Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Direct Observation of DEM Carbonylation in the Different Channels of HMOR Zeolite by Continuous-Flowing Solid-State NMR Spectroscopy

T. He[a], P.J.Ren[a], X.C.Liu[a], S.T.Xu[b] , X.W.Han[a], X.H.Bao[a]

a State Key Laboratory of Catalysis , Dalian Institute of Chemical Physic, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, *P. R.*China.

b *National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R.* China

Email: xhbao@dicp.ac.cn

NMR experiment

In situ NMR experiment was performed on a Bruker AvanceIII-600 instrument equipped with 7-mm MAS-CAT probe. The ^{13}C MAS NMR spectra was obtained with a Larmor frequency 150.92MHz using a single pulse sequence with a $\pi/2$ pulse of 5 μs and a recycle delay of 2 s, and scan 500-2000 times at 3 kHz of spinning rate. The chemical shifts were referenced to adamantane for ^{13}C. For the $^{1}H \rightarrow {}^{13}C$ CP MAS NMR experiment, the Hartmann-Hahn condition was achieved using HMB with a connect time of 5 ms, and a repetition time of 2 s.

Methoxyl

Fig.1 shows that different chemical shifts of methanol, DME and methoxyl on HMOR. The narrow signal at 60 ppm should assign to DME adsorbed on HMOR at room temperature (Fig. a). Fig. b shows ^{13}C CP MAS spectroscopy of methanol adsorbed on HMOR heated at 150° C for 0.5 hour, then desorbed on vacuum line to remove physical adsorbed species. The broad signal can be attributed to methoxyl on HMOR. Fig. c shows sample in Fig. b hydrated for days, the signal of methanol split into two signals represent DME (60 ppm) and methanol (52 ppm). These three signals are too close to identify each other, especially at in situ condition.

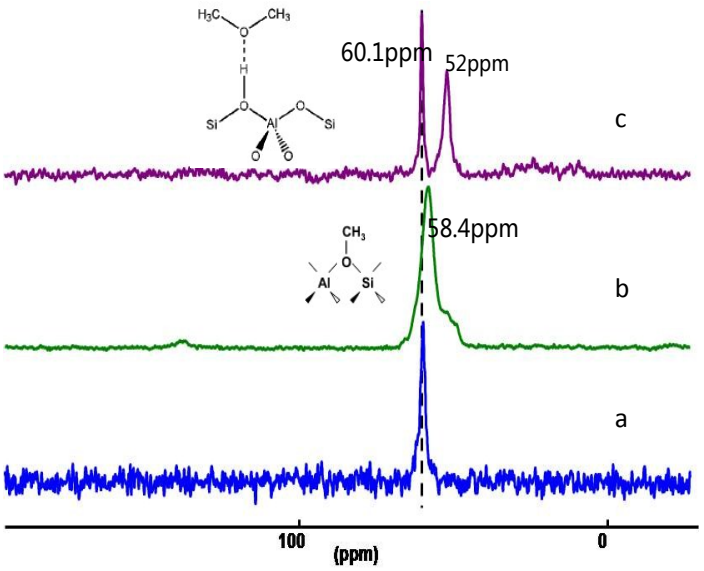


Fig.1 ^{13}C CP MAS NMR of DME adsorbed on HMOR at room temperature (a); HMOR adsorbed methanol heated at 150°C for 0.5 hour, then desorbed on vacuum line (b); sample in (b) hydrated for days(c).

Induction period

Fig.2 shows the rate of MA at 473K atmosphere with a mix gas (5% DME, 50% CO, 45% He), it has a 60minutes induction period at this condition.

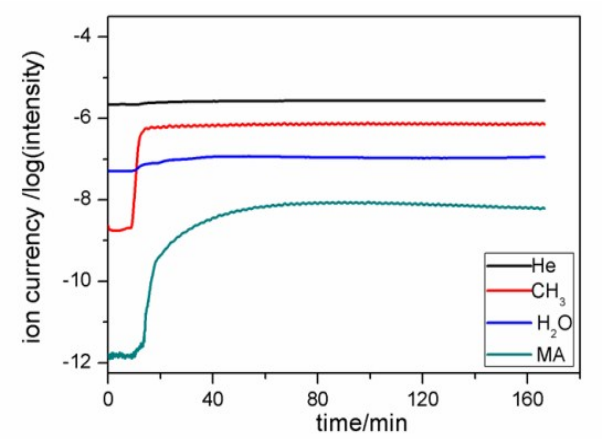


Fig.2 Mass Spectroscopy of DME carbonylation on HMOR catalyst at 473K atmosphere

DFT calculation method

Gaussian 09 package[1] was used for all DFT calculations in this paper. The structures were optimized by B3LYP[2–5] functional with 6-31G(d, p) basis set. Chemical shifts were calculated by GIAO[6] method with B3LYP functional and 6-311+G(2d, p) basis set. The structures of various species on HMOR are shown in Fig.S3 and Fig.S4.

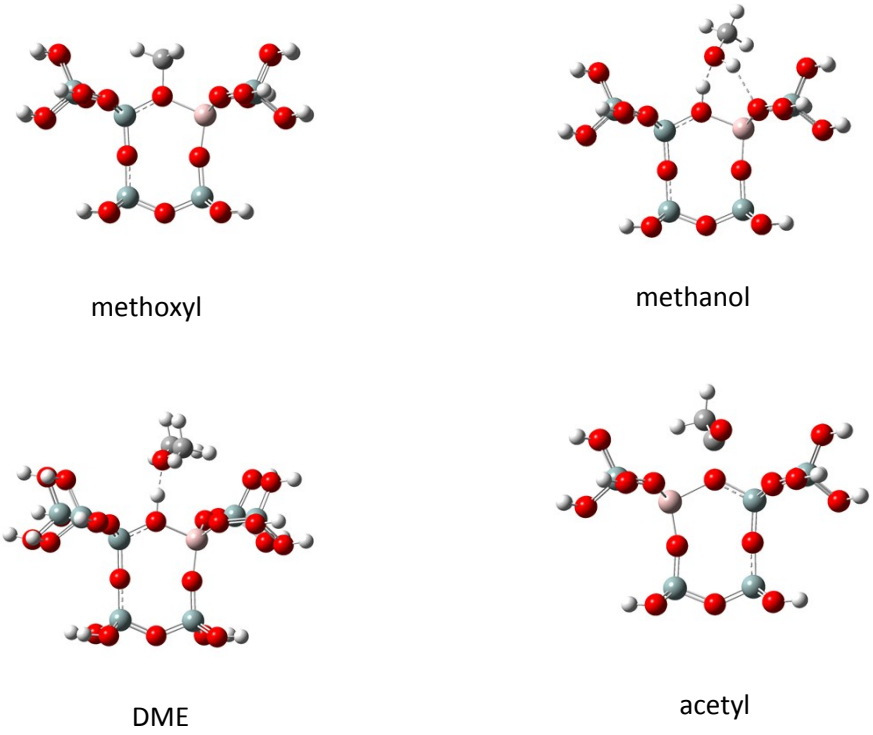
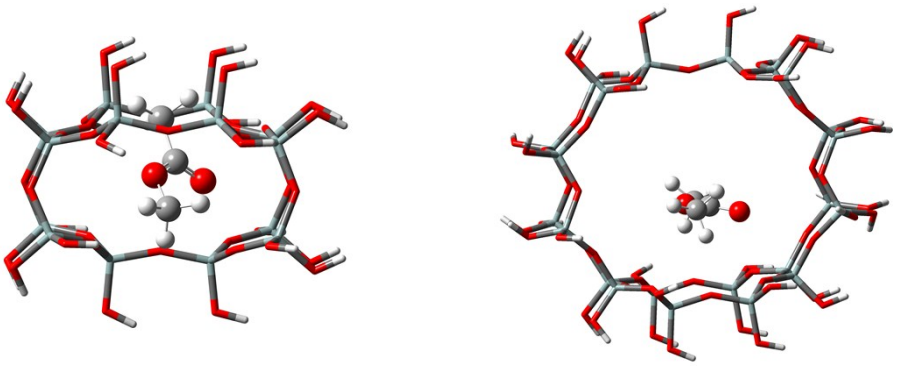


Fig.S3 Optimized structures for various species on HMOR 8T model.



MA in 8MR MA in 12MR

Fig.S4 Structures for methyl acetate adsorbed in 8MR and 12MR of MOR zeolite.

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