Supporting Information for:

Mechanochemically-Assisted Solvent-Free and Template-Free Synthesis of Zeolites ZSM-5 and Mordenite

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Contents

Table S1. The starting solid reagents for zeolite synthesis using mechanochemical grinding approach.

Table S2. Additional ICP-OES data on several mechanochemically-assisted zeolite synthesis products.

Figure S1. XRD powder patterns of starting materials used in the synthesis.

Figure S2. XRD of synthesized ZSM-5 samples after calcination (heating at 550 °C under air).

Figure S3. XRD of samples synthesized from a ball-milled reagent mixture of Na₂SiO₃, Al₂(SO₄)₃, and SiO₂ (Na₂O:Al₂O₃:SiO₂ ratio of x:1:40, where x = 3-9).

Figure S4. XRD of samples synthesized from a ball-milled reagent mixture of NaOH, Na₂SiO₃, Al₂(SO₄)₃, and SiO₂ (Na₂O:Al₂O₃:SiO₂ ratio of x:1:40, where x = 4-9).

Figure S5. Nitrogen adsorption-desorption isotherm data for selected sodium form and acid-exchanged ZSM-5 and MOR samples (Na-ZSM-5-5, H-ZSM-5-6, Na-MOR-7, and H-MOR-9).

Figure S6. Transmission IR comparison of acid-exchanged commercial ZSM-5 zeolites to selected and acid-exchanged synthesized zeolite samples (H-ZSM-5-5 and H-ZSM-5-6) before and after exposure to pyridine vapor at 100 °C.

Figure S7. Transmission IR comparison of acid-exchanged commercial MOR zeolites to selected and acid-exchanged synthesized zeolite samples (H-MOR-7 and H-MOR-9) before and after exposure to pyridine vapor at 100 °C.
Table S1. The solid starting materials for zeolite synthesis using mechanochemical grinding pre-reactions between Na$_2$SiO$_3$, Al$_2$(SO$_4$)$_3$, and SiO$_2$ with and without added NaOH.

### SiO$_2$/Al$_2$O$_3$ = 30 without NaOH

| Na$_2$O/Al$_2$O$_3$ | Mole ratio of starting materials |
|-------------------|---------------------------------|
| 3                 | 26.63 SiO$_2$ / 2.99 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 4                 | 25.80 SiO$_2$ / 3.98 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 5                 | 24.13 SiO$_2$ / 5.03 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 6                 | 23.64 SiO$_2$ / 5.88 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 7                 | 22.87 SiO$_2$ / 6.93 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 9                 | 20.64 SiO$_2$ / 8.80 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |

### SiO$_2$/Al$_2$O$_3$ = 30 with NaOH

| Na$_2$O/Al$_2$O$_3$ | Mole ratio of starting materials |
|-------------------|---------------------------------|
| 3                 | 27.96 SiO$_2$ / 1.76 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O / 2.50 NaOH |
| 4                 | 26.80 SiO$_2$ / 2.67 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O / 2.50 NaOH |
| 5                 | 25.97 SiO$_2$ / 3.69 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O / 2.50 NaOH |
| 7                 | 23.80 SiO$_2$ / 5.63 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O / 2.50 NaOH |
| 9                 | 21.64 SiO$_2$ / 7.56 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O / 2.50 NaOH |

### SiO$_2$/Al$_2$O$_3$ = 40 without NaOH

| Na$_2$O/Al$_2$O$_3$ | Mole ratio of starting materials |
|-------------------|---------------------------------|
| 3                 | 36.62 SiO$_2$ / 3.03 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 4                 | 35.12 SiO$_2$ / 3.90 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 5                 | 33.95 SiO$_2$ / 5.02 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 6                 | 33.32 SiO$_2$ / 5.84 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 7                 | 32.29 SiO$_2$ / 6.86 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 8                 | 31.62 SiO$_2$ / 7.88 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
| 9                 | 30.96 SiO$_2$ / 8.83 Na$_2$SiO$_3$•9H$_2$O / 0.98 Al$_2$(SO$_4$)$_3$•18H$_2$O |
Table S2. Additional ICP-OES measurements for some of the synthesized samples at different SiO2/Al2O3 and Na2O/Al2O3 ratios using Na2SiO3, Al2(SO4)3, and SiO2 reagents with and without NaOH addition.

| XRD phase                  | with NaOH | Equivalent reactant Na2O:Al2O3:SiO2 | Product Analysis Na2O:Al2O3:SiO2 |
|---------------------------|-----------|------------------------------------|---------------------------------|
| amorphous + trace ZSM-5   | No        | 4 : 1 : 30                          | 0.5 : 1 : 18                    |
| amorphous + trace ZSM-5   | Yes       | 4 : 1 : 30                          | 0.9 : 1 : 20                    |
| amorphous + trace ZSM-5   | No        | 7 : 1 : 40                          | 2.3 : 1 : 26                    |
| mordenite + trace ZSM-5, quartz | No      | 9 : 1 : 40                          | 5.3 : 1 : 15                    |

1) Equivalent metal oxide molar ratios are calculated based on the initial moles of the starting materials. Estimates of free sodium after reaction between Na2SiO3 and Al2(SO4)3 that use 3 molar equivalents Na2O would result in free sodium and Na2O:Al2O3 ratios would be lower by 3 Na2O (e.g., Na2O/Al2O3 of ratio of 4 becomes 1).

2) The ratios are based on bulk product compositions measured using ICP-OES analysis.
Figure S1. XRD powder patterns of starting materials used in solvent-free, template-free, seed-free zeolite synthesis.
Figure S2. XRD of synthesized ZSM-5 samples after calcination (heating at 550 °C under air). Samples were synthesized with 50 min ball mill grinding at 180 °C for 24 h (black), 48 h (red), and 72 h (blue).
**Figure S3.** XRD of samples synthesized from a reagent mixture of Na$_2$SiO$_3$, Al$_2$(SO$_4$)$_3$, and SiO$_2$ (Na$_2$O:Al$_2$O$_3$:SiO$_2$ ratio of x:1:40, where x = 3-9) that was mechanochemically ground for 50 min, then thermally treated at 180 °C for 48 h, and then washed with water. Weak peaks for Na$_2$O/Al$_2$O$_3$ of 5-7 correspond to ZSM-5 zeolite, while product for ratio of 8 is dense quartz, and peaks for ratio of 9 are mixed mordenite, ZSM-5, and quartz.
Figure S4. XRD of samples synthesized from a reagent mixture of NaOH, Na₂SiO₃, Al₂(SO₄)₃, and SiO₂ (Na₂O:Al₂O₃:SiO₂ ratio of x:1:40, where x = 4-9) that was mechanochemically ground for 50 min, then thermally treated at 180 °C for 48 h, and then washed with water. The peaks for Na₂O/Al₂O₃ of 5-8 correspond to ZSM-5 zeolite, while product for ratio of 9 is mainly dense quartz.
Figure S5. Nitrogen adsorption-desorption isotherm data for as-synthesized ZSM-5-5 sodium form (top left), and acid-exchanged H-ZSM-5-6 (top right) and for as-synthesized MOR-7 sodium form (bottom left) and acid-exchanged H-MOR-9 (bottom right). As-synthesized zeolites were subjected to maximum temperature of 300 °C during BET evacuation and acid-exchanged samples were heated to 550 °C during their synthesis. The seven-point BET surface area results for these samples are shown in Tables 2 and 3.
Pyridine surface reaction studies on acid-exchanged zeolite samples. This analysis was performed based on literature procedures from these references:

Barzetti, T.; Selli, E.; Moscotti, D.; Forni, L. Pyridine and ammonia as probes for FTIR analysis of solid acid catalysts. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1401-1407.

Connerton, J.; Joyner, R. W.; Padley, M. B. Characterisation of the Acidity of Well Defined Cu-ZSM-5 Catalysts using Pyridine as a Probe Molecule. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1841-1844.

Open glass vials with 10 - 15 mg of selected acid-exchanged synthesized and commercial zeolites were placed in a glass reactor that pre-heated to 100 °C. The sample reactor was evacuated at 100 °C for 1 hr then refilled with N₂ gas. Reagent grade pyridine (EM sciences, dried over NaOH pellets) was placed in an Erlenmeyer flask, capped with a rubber septum and degassed with an N₂ purge using a steel needle. A steel canula was used to connect the pyridine flask to the glass reactor with the samples at 100 °C and a flow of pyridine saturated N₂ was transferred into the flask through a septum. A bleed needle in the septum insured that the pyridine atmosphere above the heated zeolite samples contained sufficient available pyridine vapor. The pyridine flow was maintained for 1 hr followed by a N₂ flush and reactor/sample evacuation for 15 minutes at 100 °C to remove weakly bound pyridine. The reactor was cooled to room temperature under evacuation and then transferred into an argon-filled glovebox.

The pyridine exposed zeolites were examined by transmission IR using KBr pellets. A mixture of 1-2 mg of zeolite in 50 mg of KBr was ground to form into pressed pellets. Pellets were typically 20-30 mg in total mass and were formed in the glovebox and protected in sealed plastic bag prior to analysis. A Nicolet Nexus 670 FTIR was used with 64 scans at 2 cm⁻¹ resolution. The system was purged with N₂ for at least 5 minutes before taking each spectrum. Comparison spectra for acid-exchanged samples before pyridine exposure were obtained with 64 scans at 2 cm⁻¹ resolution under a dry air system purge using pellets prepared under ambient air conditions.
Figure S6. Transmission IR (KBr pellets) comparison of acid-exchanged commercial ZSM-5 with synthesized H-ZSM-5-5 and H-ZSM-5-6 samples before pyridine reaction (top graph) and after pyridine exposure (bottom graph). The major adsorbed water peak in acid-exchanged samples before pyridine exposure is at 1630-1632 cm$^{-1}$. Pyridine exposed spectra are plotted to highlight the region containing diagnostic peaks for adsorbed pyridine on Lewis acid sites (1621, 1576, 1455 cm$^{-1}$), molecularly adsorbed pyridine (1599, 1442 cm$^{-1}$), pyridinium (pyH$^+$, Brønsted sites - 1635, 1545 cm$^{-1}$), and overlapping pyridine/pyridinium (1490 cm$^{-1}$) vibrational bands (after Barzetti et. al. J. Chem. Soc., Faraday Trans. 1996, 92, 1401 and Connerton et al. J. Chem. Soc. Faraday Trans. 1995, 91, 1841).
Figure S7. Transmission IR (KBr pellets) comparison of acid-exchanged commercial MOR with synthesized H-MOR-7 and H-MOR-9 samples before pyridine reaction (top graph) and after pyridine exposure (bottom graph). The major adsorbed water peak in acid-exchanged samples before pyridine exposure is at 1630-1632 cm$^{-1}$. Pyridine exposed spectra are plotted to highlight the region containing diagnostic peaks for adsorbed pyridine on Lewis acid sites (1621, 1576, 1455 cm$^{-1}$), molecularly adsorbed pyridine (1599, 1442 cm$^{-1}$), pyridinium (pyH$^+$, Brønsted sites - 1635, 1545 cm$^{-1}$), and overlapping pyridine/pyridinium (1490 cm$^{-1}$) vibrational bands (after Barzetti et al. *J. Chem. Soc., Faraday Trans.* 1996, 92, 1401 and Connerton et al. *J. Chem. Soc. Faraday Trans.* 1995, 91, 1841).