 57 (52) | 34 (30) | 23 |
| $Rb_{0.95}Na_{0.05}\beta$_43 | 388 | 0.5 g, 0.80 ml | 36 | 2.9 | 360 | 2.1 (3.6) | $N_2$, 15.5 | 1-2 (9-10) | 96 (91) | 69 (70) | 59 (56) | 41 (39) | 24 |
| $Cs_{0.81}Na_{0.19}\beta$_43 | 413 | 0.5 g, 0.76 ml | 36 | 2.9 | 360 | 2.1 (3.8) | $N_2$, 15.5 | 1-2 (9-10) | 97 (87) | 70 (70) | 66 (65) | 39 (35) | 24 |
| $Na_{1.2}$ZSM-5_36 | 300 | -, 0.25 ml | 20 | 1.5 | 325 | - (6.0) | $N_2$, 32 | 1-2 (5-6) | 93 (94) | 53 (54) | - (-) | - (-) | 25 |
| 0.5P/ZSM-5-0.5AT_50 | 238 | 1.5 g, 2.0 ml | 30 | 8.0 | 350 | 1.6 (4.0) | $N_2$, 35 | 1-2 (54-55) | 98 (85) | 75 (65) | 73 (63) | 55 (41) | 26 |
| KZSM-5_150 | 263 | 0.9 g, 2.0 ml | 40 | 0.8 | 365 | 0.4 (0.4) | $N_2$, 50 | 1-2 (55-60) | 97 (91) | 77 (79) | 15 (14) | 11 (10) | 27 |
| $K_{0.97}Na_{0.03}\beta$_22 | 289 | 0.5 g, 0.75 ml | 36 | 2.9 | 360 | 2.1 (3.9) | $N_2$, 15.5 | 1-2 (30-32) | 100 (90) | 80 (67) | 82 (74) | 66 (50) | This work |
| $K_{0.97}Na_{0.03}$ZSM-5_27 | 204 | 0.5 g, 0.80 ml | 36 | 2.9 | 360 | 2.1 (3.6) | $N_2$, 15.5 | 1-2 (79-80) | 96 (80) | 82 (70) | 112 (93) | 92 (65) | This work |

[a] Left: concentration of LA in the aqueous feed; right: liquid flow rate of the feed. [b] Number outside the parenthesis shows the weight hourly space velocity of LA ($WHSV_{LA}$) and that in the parenthesis the total liquid hourly space velocity of the aqueous feed (LHSV). [c] Number after the comma shows the carrier gas flow rate. [d] $SA_{LA}$: area-specific LA consumption rate. [e] $SA_{AA}$: area-specific AA formation rate. Note: the catalytic data were compiled with the assumption that they were measured from catalytic reaction tests with satisfactory materials balance (> 95%).

**Table S2.** Framework and channel structure of the investigated zeolites in this work

| Zeolite | Framework | Pore dimension | Channels[a] | $D_i$ [Å ][b] |
|---|---|---|---|---|
| ZSM-22 | TON | 1D | [001] **10** 4.6×5.7 | 5.65 |
| ZSM-35 | FER | 2D | [001] **10** 4.2×5.4 ↔ [010] **8** 3.5×4.8 | 7.00 |
| MCM-22 | MWW | 2D | ⊥[001] **10** 4.0×5.5 \| ⊥[001] **10** 4.1×5.1 | 9.63 |
| β | BEA | 3D | <100> **12** 6.6×6.7 ↔ [001] **12** 5.6×5.6 | 6.62 |
| ZSM-11 | MEL | 3D | <100> **10** 5.3×5.4 | 7.66 |
| ZSM-5 | MFI | 3D | [100] **10** 5.1×5.5 ↔ [010] **10** 5.3×5.6 | 6.30 |

[a] A shorthand notation has been adopted to describe the channels in various zeolites, including channel direction, the number of T-atoms forming the rings of the channels and the crystallographic free diameters of the channels in angstrom. The number in bracket gives the channel direction by the crystallographic axis, and angle bracket marks cubic structure. The numbers in bold font show the number of T-atoms in the pore rings. The two numbers connected by "×" show the crystallographic free diameters of the channel in angstrom. Interconnecting channel systems are separated by a double arrow (↔). A vertical bar (|) denotes that the channel systems are not interconnected.[s1]

[b] Largest included sphere diameter according the calculation on packing of spheres into rigid zeolite framework.[s2]

**Table S3.** Composition and textural properties of the $K^+$-exchanged zeolite samples investigated in this study

| Sample[a] | Parent zeolite | $SiO_2/Al_2O_3$ (molar)[b] | K-loading (wt%)[c] | K/Al (molar)[d] | Surface area[e] ($m^2·g^{-1}$) | Pore volume[e] ($cm^3·g^{-1}$) |
|---|---|---|---|---|---|---|
| $K_{0.96}Na_{0.04}$ZSM-22_50 | NaZSM-22 | 50.3 | 3.8 | 1.6 | 321 (393) | 0.15 (0.19) |
| $K_{0.90}Na_{0.10}$ZSM-35_28 | HZSM-35 | 27.7 | 7.4 | 2.1 | 289 (322) | 0.17 (0.24) |
| $K_{0.99}Na_{0.01}$MCM-22_26 | NaMCM-22 | 25.6 | 8.1 | 2.2 | 332 (472) | 0.36 (0.67) |
| $K_{0.96}Na_{0.04}$ZSM-11_46 | NaZSM-11 | 45.6 | 5.1 | 2.1 | 291 (363) | 0.23 (0.30) |
| $K_{0.93}Na_{0.07}$ZSM-5/ZSM-11_50 | NaZSM-5/ZSM-11_50 | 49.9 | 4.9 | 2.2 | 374 (380) | 0.21 (0.22) |
| $K_{0.97}Na_{0.03}$β_22 | Hβ | 22.2 | 5.1 | 1.1 | 289 (320) | 0.21 (0.24) |
| $K_{0.92}Na_{0.08}$β_31 | Hβ | 31.2 | 5.5 | 1.5 | 489 (566) | 0.32 (0.36) |
| $K_{0.94}Na_{0.06}$β_42 | Hβ | 42.3 | 5.6 | 2.1 | 420 (490) | 0.26 (0.28) |
| $K_{0.93}Na_{0.07}$β_58 | Hβ | 57.9 | 5.0 | 2.4 | 318 (525) | 0.23 (0.30) |
| $K_{0.90}Na_{0.10}$β_111 | Hβ | 110.7 | 3.9 | 3.5 | 263 (624) | 0.19 (0.32) |
| $K_{0.97}Na_{0.03}$ZSM-5_27 | NaZSM-5 | 27.0 | 4.9 | 1.1 | 204 (222) | 0.10 (0.10) |
| $K_{0.95}Na_{0.05}$ZSM-5_36 | NaZSM-5 | 36.2 | 5.2 | 1.8 | 224 (253) | 0.11 (0.12) |
| $K_{0.94}Na_{0.06}$ZSM-5_43 | NaZSM-5 | 43.2 | 5.3 | 2.1 | 212 (222) | 0.10 (0.10) |
| $K_{0.95}Na_{0.05}$ZSM-5_68 | HZSM-5 | 68.0 | 5.2 | 3.1 | 245 (285) | 0.14 (0.16) |
| $K_{0.92}Na_{0.08}$ZSM-5_75 | HZSM-5 | 74.9 | 6.0 | 4.1 | 261 (354) | 0.17 (0.21) |
| NaZSM-5_27 | — | 27.9 | 0 | 0 | 222 | 0.10 |
| $K_{0.54}Na_{0.46}$ZSM-5_27 | NaZSM-5 | 25.8 | 2.6 | 0.6 | 216 | 0.10 (0.10) |
| $K_{0.89}Na_{0.11}$ZSM-5_27 | NaZSM-5 | 26.4 | 4.8 | 1.0 | 208 | 0.10 (0.10) |

[a] The $K^+$-exchanged zeolites were denoted as $K_xNa_{1-x}Z\_y$, according to zeolite type (***Z***), fractional exchange degree of each alkali ion ($K^+$: ***x***, $Na^+$: ***1-x***) and $SiO_2/Al_2O_3$ ratio (***y***). [b] Measured by XRF. [c] K-loading by weight percentage in the $K_xNa_{1-x}Z\_y$ samples measured by XRF. [d] The molar K/Al ratio in the $K_xNa_{1-x}Z\_y$ samples measured by XRF. [e] Surface area was determined by BET method and pore volume was measured at $P/P_0$ = 0.975. Number in the parenthesis shows the specific BET surface area or pore volume for the corresponding parent zeolite.

**Table S4.** Effect of $SiO_2/Al_2O_3$ ratio (***y***) on the catalytic performance of $K_{0.9+m}Na_{0.1-m}β\_y$ for gas-phase dehydration of aqueous lactic acid[a]

| Catalyst | K/Al (molar) | LA conv. (%) | Product selectivity (mol%) | | | | | | AA yield (mol%) | Carbon deposits[b] ($mg_{carbon}·m_{cat}^{-2}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | AA | AD | 2,3-PD | PA | 1-HA | Others | | |
| $K_{0.97}Na_{0.03}β\_22$ | 1.1 | 99 (94) | 80 (71) | 7 (9) | 3 (7) | 7 (9) | 1 (2) | 2 (2) | 80 (67) | 0.69 (32 h) |
| $K_{0.92}Na_{0.08}β\_31$ | 1.5 | 100 (95) | 71 (62) | 16 (15) | 7 (9) | 3 (8) | 0 (2) | 3 (4) | 71 (58) | 0.51 (20 h) |
| $K_{0.94}Na_{0.06}β\_42$ | 2.1 | 99 (90) | 63 (58) | 21 (18) | 9 (12) | 3 (7) | 0 (0) | 4 (5) | 62 (52) | 0.32 (10 h) |
| $K_{0.93}Na_{0.07}β\_58$ | 2.4 | 98 (91) | 49 (46) | 22 (20) | 11 (16) | 4 (7) | 1 (1) | 13 (10) | 48 (42) | 0.53 (10 h) |
| $K_{0.91}Na_{0.09}β\_111$ | 3.5 | 97 (87) | 34 (35) | 21 (21) | 14 (22) | 5 (6) | 1 (2) | 25 (14) | 33 (31) | 0.94 (10 h) |

[a] Catalyst loading: 500 mg; $WHSV_{LA}$: 2.1 $h^{-1}$; rxn temp.: 360 $^{o}C$; TOS = 1~2 h (data outside the parenthesis) and 9~10 (data in the parenthesis). [b] The times given in the parenthesis show the reaction TOS, during which the carbon deposits accumulated on the catalyst surface.

**Table S5**. Acid-base property of the $K^+$-exchanged zeolite samples by $NH_3$- and $CO_2$-TPD measurements

| Sample | $NH_3$-TPD[a] | | $CO_2$-TPD[b] | | $T_{NH3}/T_{CO2}$[c] | Acidity/basicity[d] |
|---|---|---|---|---|---|---|
| | Peak temp. (°C) | Acidity × $10^3$ ($\mu mol_{NH3} \cdot m^{-2}$) | Peak temp. (°C) | Basicity × $10^3$ ($\mu mol_{NH3} \cdot m^{-2}$) | | |
| $K_{0.96}Na_{0.04}$ZSM-22_50 | 200 | 275 | 177 | 8 | 1.13 | 34.4 |
| $K_{0.99}Na_{0.01}$MCM-22_26 | 192 | 114 | 186 | 82 | 1.03 | 1.4 |
| $K_{0.90}Na_{0.10}$ZSM-35_28 | 183 | 110 | 184 | 127 | 0.99 | 0.9 |
| $K_{0.96}Na_{0.04}$ZSM-11_46 | 208 | 466 | 172 | 27 | 1.21 | 17.3 |
| $K_{0.93}Na_{0.07}$ZSM-5/ ZSM-11_50 | 200 | 240 | 190 | 31 | 1.05 | 6.7 |
| $K_{0.94}Na_{0.06}\beta$_42 | 208 | 238 | 170 | 19 | 1.23 | 14.8 |
| $K_{0.94}Na_{0.06}$ZSM-5_43 | 199 | 672 | 190 | 31 | 1.05 | 21.7 |
| $K_{0.97}Na_{0.03}\beta$_22 | 233 | 608 | 160 | 13 | 1.46 | 46.8 |
| $K_{0.92}Na_{0.08}\beta$_31 | 219 | 417 | 164 | 16 | 1.34 | 26.1 |
| $K_{0.94}Na_{0.06}\beta$_42 | 207 | 226 | 169 | 19 | 1.23 | 11.9 |
| $K_{0.93}Na_{0.07}\beta$_58 | 194 | 114 | 173 | 28 | 1.12 | 4.1 |
| $K_{0.90}Na_{0.10}\beta$_111 | 186 | 46 | 175 | 45 | 1.06 | 1.0 |
| $K_{0.97}Na_{0.03}$ZSM-5_27 | 218 | 1495 | 180 | 20 | 1.21 | 74.8 |
| $K_{0.95}Na_{0.05}$ZSM-5_36 | 206 | 782 | 185 | 25 | 1.11 | 31.3 |
| $K_{0.94}Na_{0.06}$ZSM-5_43 | 199 | 672 | 190 | 31 | 1.05 | 21.7 |
| $K_{0.95}Na_{0.05}$ZSM-5_68 | 195 | 395 | 195 | 44 | 1.00 | 9.0 |
| $K_{0.92}Na_{0.08}$ZSM-5_75 | 187 | 115 | 190, 270 | 49 | 0.69 | 2.3 |
| NaZSM-5_27 | 218, 320 | 4112 | 171 | 6 | 1.87 | 685.3 |
| $K_{0.54}Na_{0.46}$ZSM-5_27 | 201, 272 | 3148 | 174 | 10 | 1.56 | 314.8 |
| $K_{0.89}Na_{0.11}$ZSM-5_27 | 230 | 2502 | 177 | 16 | 1.30 | 156.4 |
| $K_{0.97}Na_{0.03}$ZSM-5_27 | 218 | 1495 | 182 | 20 | 1.20 | 74.8 |

[a] The density and strength of acid sites were measured according to the amount of desorbed $NH_3$ molecule and the peak temperature of $NH_3$ desorption, respectively, as shown in Figures 5A, 6A, 7A and 9A. [b] The density and strength of basic sites were measured according to the amount of desorbed $CO_2$ molecule and the peak temperature of $CO_2$ desorption, respectively, as shown in Figures 5B, 6B, 7B and 9B. [c] The ratio of the $NH_3$-TPD-peak temperature to the $CO_2$-TPD-peak temperature. [d] The ratio of surface acidity to basicity.

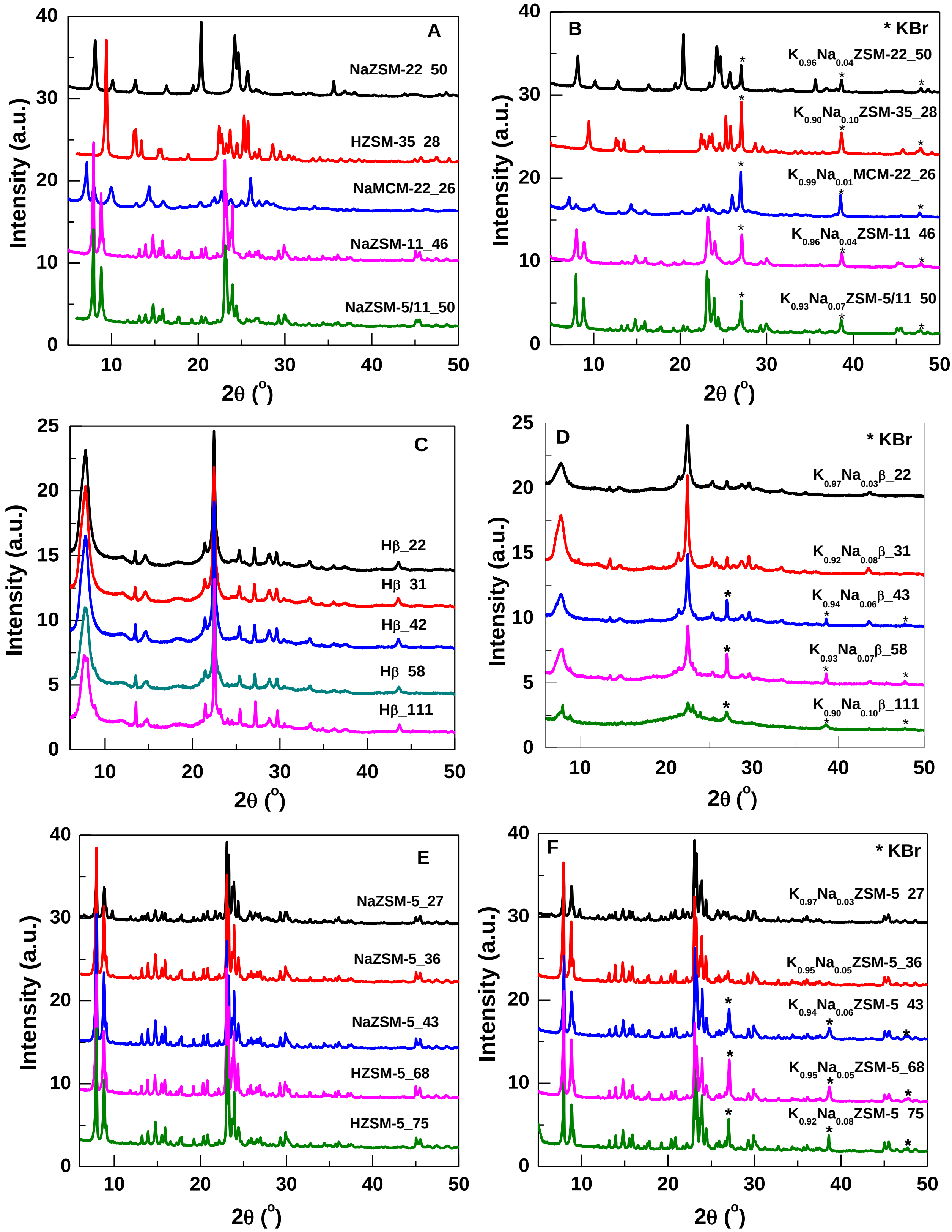


**Figure S1** XRD patterns of the parent zeolites and their derived $K_xNa_{1-x}Z\_y$ samples. The asterisked diffractions denote the presence of crystalline KBr residues.

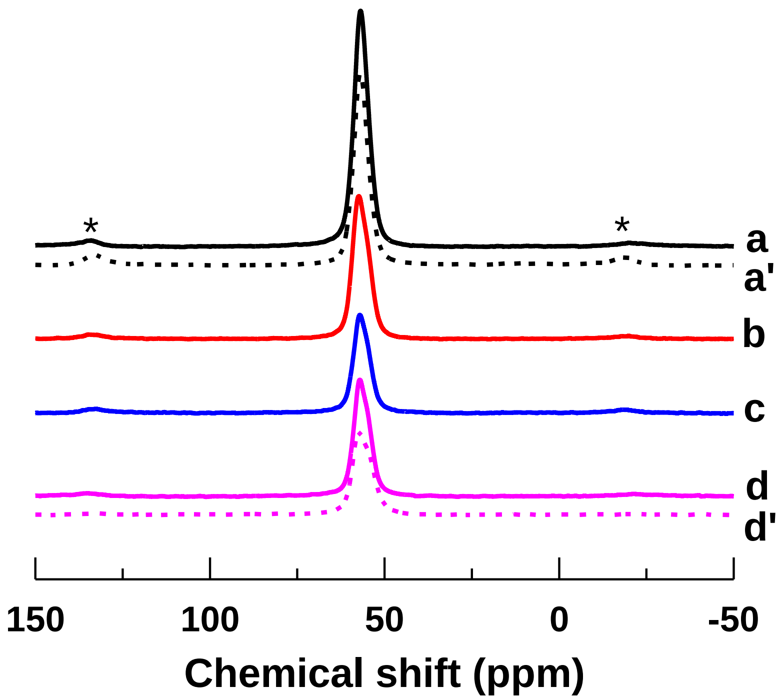


**Figure S2** $^{27}$Al MAS NMR of the fresh $K_{0.97}Na_{0.03}$ZSM-5_27 (a), $K_{0.95}Na_{0.05}$ZSM-5_36 (b), $_{0.94}Na_{0.06}$ZSM-5_43 (c) and $K_{0.95}Na_{0.05}$ZSM-5_68 (d) catalysts. The dashed spectra were obtained with the used $K_{0.97}Na_{0.03}$ZSM-5_27 (a') and $K_{0.95}Na_{0.05}$ZSM-5_68 (d') catalysts. The asterisks denote the spinning sidebands.

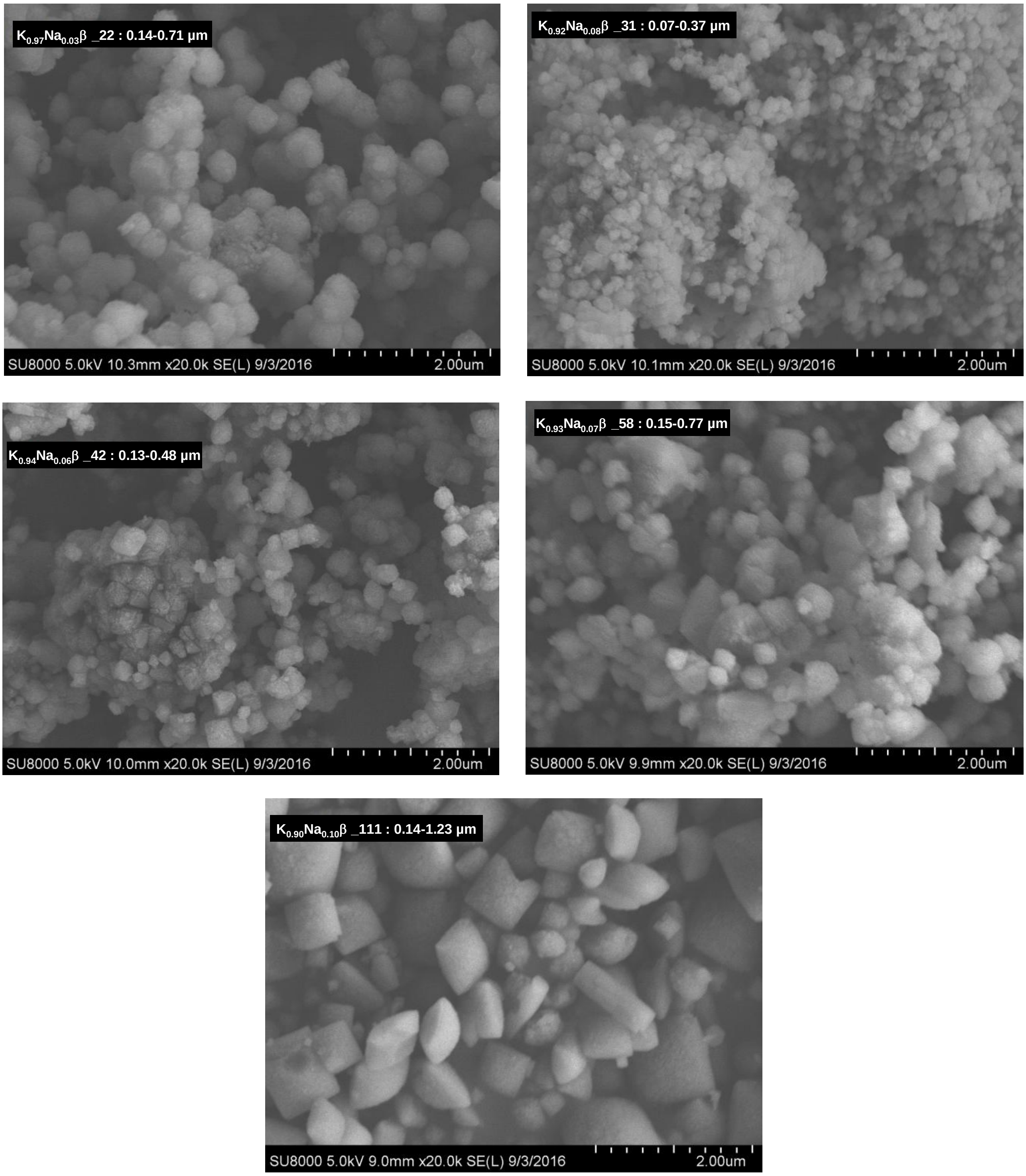


**Figure S3** SEM images of the $K_xNa_{1-x}\beta\_y$ samples with varying $SiO_2/Al_2O_3$. The numbers after the sample code show the particle sizes.

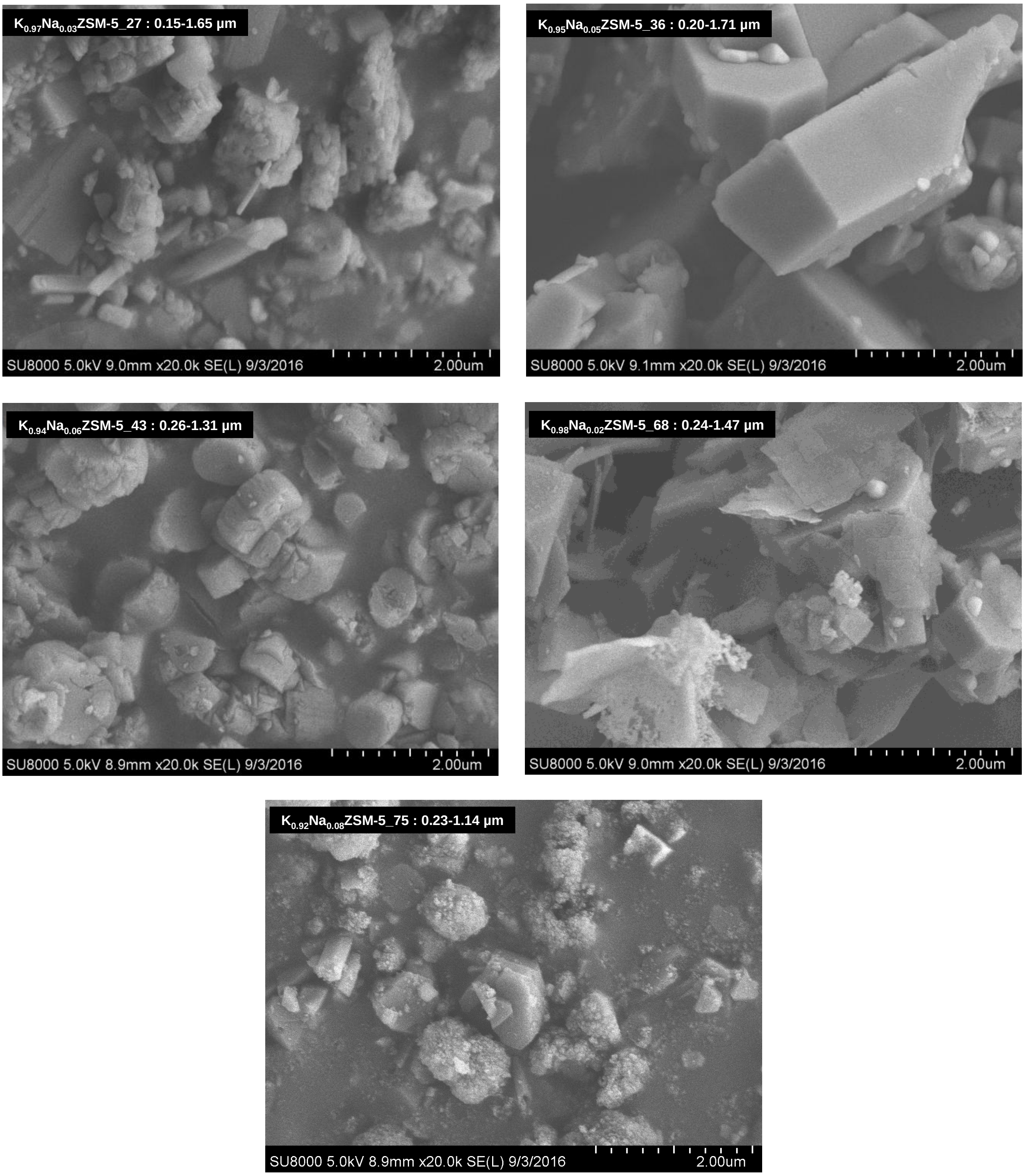


**Figure S4** SEM images of the $K_xNa_{1-x}$ZSM-5_*y* samples with varying $SiO_2/Al_2O_3$. The numbers after the sample code show the particle sizes.

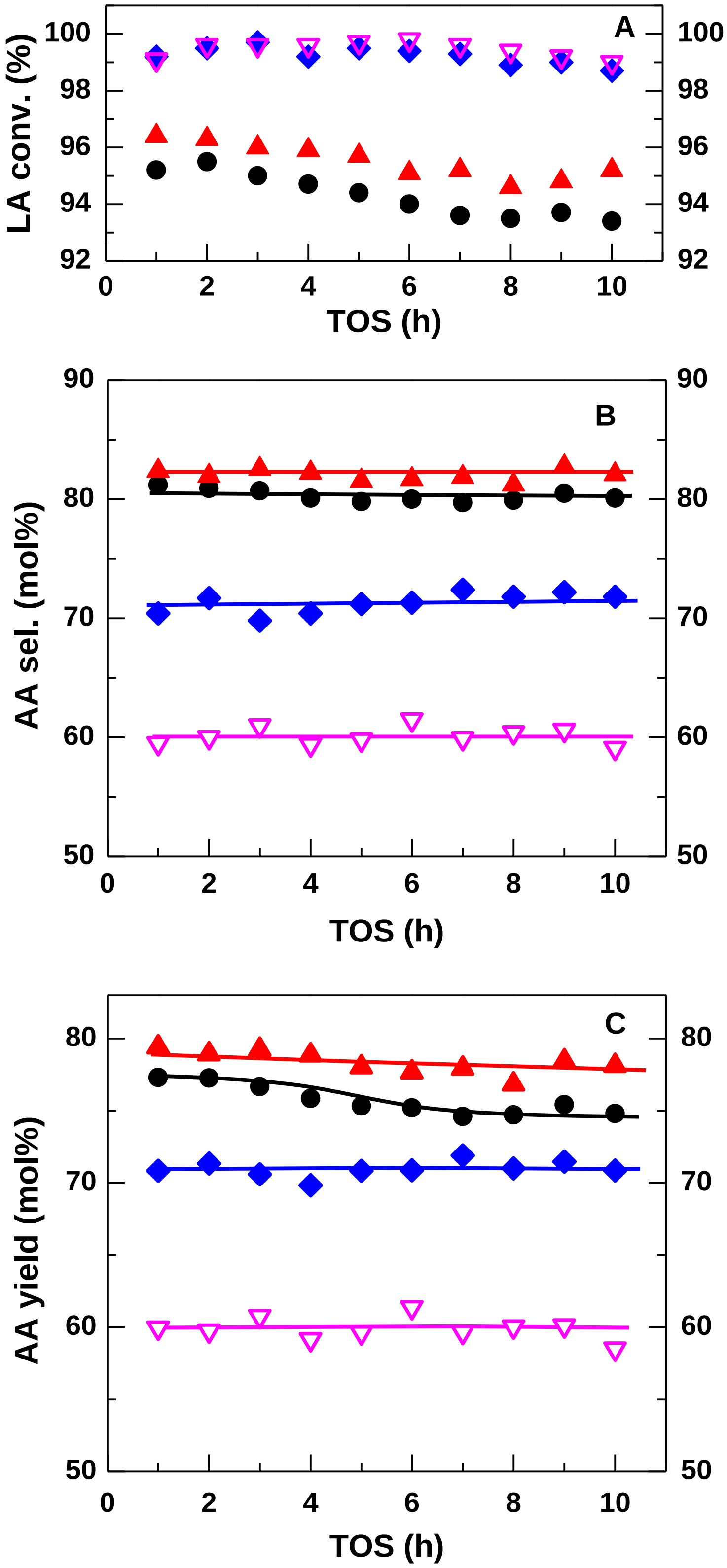


**Figure S5** Catalytic performance by the time courses of LA conversion (A), AA selectivity (B) and AA yield (C) for $K_xNa_{1-x}$ZSM-5_27 of $x$ = 0.97 (●), $x$ = 0.89 (▲), $x$ = 0.54 (◆) and $x$ = 0 (▽).

## Additional References

(1) Baerlocher, Ch.; McCusker, L. B.; Olson, D. H. J. In *Atlas of Zeolite Framework Types*, 6th ed.; Elsevier: Amsterdam, 2007; p 8–213.

(2) Foster, M. D.; Rivin, I.; Treacy, M. M. J.; Friedrichs, O. D. *Microporous Mesoporous Mater.* **2006**, *90*, 32–38.