Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Ethane Dehydrogenation over Manganese Oxides Supported on ZSM-5 Zeolites

Jian Pan and Raul F. Lobo*

J. Pan, Prof. R. F. Lobo
Center for Catalytic Science and Technology
Department of Chemical and Biomolecular Engineering
University of Delaware
Newark, Delaware, 19716, United States
E-mail: lobo@udel.edu

Table S1. Mn-based catalysts synthesized in this report and their contents.

	Si/Al ratio	Mn loading (wt. %)	Mn speciation
Mn-ZSM5, IWI	12	0	No Mn
	12	2.1	MnO_x, $(MnOH)^+$
	12	3.4	MnO_x, $(MnOH)^+$
	12	4.6	MnO_x, $(MnOH)^+$
	12	6.4	MnO_x, $(MnOH)^+$
	12	9.2	MnO_x, $(MnOH)^+$
	12	11.7	MnO_x, $(MnOH)^+$
	25	3.4	MnO_x, $(MnOH)^+$
	40	3.4	MnO_x, $(MnOH)^+$
Mn-ZSM5, IE	12	4.6	$(MnOH)^+$
Mn-Si-ZSM5, IWI	-	4.6	MnO_x

Table S2. Reaction rates and selectivity of EDH over Mn-ZSM5 with different conditions.

	Mn-ZSM5, IE	Mn-ZSM5, IWI	Mn-Si-ZSM5, IWI
Si/Al ratio	12	12	-
Mn loading (wt.%)	4.6	4.6	4.6
Reaction rate (mmol/g_{cat}/hr)	1.02	11.98	2.72
Selectivity (%)	94.71	98.72	94.94

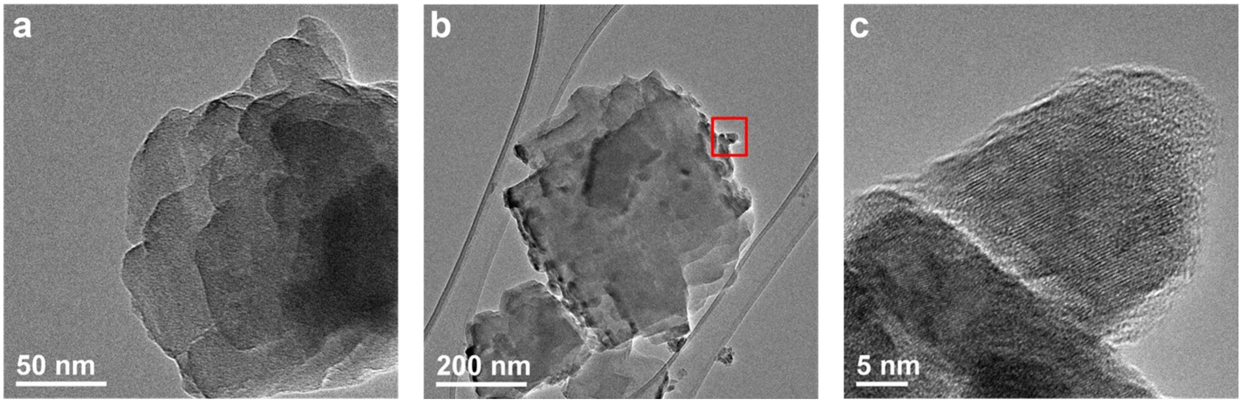

Fig. S1 High resolution TEM images of a) H-ZSM5 and b) Mn-ZSM5; c) manganese oxide particle on the zeolite surface (enlarged image of the area highlighted with red rectangular in b)).

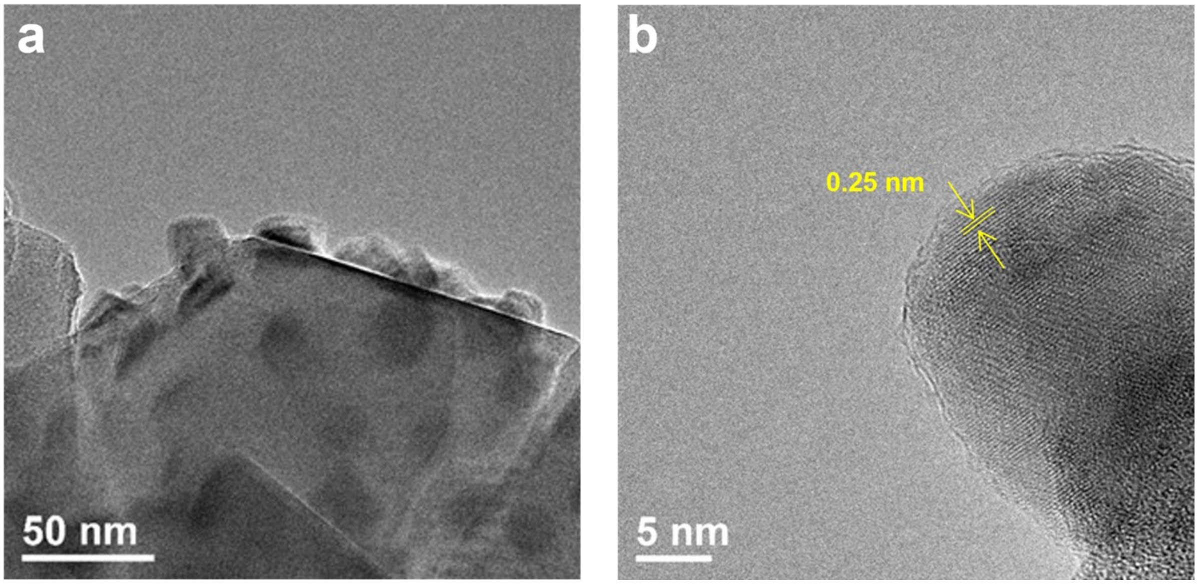

Fig. S2 TEM images of Mn-ZSM5 after EDH in a) lower and b) higher resolution. Si/Al = 12 and Mn loading: 6.4 wt.%.

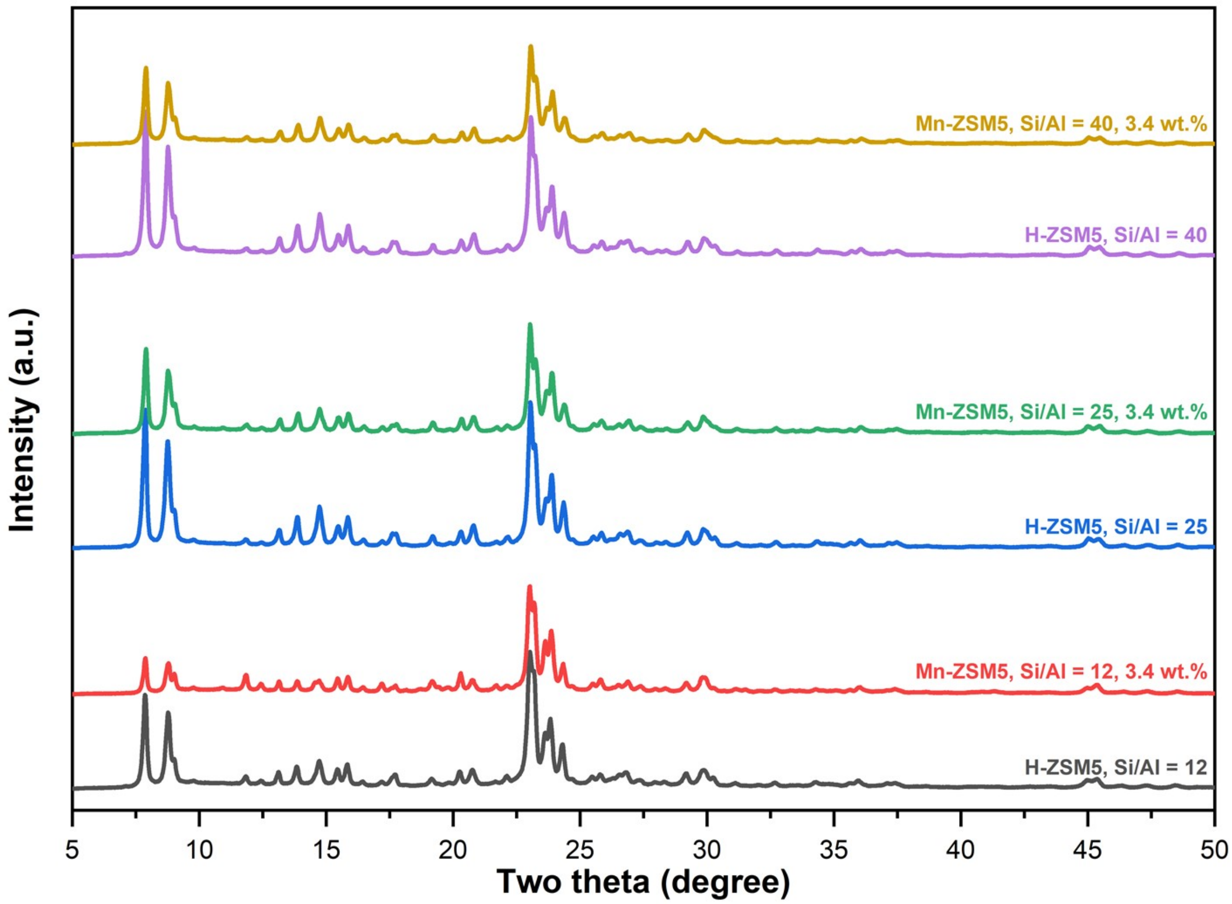

Fig. S3 XRD patterns of Mn-ZSM5 samples with different Si/Al ratios of 12, 25, and 40 but same Mn loading of 3.4 wt.%.

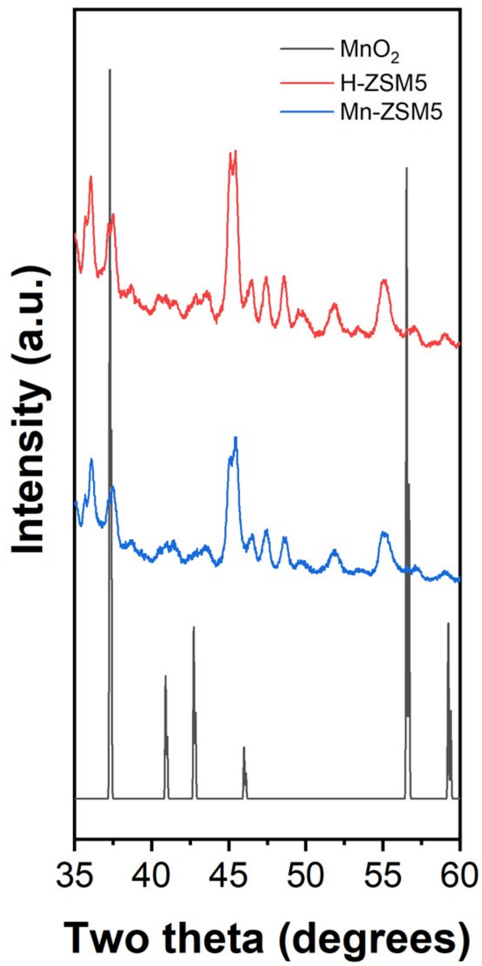

Fig. S4 XRD patterns of H-ZSM5, Mn-ZSM5 samples (Si/Al = 12, Mn loading: 4.6 wt.%), and MnO_2.

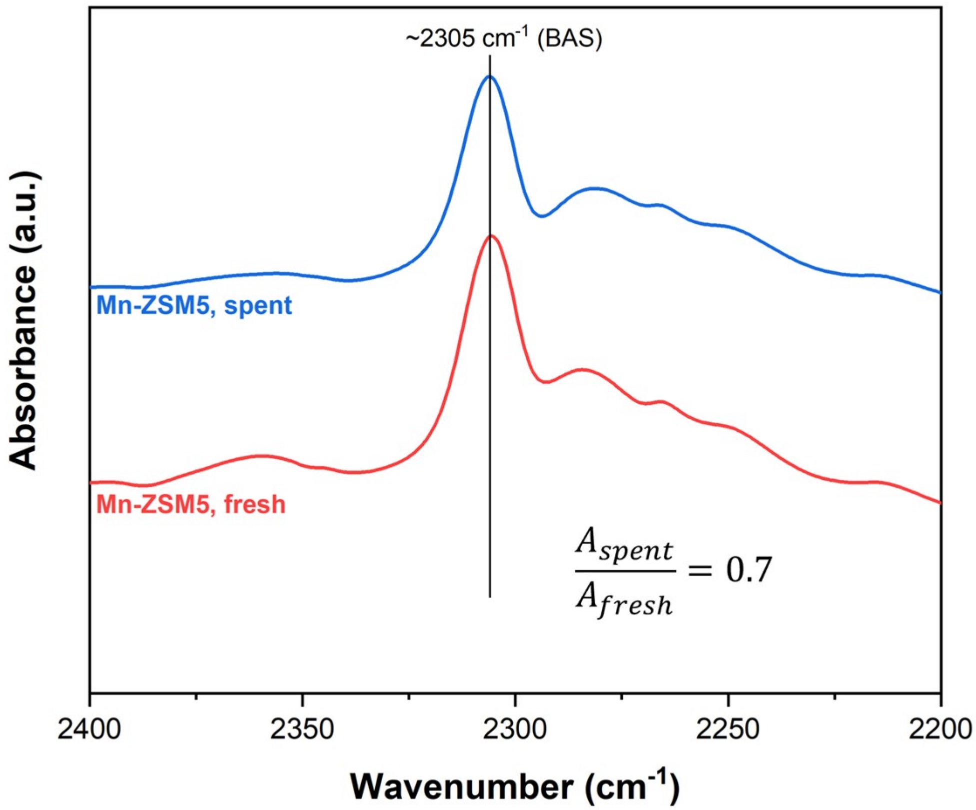

Fig. S5 *In situ* DRIFTS spectra of Mn-ZSM5 before and after EDH at 50 °C saturated with CD_3CN. The presence of BAS and its decrease in concentration after EDH were observed. The BAS peak area of each sample was calculated by integration of the single peak at 2305 cm^{-1}. Peaks overlap was not considered.

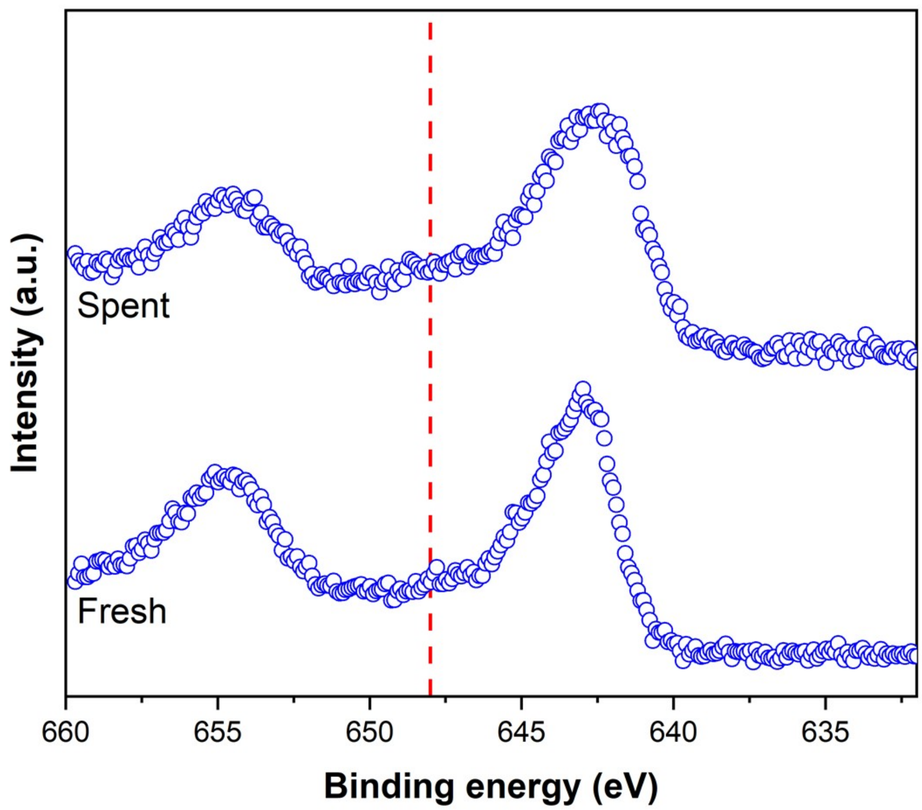

Fig. S6 Mn 2p scan spectra from XPS of Mn-ZSM5 before and after EDH.

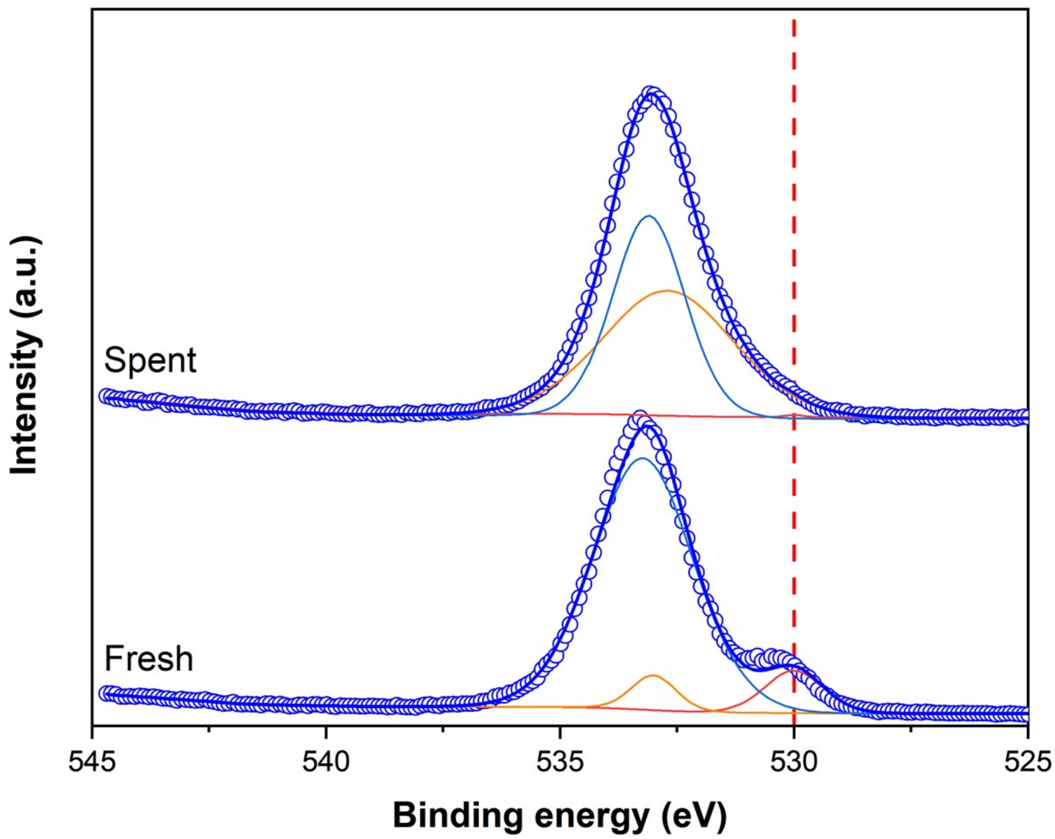

Fig. S7 O 1s scan spectra from XPS of Mn-ZSM5 before and after EDH.

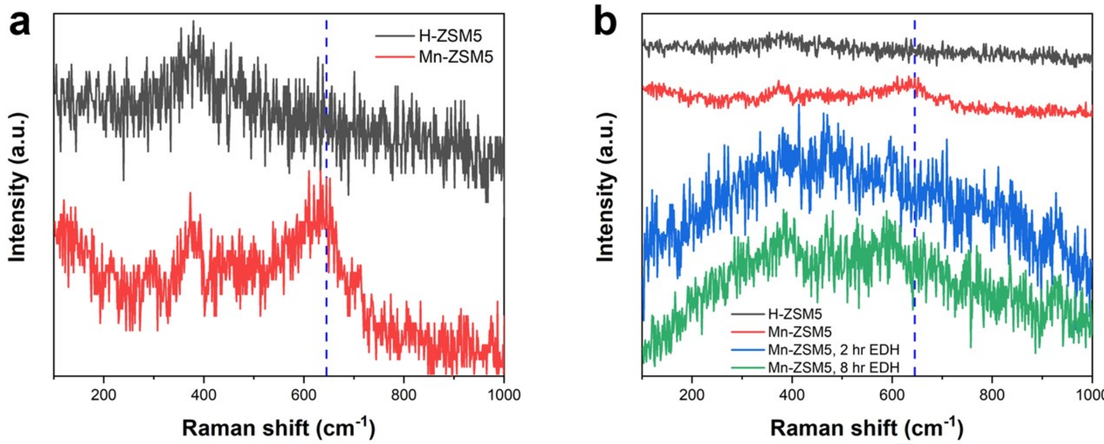

Fig. S8 Comparison of Raman spectra between a) fresh H-ZSM5 and Mn-ZSM5; b) Mn-ZSM5 before and after EDH for two or eight hours.

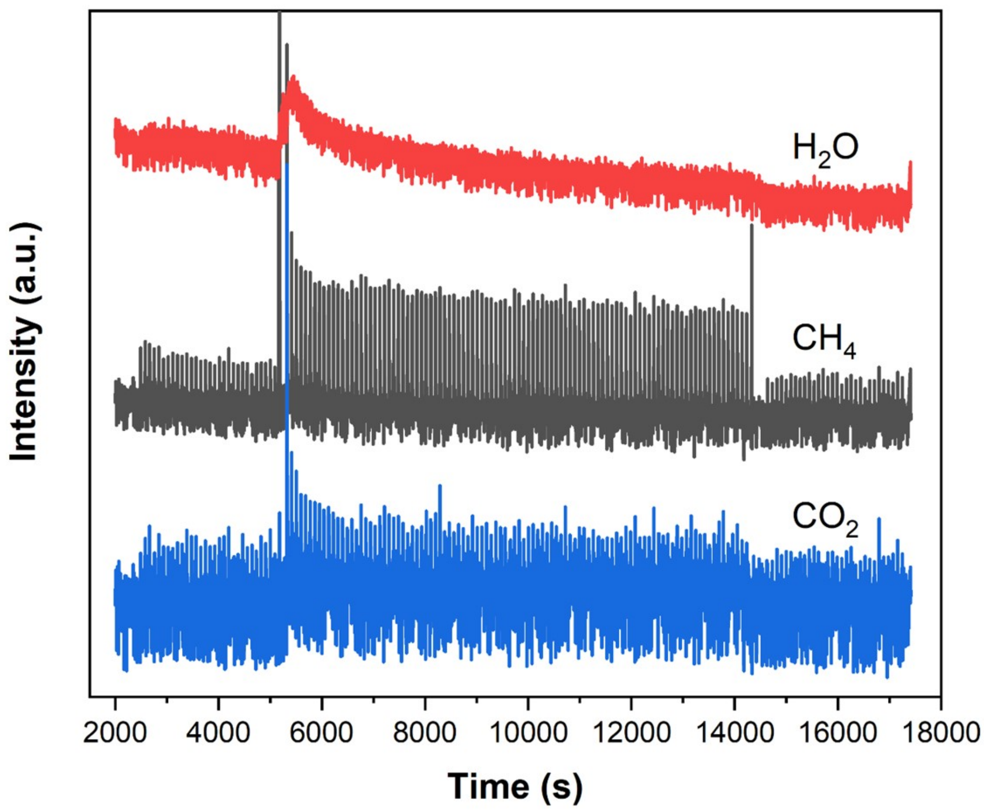

Fig. S9 Production of H_2O, CH_4, and CO_2 during EDH over Mn-ZSM5 in an inhouse-built pulse reactor. Pulses of 10% C_2H_6/Ar were introduced into the reactor every 1.5 minutes via a computer-controlled six-way valve with a 0.67 mL loop at 600 °C.

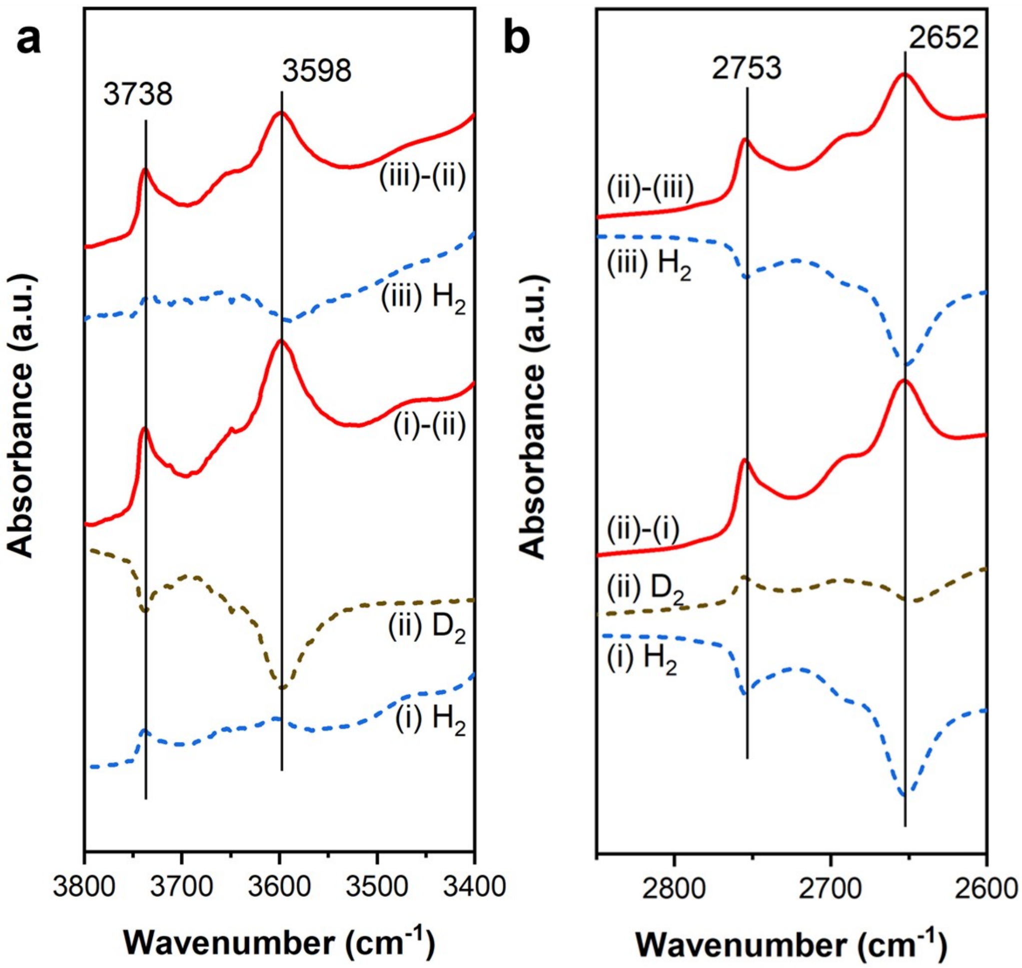

Fig. S10 *In situ* DRIFTS spectra of H-ZSM5 feeding H_2 and D_2 at a) higher and b) lower spectral regions.

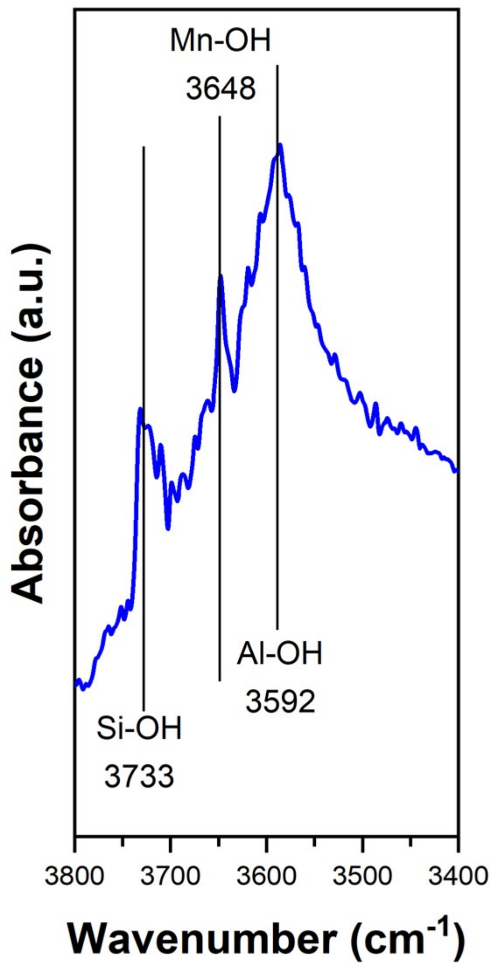

Fig. S11 DRIFTS spectra of Mn-ZSM5 prepared by ion-exchange after EDH and purging with Ar.

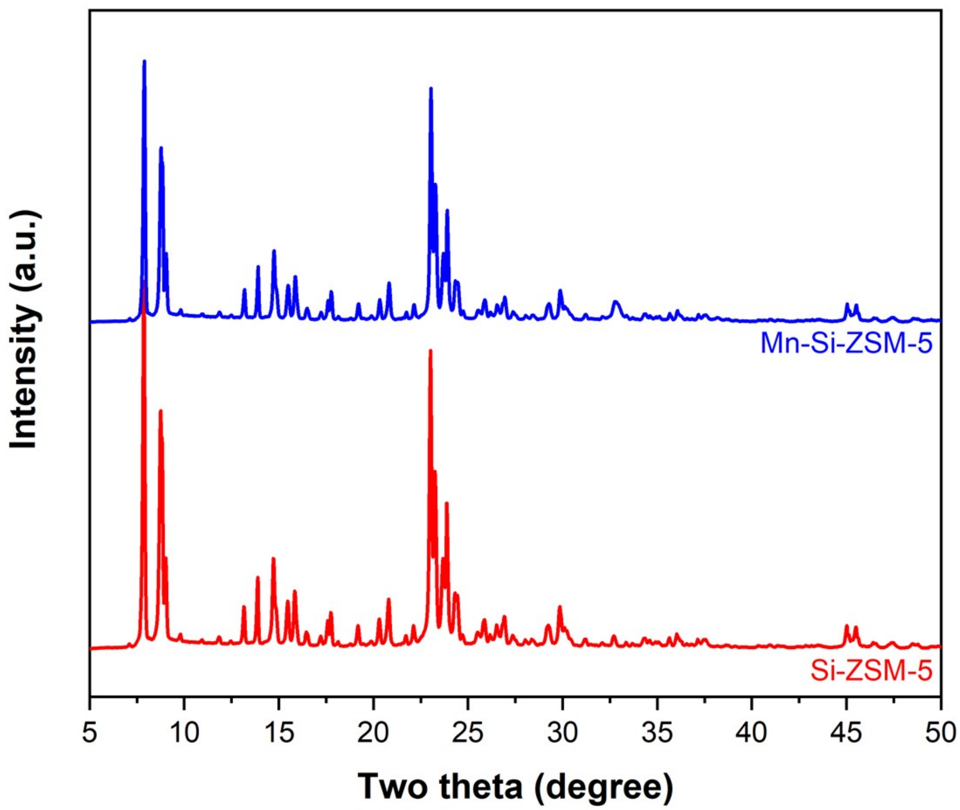

Fig. S12 XRD pattern of Si-ZSM-5 samples and the Mn-Si-ZSM-5 samples prepared using the same zeolite.

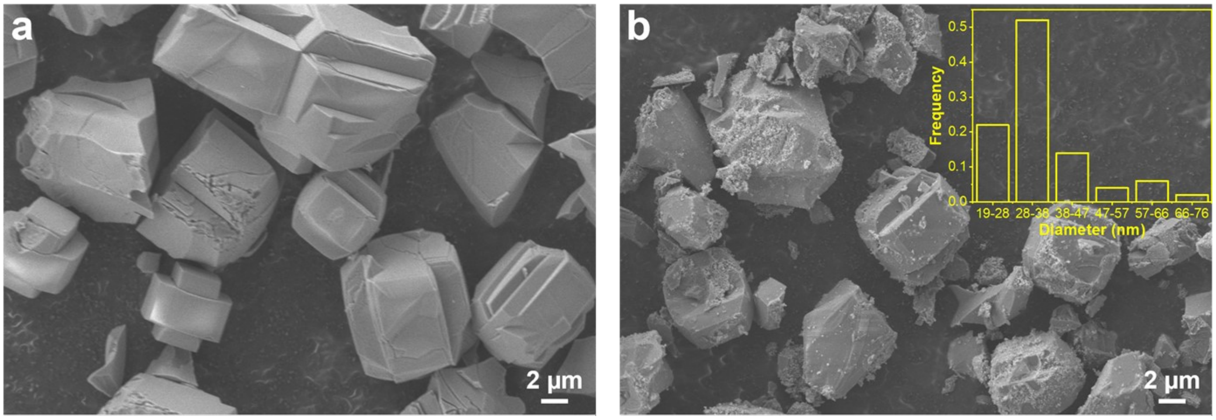

Fig. S13 SEM images of fresh a) Si-ZSM-5 and b) Mn-Si-ZSM-5 samples (inset: histogram of particle size distribution). The average particle size is 35 nm.

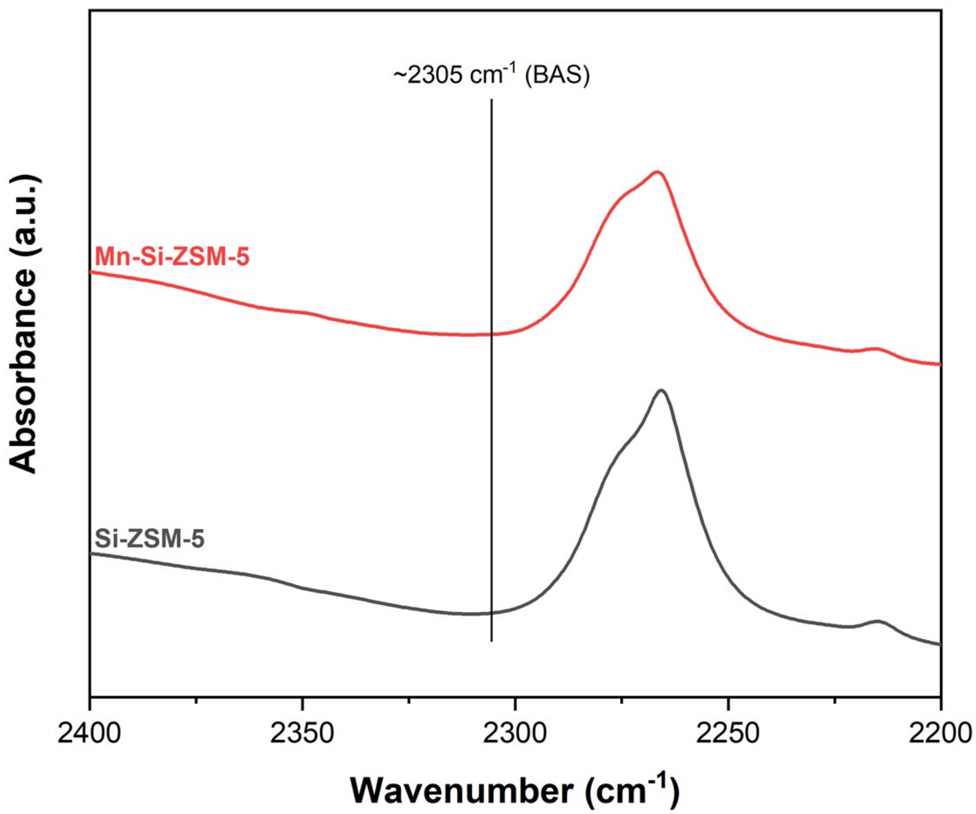

Fig. S14 *In situ* DRIFTS spectra of Si-ZSM-5 and Mn-Si-ZSM-5 at 50 °C saturated with CD_3CN. No BAS were observed as expected due to the absence of framework Al sites.

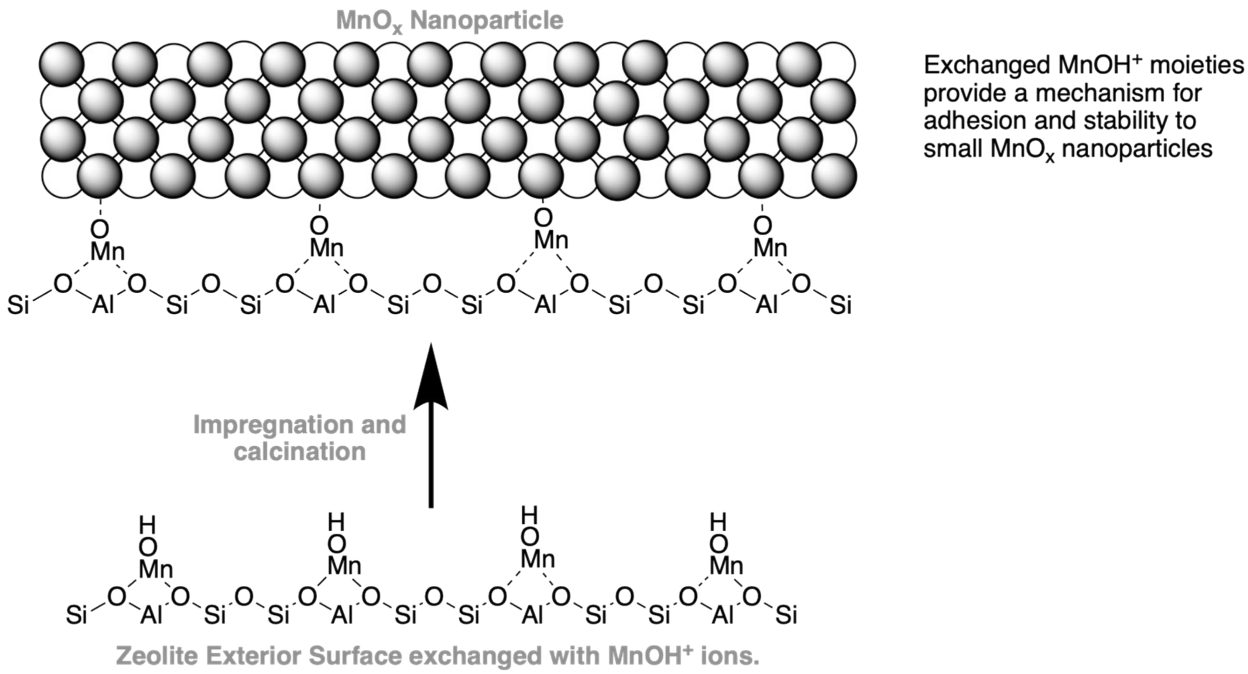

Fig. S15 Schematic of the process of MnO$_x$ particles stabilization with (Mn-OH)$^+$ groups in Mn-ZSM5.

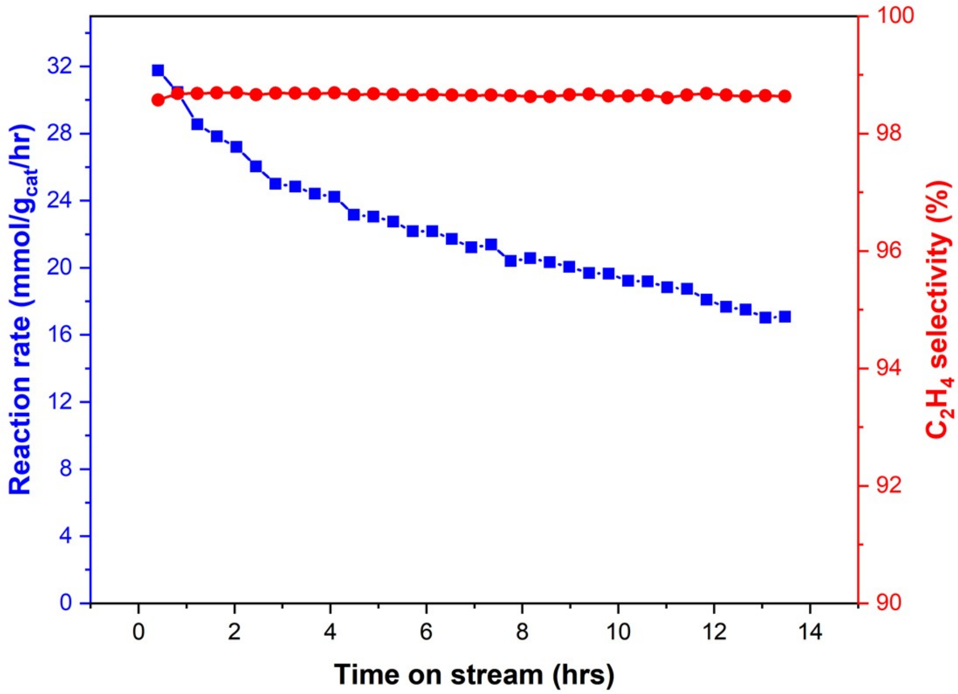

Fig. S16 Specific reaction rate and C_2H_4 selectivity of EDH over Mn-ZSM5 (50 mg, Si/Al = 12, Mn loading = 6.4 wt.%). Reaction conditions: 25 mL/min of 20% C_2H_6/He, 600 °C.

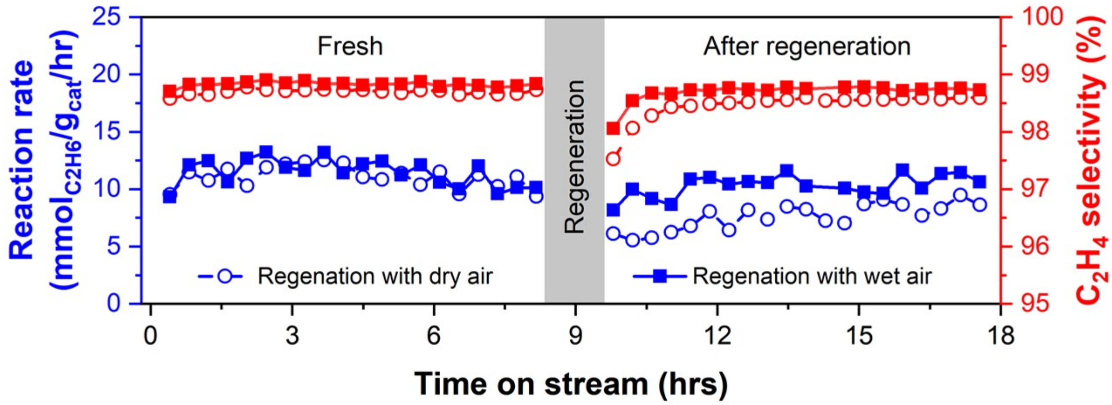

Fig. S17 Reaction and regeneration of Mn-ZSM5 catalysts (Si/Al = 12, Mn loading = 3.4 wt.%) with either dry air or wet air (3% steam). Reaction conditions: 50 mL/min of 10% C_2H_6/He, 600 °C. Regeneration conditions: feeding either dry air or wet air (3% steam) into the reactor at 600 °C for two hours, followed by purging with 50 mL/min Ar for one hour.