Supporting Information

Insights into the Pyridine-modified MOR Zeolite Catalysts for DME Carbonylation

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Table S1 Molar compositions of the initial gels for the synthesis of MOR zeolites

Samples	SiO_2	Al_2O_3	Na_2O	$(TEA)_2O$	H_2O
MOR(7.0)	30	2.0	3.9	3.0	480
MOR(9.7)	30	1.5	3.0	3.0	480
MOR(13.8)	30	1.0	2.4	3.0	480
MOR(16.5)	30	0.8	2.4	3.0	480
MOR(19.4)	30	0.65	2.4	3.0	480

Table S2 Summary of the product STY in the MOR-catalyzed DME carbonylation reaction.

Literature	Reaction conditions				STY of MA	Pyridine
	DME : CO (%)	T (^oC)	P (MPa)	GHSV (mL/g/h)	(mmol/h/g)	modification
[1]	2:93	165	1	12024	1.9	
[2]	5:50	200	1	1250	0.8	Yes
[3]	5:50	200	1	1250	1.7	
[4]	3:95.5	210	1.5	5280	4.0	
[5]	5:35	200	2	1500	1.3	
[6]	1:47	200	1.5	4500	1.8	
[7]	5:35	200	3	1500	2.8	
[8]	2.4:50	210	2	2100	3.2	
[9]	1:49	200	1.5	6000	1.6	
[10]	5:50	200	1	1250	1.3	
[11]	5:35	200	2	1500	3.0	Yes
[12]	1:47	200	1.5	3000	1.1	Yes
[13]	5:76	200	1	2500	2.5	
[14]	1:49	200	1.5	6000	1.6	
[15]	2:98	190	2	2000	1.8	
[16]	3:95.5	190	1.5	2640	2.8	
Our work	**5:35**	**200**	**2**	**3600**	**7.2**	**Yes**

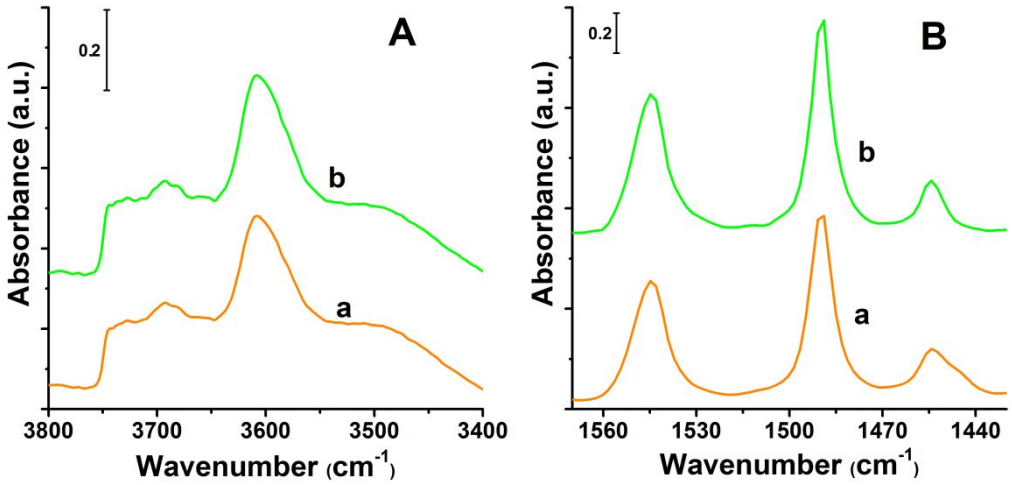


Figure S1 FTIR spectra in the ν(OH) vibration region (A) and pyridine ring-related vibration regions (B) of H-MOR(13.8) pretreated with different heating rates (heating rate 1 °C/min (a); heating rate 5 °C/min (b)). Pyridine desorption temperature: 200 °C.

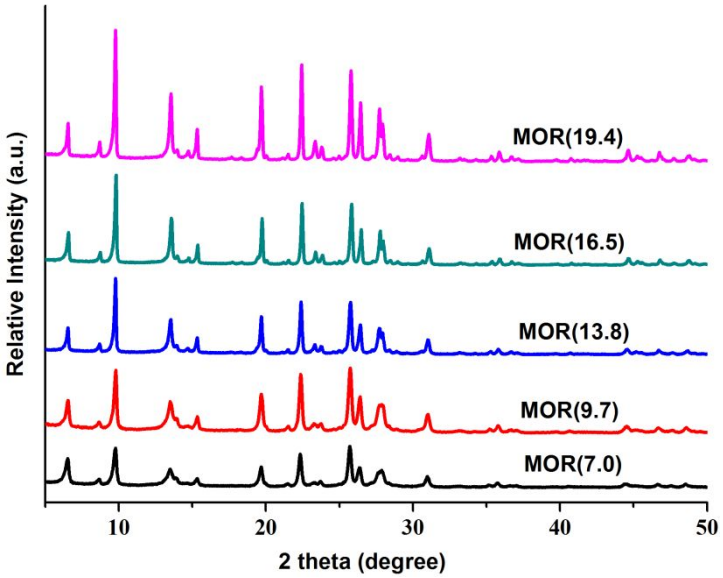


Figure S2 XRD patterns of the as-synthesized MOR zeolites with different Si/Al ratios.

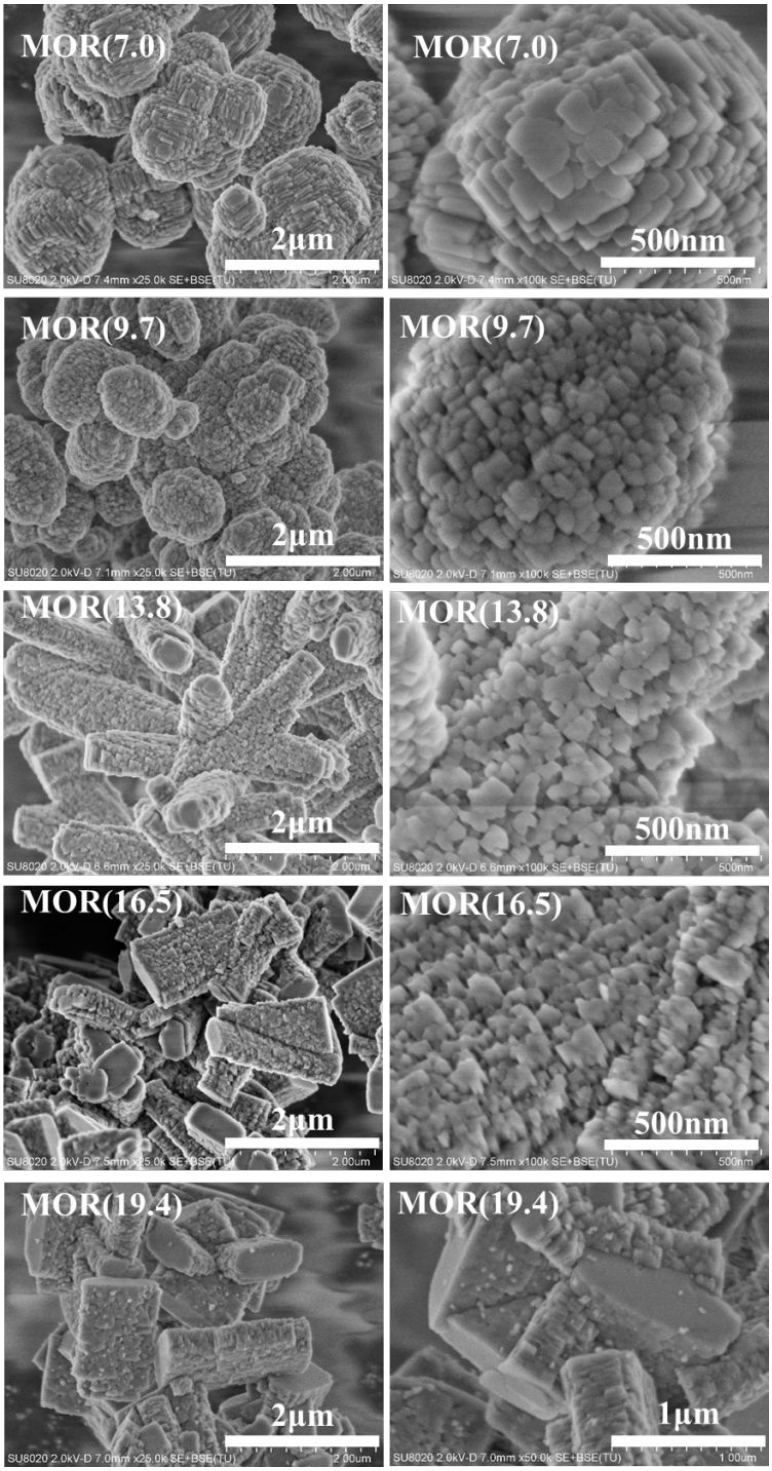


Figure S3 SEM images of the as-synthesized MOR samples with different Si/Al ratios.

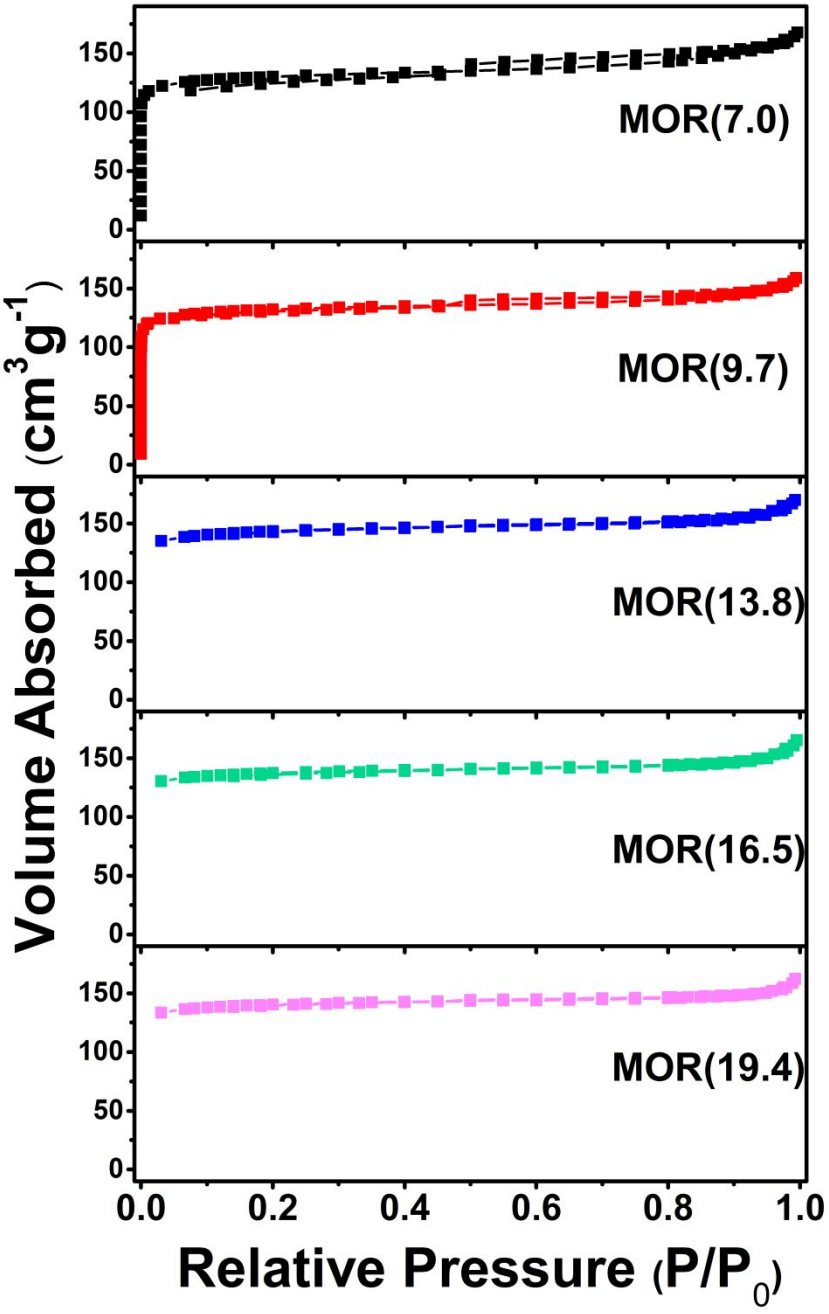


Figure S4 N_2 adsorption-desorption isotherms of the H-MOR samples.

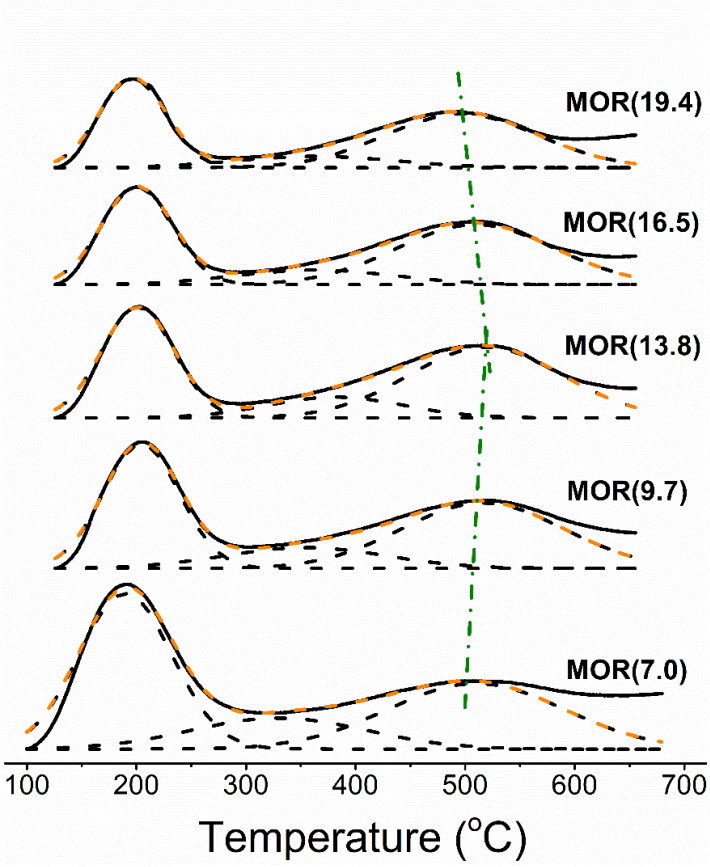
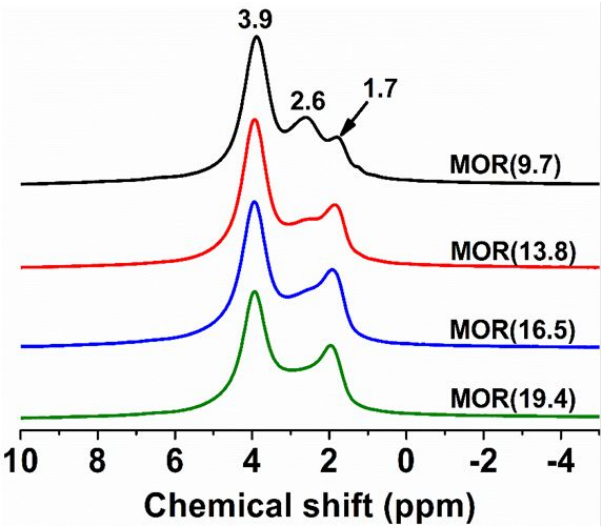


Figure S5 NH_3-TPD profiles (solid line) and deconvoluted results (dotted line) of the H-MOR samples. The arrows indicate the variation of the maximum desorption temperature.



Samples	Si-OH-Al	Al-OH	Si-OH
MOR(7.0)	59.10	30.28	10.61
MOR(13.8)	65.79	18.26	15.95
MOR(16.5)	59.81	16.28	23.91
MOR(19.4)	59.78	12.24	26.24

Figure S6 ^1H MAS NMR spectra of the H-MOR samples (left) and the relative percentage of Si-O(H)-Al (3.9 ppm), Al-OH (2.6 ppm) and Si-OH (1.7 ppm) calculated based on the deconvoluted spectra (right).

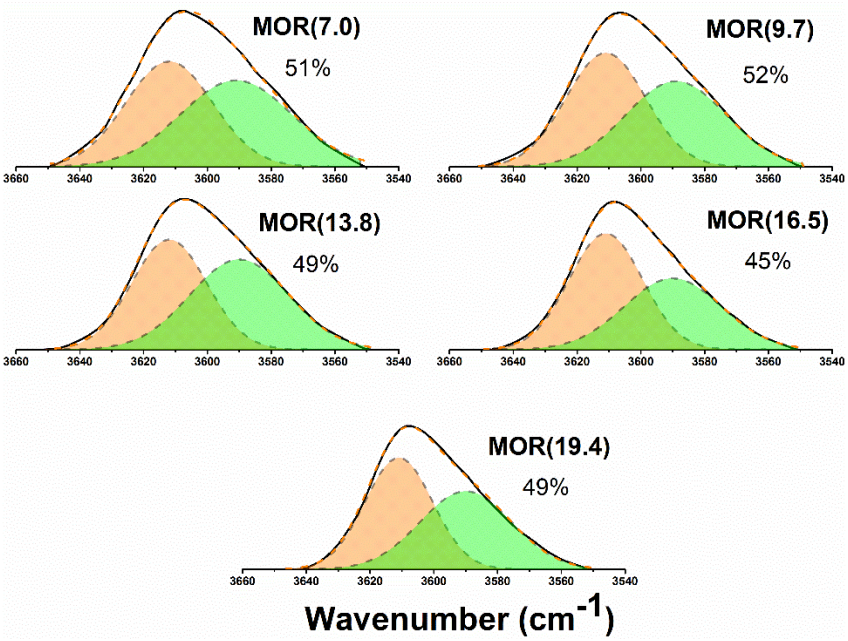


Figure S7 Deconvoluted bands corresponding to the acid hydroxyls in the 12-MR channels (HF) and 8-MR pockets (LF) of H-MOR samples. The percentage shown in each figure is the ratio of H^+ in 8-MR pockets. Note that the possible difference in absorption coefficient of the acid hydroxyls located in 12-MR channels and 8-MR pockets is not considered in the calculation[1, 17-18].

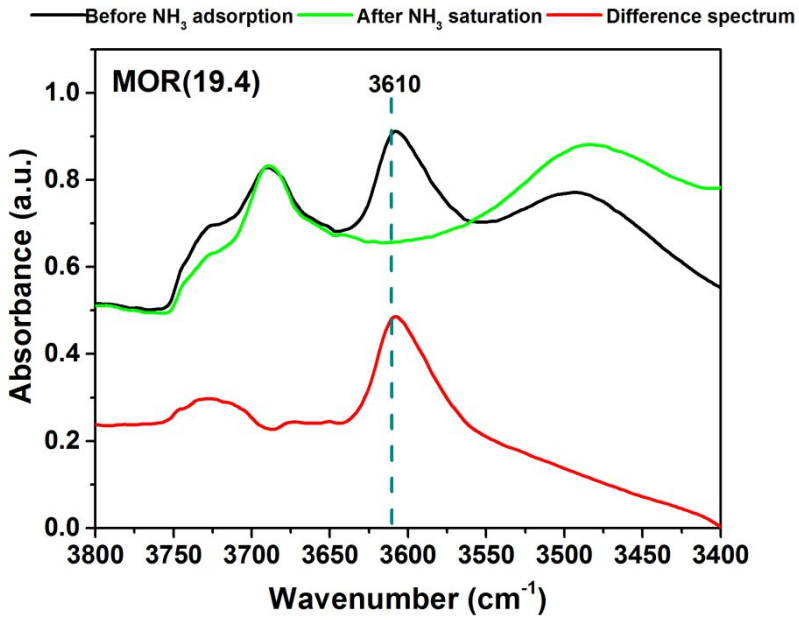


Figure S8 The derivation of the acidic hydroxyl band for deconvolution by subtracting the NH_3-titrated spectrum from the original one.

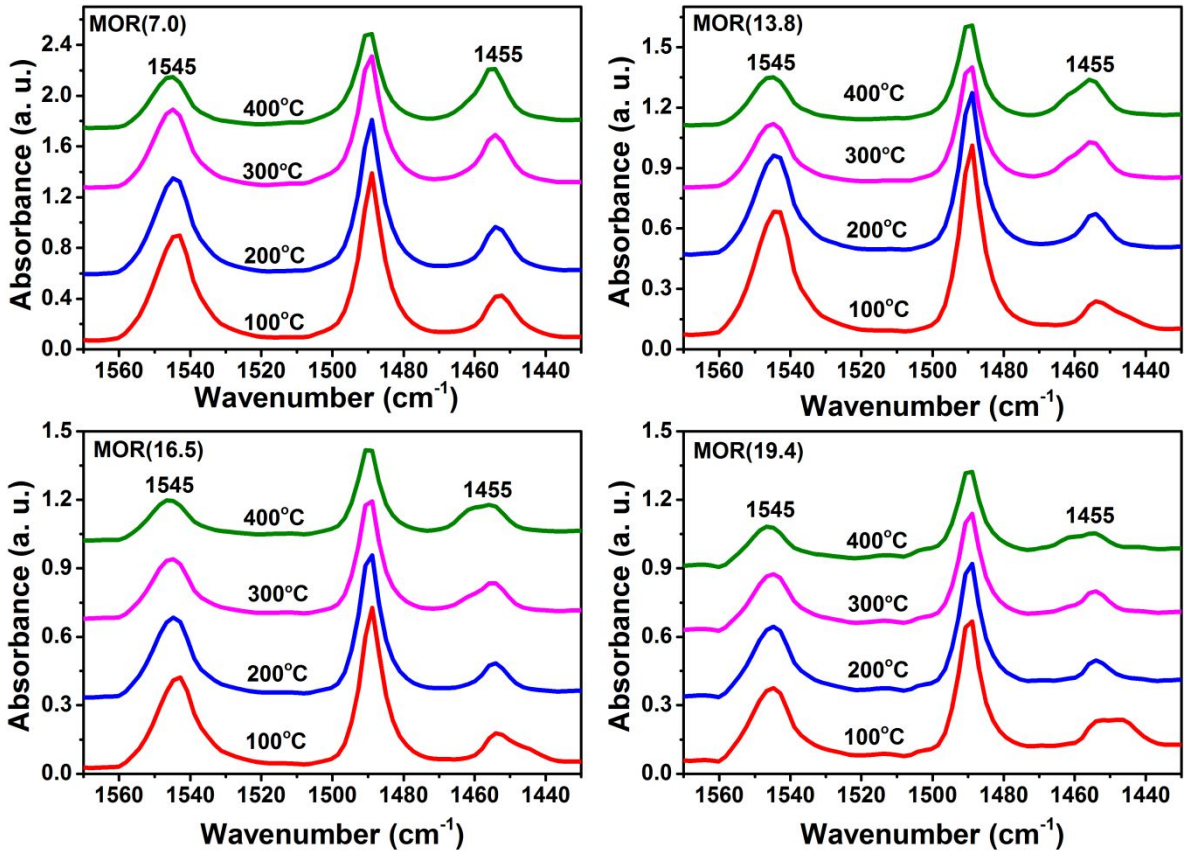


Figure S9 FTIR spectra of pyridine ring-related vibration regions on the H-MOR samples after pyridine desorption at 100, 200, 300 and 400 °C.

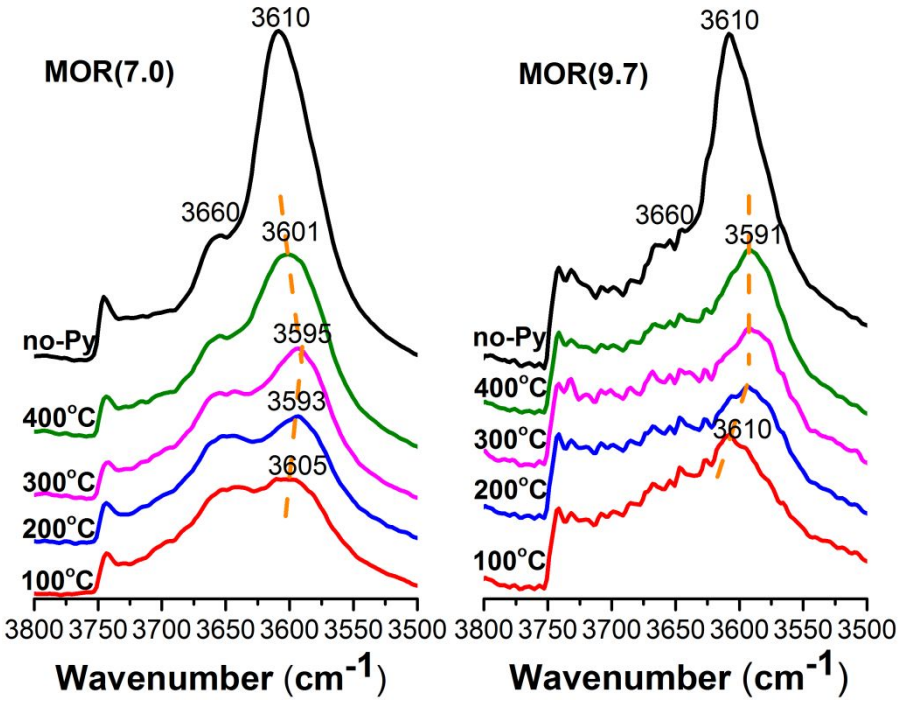


Figure S10 The ν(OH) bands of the low-Si sample H-MOR(7.0) and H-MOR(9.7) after pyridine desorption at different temperatures (pyridine adsorption temperature: 100 °C).

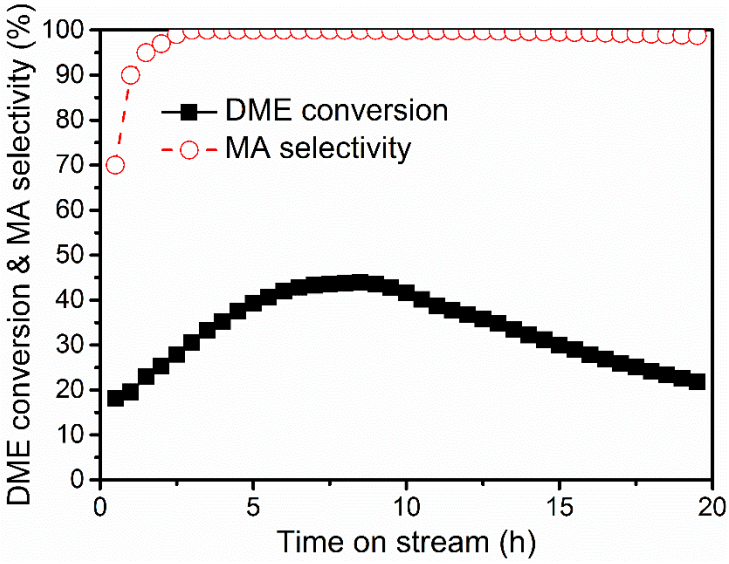


Figure S11 DME conversion and MA selectivity over pyridine-modified H-MOR(13.8) catalysts after pyridine desorption at 500°C. Reaction conditions: 200°C, 2 MPa, DME/CO/N_2 = 5/35/60, GHSV=3600 mL/g/h.

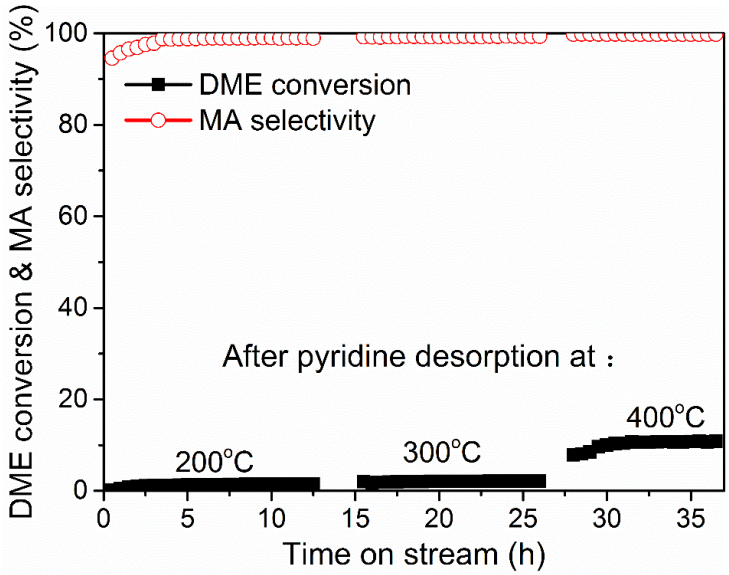


Figure S12 DME conversion and MA selectivity over pyridine-exchanged MOR(13.8) after pyridine desorption at different temperatures. Pretreatment condition: 0.5 g of the catalyst (40-60 mesh) was loaded into the reactor and pretreated (heating rate 1 °C/min) in Ar at 200 °C for 4 h; Reaction conditions: 200 °C, 2 MPa, DME/CO/N_2 = 5/35/60, GHSV = 3600 mL/g/h.

Pyridine exchange condition: Mixed solution of pyridine and HCl (pyridine: 1 mol/L; pH ≈ 7), solid/liquid = 1 g/20 mL (12 h@60 °C, repeated 3 times). The Na/Al ratio of the sample decreased from 0.76 to 0.13 after ion exchange.

References

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