Supporting information

Preparation and Characterization of Silicalite-1 Zeolites with High Manganese Content from Mechanochemically Pretreated Reactants

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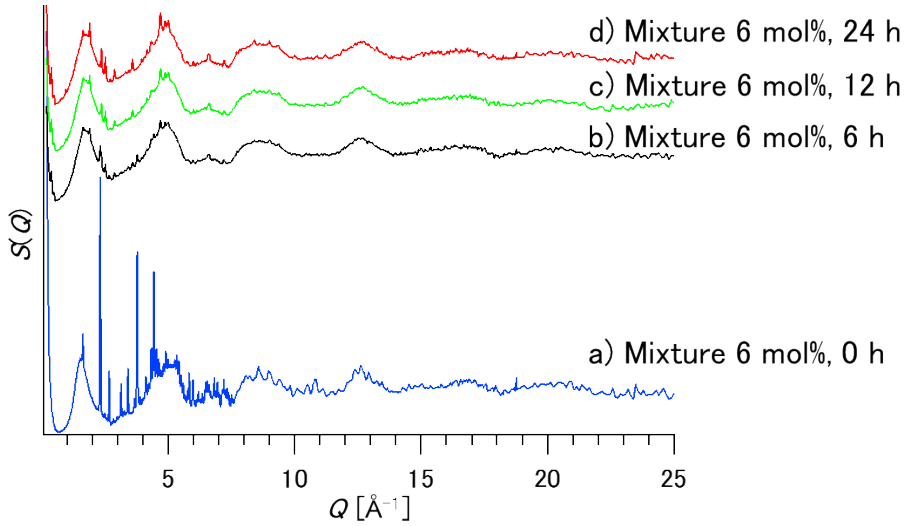

Figure S1. Total structure factor $S(Q)$ of Mn_2O_3/fumed silica mixtures during mechanochemical treatment. a) Initial 6 mol% Mn mixture, b) 6 mol% Mn mixture after 6 h, c) 6 mol% Mn mixture after12 h, and d) 6 mol% Mn mixture after 24 h.

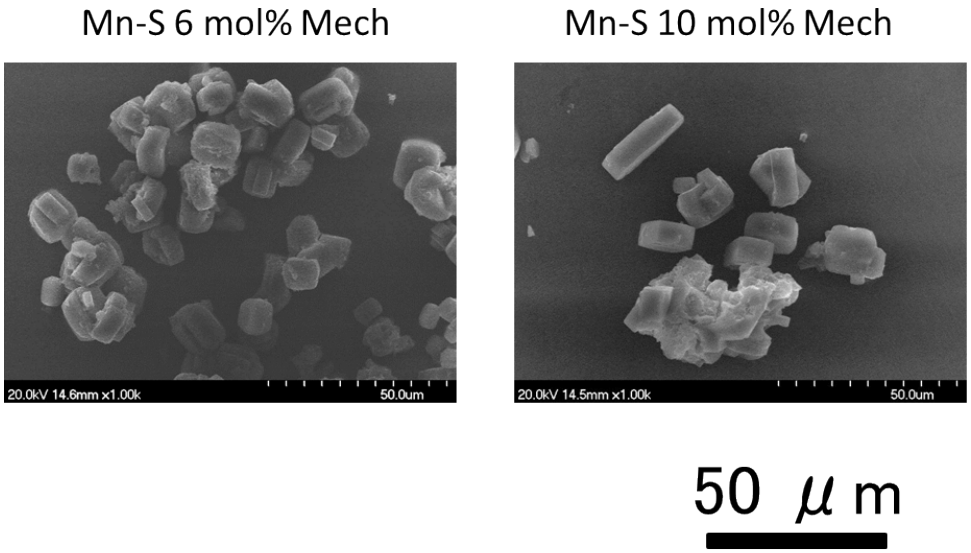

Figure S2. SEM images of Mn-Silicalite-1 zeolite samples. (Left) Mn-S 6 mol% Mech and (Right) Mn-S 10 mol% Mech.

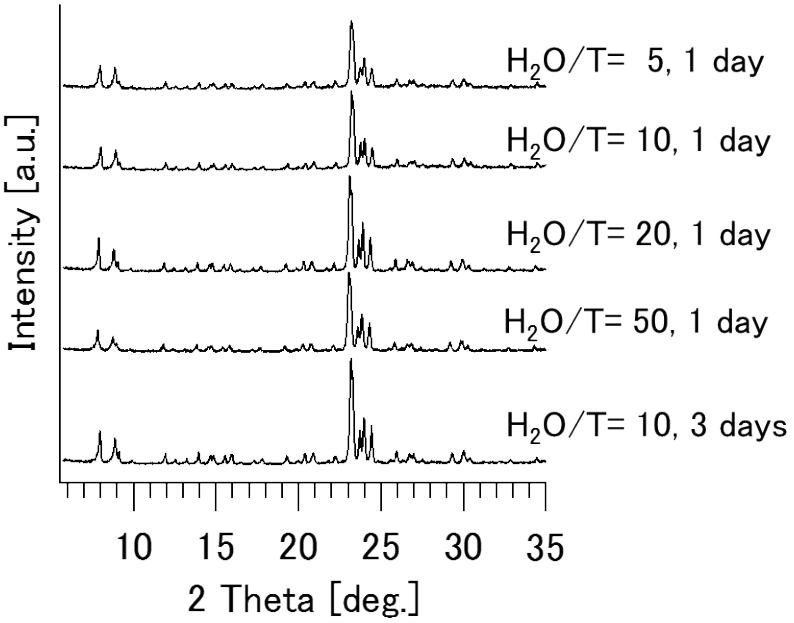

Figure S3. XRD patterns of Mn-S samples synthesized using Mn-Si mixed oxide composite with Mn/(Mn+Si) = 10 mol% at various synthetic periods and H_2O/T ratio.

It is clarified by comparing the crystallinity of Mn-S samples synthesized in 1 day and 3 days using H_2O/T= 10 that one day treatment was not enough for the complete crystallization of Mn silicalite-1 from Mn-Si mixed oxide composite with Mn/(Mn+Si) = 10 mol%. The effect of H_2O/T on the crystallization kinetics was also investigated (H_2O/T = 5, 10, 20, and 50). The amount of water has little effect on the crystallization kinetics because the crystallization occurs via a solid transformation mechanism, unlike solution-mediated crystallizations. This crystallization mechanism can explain the successful incorporation of manganese into the framework.

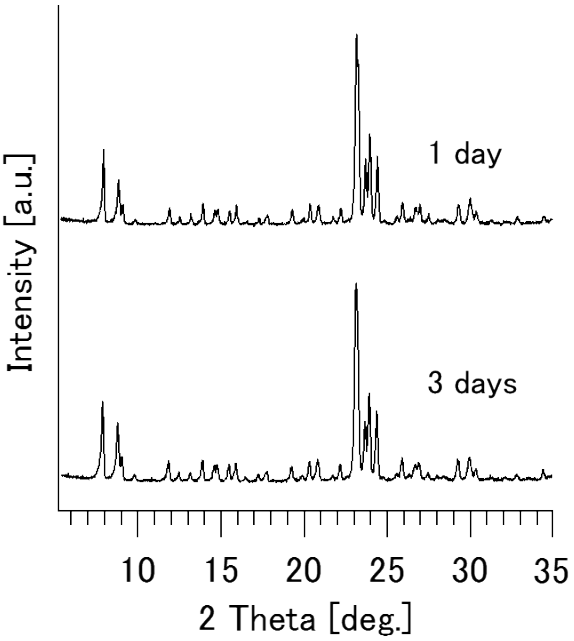

Figure S4. XRD patterns of Mn-S samples synthesized using Mn-Si mixed oxide composite with Mn/(Mn+Si) = 6 mol% at synthesis periods of 1 day and 3 days.

From Figure S4, complete crystallization has proceeded in one day when Mn-Si mixed oxide composite with Mn/(Mn+Si) = 6 mol% was used. This is in contrary with the case when using Mn-Si mixed oxide composite with Mn/(Mn+Si) = 10 mol% shown in Figure S3.

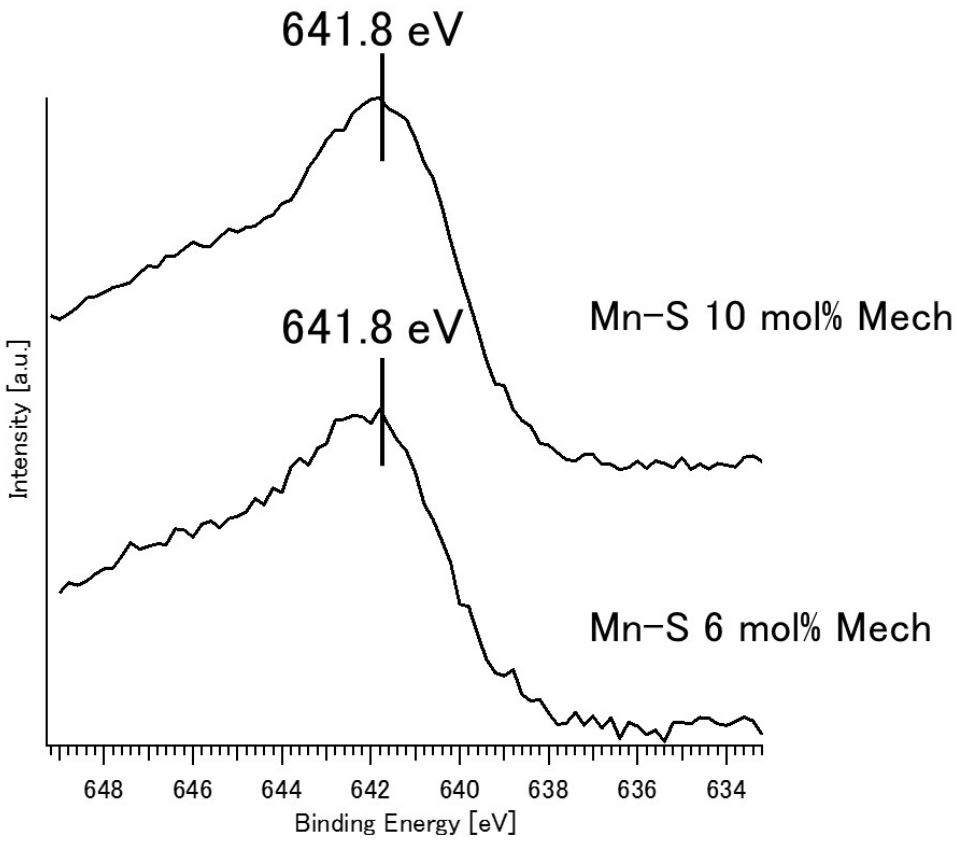

Figure S5. XPS results of Mn-Silicalite-1 zeolite samples.

The signals observed at 641.8 eV are attributed to the Mn^{3+}. According to literature [H. Nesbitt, D. Banerjee, *Am. Mineral.*, 1998, **83,** 305–315.], signals from Mn^{2+} are present at 640.8±0.3 eV, while signals from Mn^{3+} are present around 641.8±0.1 eV.