

Electronic Supplementary Information (ESI)

Regulating the location of framework aluminum in mordenite for the carbonylation of dimethyl ether

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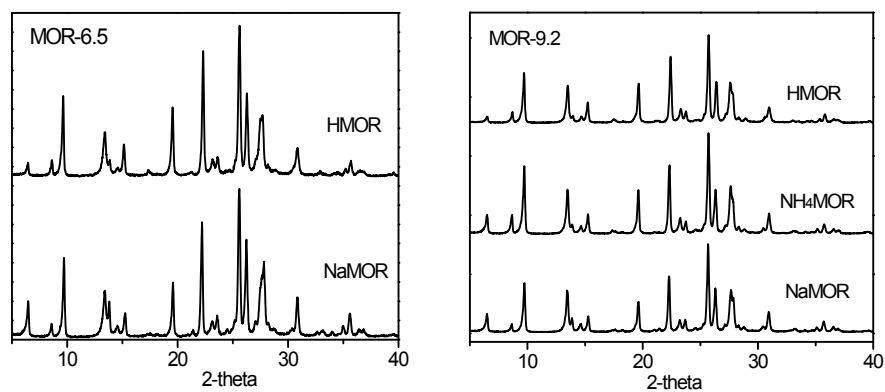


Fig. S1 XRD patterns of the mordenites with varied SARs.

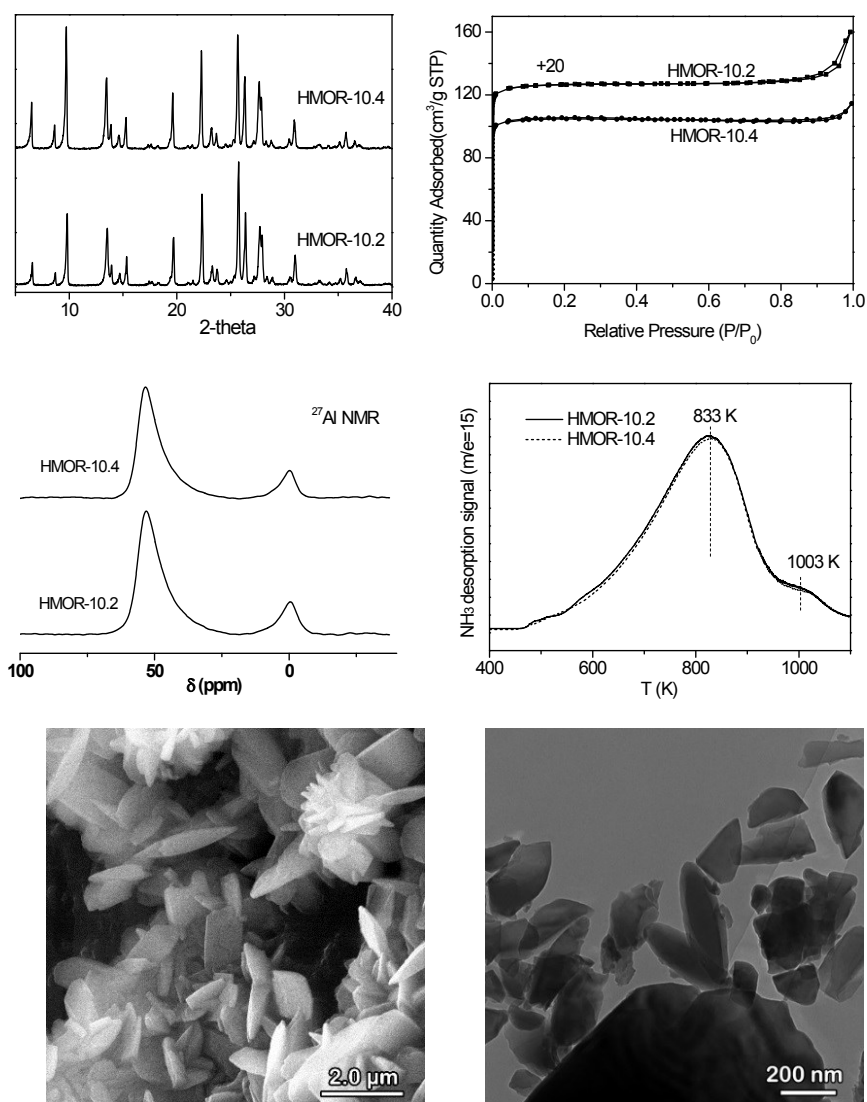


Fig. S2 XRD, N_2 adsorption-desorption isotherms, ^{27}Al NMR spectra, NH_3 -TPD profiles of the HMOR-10.4 sample and SEM/TEM images of the corresponding NaMOR-10.4 sample.

Another sample with a framework SAR of 10.4 (HMOR-10.4) was prepared by decreasing the Al content in the raw gel to a Si/Al ratio of 20. Structural characterizations indicated that the textural and chemical properties resembled ~~those that~~ of the HMOR-10.2 sample (Table S1 & Fig. S2). It consisted of irregular spindle-like plates with an elongated diameter of about 1 μm and a short diameter around 0.5 μm , but rectangular nanosheets became more significantly than that in the MOR-10.2 sample. The MOR-10.4 sample exhibited a typical type-I isotherm, evidencing the exclusive presence of micropores with a pore volume of 0.159 cm^3/g . The BET surface area was 303 m^2/g in which the micropore area of 293 m^2/g .

Table S1 Framework properties and the amounts of Brønsted acid sites of the HMOR samples

Sample	Raw gel		^{29}Si NMR			Si/Al		Brønsted acid sites (mmol/g)	
	Si/Al ratio	^{27}Al NMR	Si(0Al) %	Si(1Al) %	Si(2Al) %	^{29}Si NMR	^{29}Si NMR	NH_3 -TPD	
HMOR-10.2	15	15.4	63.2	34.5	2.3	10.2	1.29	1.25	
HMOR-10.4	20	15.3	63.7	34.0	2.2	10.4	1.27	1.20	

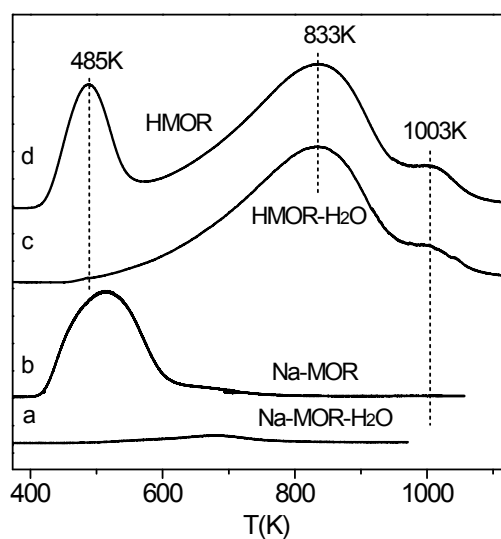


Fig. S3 NH_3 -TPD profiles of NaMOR-9.2 and HMOR-9.2. (a) NaMOR-9.2 with H_2O purging at 413 K, (b) NaMOR-9.2 without H_2O purging, (c) HMOR-9.2 with H_2O purging at 413 K, (d) HMOR-9.2 without H_2O purging after NH_3 adsorption.

On the NaMOR-9.2, only weakly adsorbed ammonia at around 485 K was observed, which vanished upon sweeping with water vapor at 413 K. On the HMOR-9.2, two distinct ammonia desorption peaks appeared at 485 and 833 K. Sweeping with water vapor relieved the weakly adsorbed signal, leaving

only the high-temperature peak relating to the strongly adsorbed NH_3 . By comparing the profiles of NaMOR and HMOR, it was inferred that the high-temperature peak was related to the exchangeable H^+ , namely the Brønsted acid sites, while the low temperature peak was related with the physically adsorbed NH_3 on $\text{NH}_4^+/\text{Na}^+$ cations (N. Katada & M. Niwa, Analysis of acidic properties of zeolitic and non-zeolitic solid acid catalysts using temperature-programmed desorption of ammonia, *Catal. Surv. Asia*, 2004 **8(3)** 161-170). Therefore, NH_3 -TPD, together with water sweeping, is workable for quantitatively determining the Brønsted acid sites on HMORs.

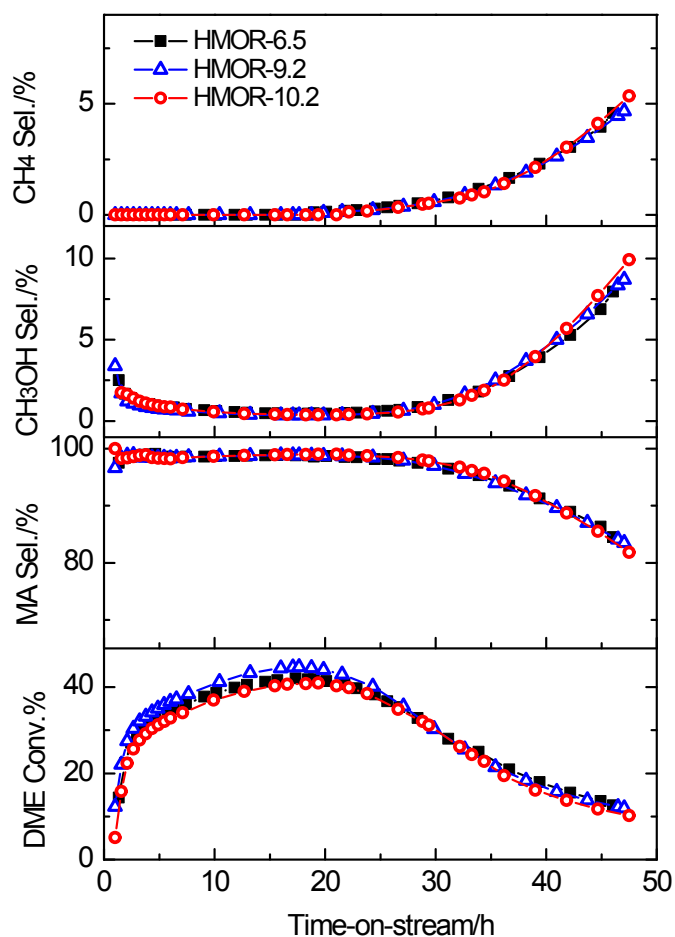


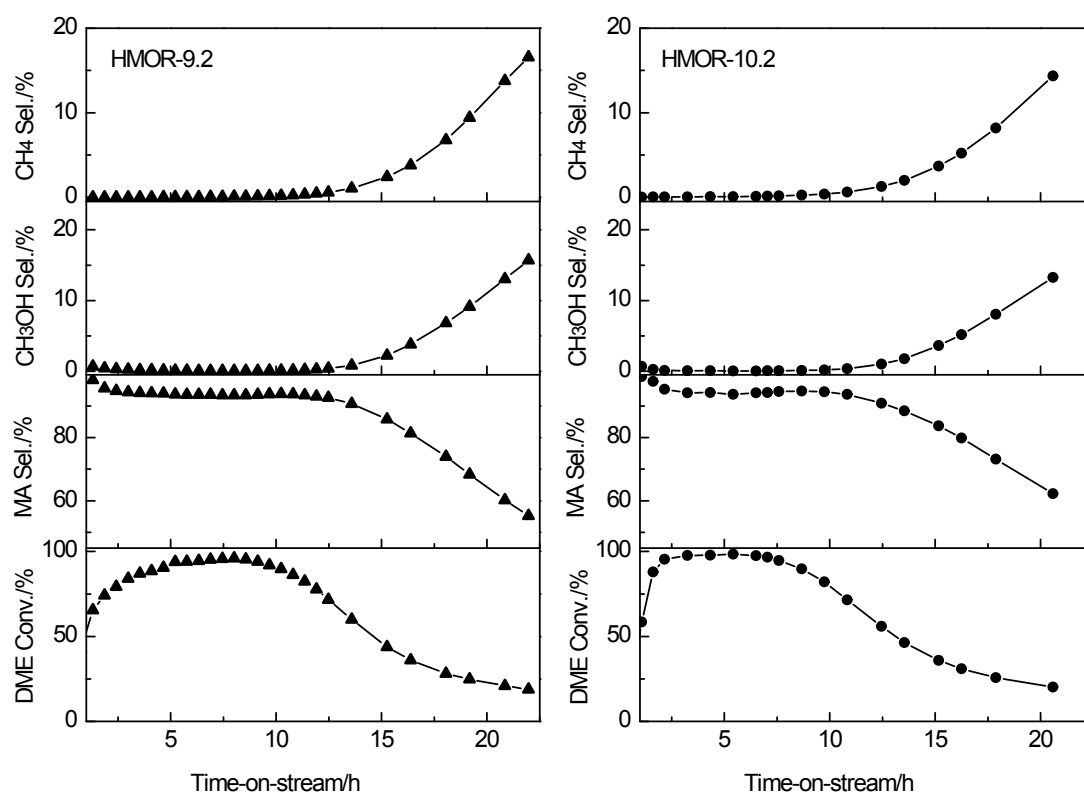
Fig. S4 DME carbonylation over the HMOR catalysts.

Reaction conditions: 453 K, DME/CO/N₂/He/=5/50/2.5/42.5 vol%, 1.0 MPa, 1250 ml/(g_{cat}·h).

Table S2 DME carbonylation over the HMORs at 453 K

Sample	DME Conv.% (MA Sel.%) with time-on-stream						
	2.0 h	5.6 h	10.2 h	18.0 h	24.5 h	33.5 h	46.3 h
MOR-6.5	22.3 (98.3)	34.2 (98.6)	38.7 (98.7)	42.0 (98.8)	38.3 (98.2)	25.0 (95.3)	12.6 (84.5)
MOR-9.2	27.5 (98.8)	35.9 (98.4)	41.3 (98.6)	44.7 (98.9)	40.1 (98.5)	24.4 (95.0)	12.2 (84.1)
MOR-10.2	22.3 (98.4)	32.1 (98.3)	37.0 (98.6)	40.9 (99.0)	38.4 (98.7)	24.3 (96.1)	11.0 (83.8)

* The number in the bracket indicates the selectivity of MA.

**Fig. S5** DME carbonylation over the HMOR catalysts.

Reaction conditions: 473 K, DME/CO/N₂/He/=5/50/2.5/42.5 vol%, 1.0 MPa, 1250 ml/(g_{cat}·h).

Table S3 DME carbonylation over the HMORs at 473 K

Sample	DME Conv.% (Ac Sel.%) with time-on-stream					
	1.8 h	5.3 h	8.0 h	9.7 h	15.2 h	20.7 h
MOR-9.2	74.2 (99.6)	93.9 (99.8)	96.0 (99.8)	91.9 (99.7)	43.8 (95.3)	20.9 (72.9)
MOR-10.2	87.9 (99.7)	98.4 (99.9)	94.7 (99.8)	82.1 (99.4)	35.8 (92.6)	20.6 (72.1)

* The number in the bracket indicates the total selectivity of MA and AcOH.

The selectivity of AcOH was much higher at 473 K, it was 5-6% at maximum conversion and 10-12% at 20.7 h time-on-stream.

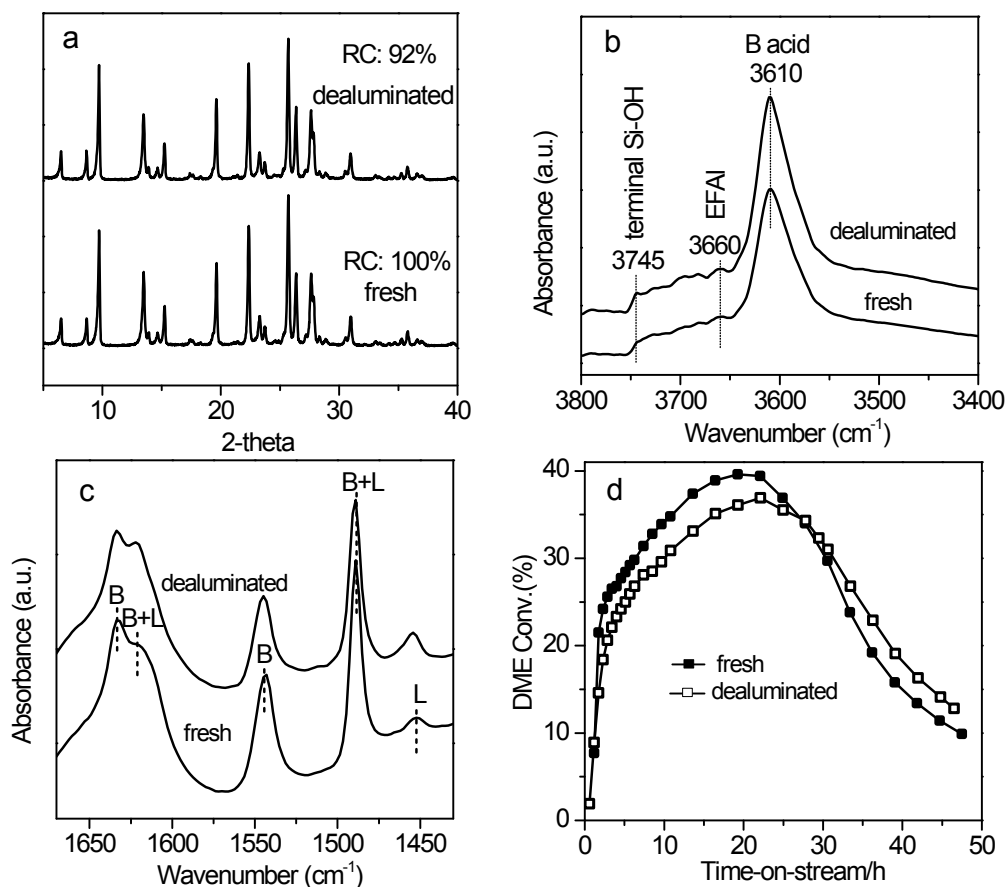


Fig. S6 Structure properties and catalytic activity of the dealuminated HMOR-10.2. (a) XRD pattern, (b) IR spectra in the -OH region, (c) Pyridine-IR spectra, and (d) DME conversion. Reaction conditions: 453 K, DME/CO/N₂/He/=5/50/2.5/42.5 vol%, 1250 ml/(g_{cat}·h), 1.0 MPa.

Dealumination of the HMOR-10.2 sample

For further increasing the SAR, the HMOR-10.2 sample was dealuminated by acid-leaching. The NH₄MOR-10.2 precursor was treated with 0.12 M nitric acid aqueous solution at 333 K for 1 h, followed by calcination at 773 K in flowing air. ICP analysis for the pristine and dealuminated samples was conducted (Table S4). The overall Si/Al ratio in the pristine NH₄MOR-10.2 was 8.67, and the estimated framework SAR was 10.3, in accordance with the SAR of 10.2 measured by ²⁹Si NMR. On the dealuminated sample, the Si/Al ratio slightly decreased to 9.46, equivalent to a framework SAR of around 11.2. In both cases, the extra-framework alumina was assumed to be 15.4%, based on the ²⁷Al NMR result and the IR spectra (Fig. S6b). The relative crystallinity of the dealuminated sample slightly decreased to 92% (Fig. S6a). The intensity of IR band at 3660 cm⁻¹ and 3745 cm⁻¹ on the dealuminated HMOR-10.2 sample enhanced slightly, implying that traceable extra-framework alumina and defect

sites were generated during the dealumination. Pyridine-IR spectra indicated a slight loss in the Brønsted acid sites (IR band at 1545 cm^{-1}) and the creation of new Lewis acid sites (IR band at 1454 cm^{-1}). The dealumination with acid washing induced the loss of framework Al species but did not alter the size and shape (Fig. not given). Consequently, maximum DME conversion was lowered and the catalytic stability slightly promoted (Fig. S6d).

Table S4 Si/Al ratio of the dealuminated HMOR-10.2

Sample	Si/Al by ICP	EFAI ^{27}Al NMR	Framework SAR by ICP	Framework SAR by ^{29}Si NMR
HMOR-10.2	8.67	15.4	10.3	10.2
Dealuminated HMOR-10.2	9.46	15.4	11.2	/

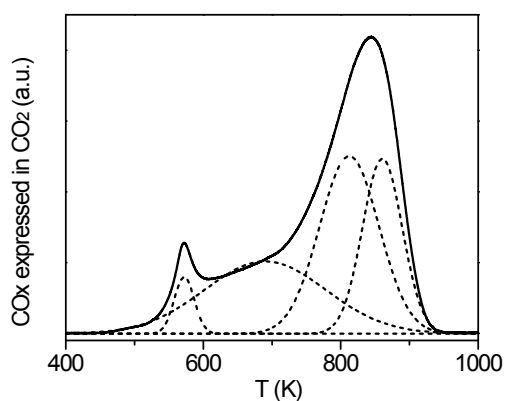


Fig. S7 TPO profile of the spent HMOR-10.2 catalyst after reaction at 473 K for 22 hours.

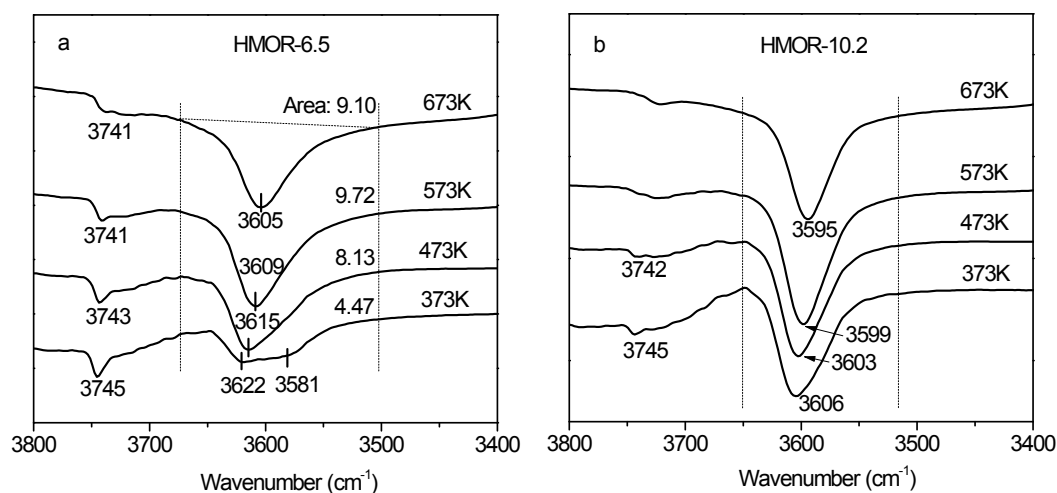


Fig. S8 Subtracted v-OH spectra of the background from that after Py adsorption.