Supporting Information for

Dynamic Activation of C1 Molecules Evoked by Zeolite Catalysis

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1. Characterization of the Materials

1.1 Materials
1.2 Powder X-ray diffraction (XRD)
1.3 Scanning electron microscopy (SEM)
1.4 X-ray fluorescence (XRF)
1.5 NH$_3$-TPD profiles
1.6 Fourier Transform Infrared (FTIR) Spectroscopy
1.7 $^1$H MAS ssNMR spectroscopy
1.8 Ab initio molecular dynamics (AIMD) simulation

2. Experimental Section

2.1 Methanol conversion on a fix-bed reactor
2.2 ssNMR experiment
2.3 DRIFTS experiment

3. Results and Discussion

3.1 GC-MS detection of methanol conversion on NaZSM-5 and silicate-1
3.2 DRIFTS study of methanol conversion over HZSM-5, NaZSM-5, and silicate-1
3.3 Dynamic evolution of C-O distance in (a) ethoxy, (b) isopropoxy, (c) tert-butoxy along with the temperature increase from 273K to 673K on ZSM-5 zeolite.

1.1 Materials

ZSM-5 was purchased from Nankai Catalyst factory and silicate-1 was prepared according to the method reported in the literature.\textsuperscript{[1]}

1.2 Powder X-ray diffraction (XRD)
Figure S1. XRD patterns of HZSM-5, NaZSM-5, and silicate-1.

The powder XRD patterns, recorded using a PANalytical X’Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV and 40 mA, indicated that three samples have the same topological structure of MFI.

1.3 Scanning electron microscopy (SEM)
Figure S 2. The Scanning electron microscope (SEM) images of HZSM-5(a), NaZSM-5(b) and silicate-1(c).

To investigate crystallite size and morphology of the used molecular sieve, a HITACHI SU8020 Scanning Electron Microscope was employed. Three samples consist of small crystal particles with the size of 20-100 nanometer.

1.4 X-ray fluorescence (XRF)

The chemical composition of parent ZSM-5(Si/Al=20) was determined with a Philips Magix-601 X-ray fluorescence (XRF) spectrometer.
1.5 NH₃-TPD

NH₃-TPD profiles of HZSM-5, NaZSM-5 and silicate-1 are shown in Figure S 3. A low-temperature desorption peak at ca. 100-350 °C and a high-temperature desorption peak at ca. 350-600 °C correspond to the NH₃ desorption from weak/medium acid sites and from strong acid sites, respectively. The weak and medium acid sites usually assigned as silanol groups (Si-OH) at the external surface or at lattice defects and hydroxyl (Al-OH) bounded to the extra-framework aluminum species. The strong acid sites that are important for the catalysis were generally resulted from the bridge hydroxyl groups (Si (OH)Al). On silicate-1, only a broad desorption peak at ca. 100-350 °C represents the NH₃ desorption from silanol groups.

1.6 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were collected on a Bruker Tensor 27 instrument supplied with an MCT detector. The catalyst powder was loaded in a diffuse reflectance infrared cell with ZnSe window which can work at high temperatures and high pressures. Direct observation of the potential active sites is conducted before the reactants were introduced (Figure S 4). The stretching vibration of bridge hydroxyl give rise to the peak
at 3600 cm$^{-1}$. The signals at 3730-3740 cm$^{-1}$ are often attributed to silanols group at the external surface or at lattice defects. The signals at 3680-3640 cm$^{-1}$ are attributed to hydroxyl bounded to the extra-framework aluminum species.

Figure S 4. FTIR spectra of the hydroxyl groups of HZSM-5, NaZSM-5, and silicate-1.

1.7 $^1$H MAS ssNMR spectra

Figure S 5. $^1$H MAS NMR spectra of HZSM-5, NaZSM-5, and silicate-1.
From $^1$H MAS NMR spectra, the peak at 3.6 ppm, 2.4 ppm and 1.6-1.8 ppm can be assigned to Si (OH)Al, Al (OH) and Si (OH), respectively. The Brønsted acid site concentration of HZSM-5 (0.75 mmol/g) is determined by the peak intensity, using adamantane as the external standard.

1.8 Ab initio molecular dynamics (AIMD) simulation

All AIMD simulations were employed by CP2K software. The Perdew–Burke–Ernzerhof (PBE) functional\cite{2} with consideration of Grimme D3 dispersion corrections,\cite{3} valence polarized (DZVP) basis set\cite{4} together with the Goedecker-Teter-Hutter (GTH) pseudopotential\cite{5} were used for the system. During the self-consistent field (SCF) procedure, a 360 Ry density CUTOFF criterion with finest grid level was employed along with multi-grids number 4 (NGRID 4 and REL CUTOFF 70). The temperature was controlled by a chain of five Nosé-Hoover thermostats,\cite{6} and the integration time step was set to 0.5 fs during the AIMD simulations. The topologies of MFI were extracted from the official website of the International Zeolite Association (IZA). On the basic of approachability of the adsorbed molecules, the T12-O24-T12 site in the intersection channel of ZSM-5 zeolite was chosen as the Bronsted acid site (BAS). To account for zeolite framework flexibility at designated reaction temperatures, ab initio molecular dynamic (AIMD) simulations were performed by periodic density functional theory (DFT). This is carried out by first performing equilibrium AIMD simulations of surface methyl species for 5 ps at the isothermal-isobaric (NPT) ensemble, in which the amount of substance (N), pressure (P) and temperature (T) are conserved, to relax the cell parameters and atom positions. Subsequently, 50 ps AIMD simulation at NVT ensemble was performed to sample the C-O distance.

2.1 Methanol conversion in a fix-bed reactor

Three samples of HZSM-5, NaZSM-5 and silicate-1 were calcined at 823 K for 4 h, and then was extruded and sieved into 40-60 meshes. Methanol conversion was carried out in a fixed-bed quartz tubular reactor under atmospheric pressure. The methanol was fed by passing helium through a saturation evaporator with a WHSV of
2.0 h\(^{-1}\). The reaction products were analyzed both by an Agilent 7890A/5975C GC/MSD and an on-line MS (Omni star).

2.2 NMR Spectroscopy

All the solid-state NMR experiments were performed on a Bruker Avance III 600 spectrometer equipped with a 14.1 T wide-bore magnet using a 4 mm or 7 mm MAS-CAT probe. In the temperature programmed ssNMR experiments, about 200 mg of pre-dehydrated samples were filled and pressed into a hollow cylinder with a specially constructed tool into a 7 mm NMR rotor reactor under dry nitrogen in a glove box. After transferred to the 7 mm high temperature MAS-CAT NMR probe, the catalyst was activated at 573 K for 1 h under flowing helium (40 ml/min) which was injected into the spinning MAS rotor via the injection tube. After the temperature decreased to the target value, \(^{13}\)C-enriched methanol was fed into the MAS NMR rotor reactor by passing the carrier gas through a saturator kept at 283 K with a WHSV of 1 h\(^{-1}\). \(^{13}\)C MAS NMR spectra were recorded using one pulse sequence with a spinning rate of 3 kHz. The chemical shifts were referenced to adamantane with the peak at 29.5 ppm.

2.3 DRIFTS

In-situ DRIFT spectra were collected on a Bruker Tensor 27 instrument supplied with an MCT detector. The catalyst powder was contained in a diffuse reflectance infrared cell with ZnSe window which can work at high temperatures and high pressures. The absorbance spectra were obtained by collecting 16 scans at 4 cm\(^{-1}\) resolution. Methanol was fed by passing the carrier gas (N\(_2\), the purity is 99.999\%) through a methanol saturator maintained at 283 K into the reactor. Before the adsorption of reactants, the sample was first calcined in N\(_2\) flow of 20 ml/min at 773 K for 150 min. With the temperature decreasing to the target value, methanol was introduced to the activated catalyst for 10 min with the total gas flow rate of 5 ml/min\(^{-1}\). Then, the cell was heated at a constant heating-rate of 10 k/min to 573 K under N\(_2\) sweeping (5 ml/min) and the spectra was recorded at the relevant temperatures.
3.1 GC-MS detection on NaZSM-5 and Silicate-1

As shown in Figure S 6, besides methanol and DME, no hydrocarbons could be detected below 523 K, indicating that the methanol dehydration to DME should be the main chemical reaction. Trace amounts of methane and ethene might be generated over Lewis acid site. The hydroxyl bounded to the extra-framework aluminum species was also considered as an active center for the methanol conversion to hydrocarbons.
As shown in Figure S 7, methanol was the only compound detected in the effluent and no hydrocarbons could be formed during the methanol feeding onto silicate-1 at 573 K.

3.2 Temperature-programmed DRIFTS study of methanol conversion of HZSM-5, NaZSM-5, and silicate-1
In-situ DRIFT spectra of methanol conversion on HZSM-5 (A), NaZSM-5 (B), silicate-1 (C) in temperature range of 373 - 573 K.

The characteristic peak of SMS at 2977, 2868 cm\textsuperscript{-1} could be observed on HZSM-5 above 473 K. In contrast, they are absent over NaZSM-5 or silicate-1 and the signal of surface-adsorbed DME and methanol dominated the catalyst surface. The significant differences in surface composition and reaction performance on these three catalysts well supported that SMS must play a crucial role in activating C1 reactants and launching an efficient MTH reaction.

3.3 Dynamic evolution of C-O distance in (a) ethoxy, (b) isopropoxy, (c) tert-butoxy along with the temperature increase from 273K to 673K on ZSM-5 zeolite
We have extended the supramolecular system from methoxy to ethoxy, isopropoxy, and tert-butoxy surface species over HZSM-5 zeolite to confirm the universality of alkyl-Zeo system with dynamic evolution and illustrate the covalent-ionic transition at C-O bond along with the alkoxy groups (Scheme S1). The evolution of the covalent-ionic transition of C-O bond in this alkyl-Zeo system would help to understand the role of them in those hydrocarbon-related reactions. Like the evolution of C-O bond in SMS (Figure 3.a-b), the distribution of C-O distance in these three alkoxy species are also widened with the temperature increase as displayed in Figure S 9. Notably, the increased ionic property of surface species, in terms of the percentage of D > 1.60 Å, increases gradually from SMS to surface tert-butoxy with the order: CH₃-Zeo (5.79%) < CH₃CH₂-Zeo (8.16%) < (CH₃)₂CH-Zeo (35.49%) < (CH₃)₃C-Zeo (100%) of 5.79 % at 673 K. Notably, with temperature increase from 273 K to 673K, the surface isopropoxy shows the inevitable tendency to transform to the isopropyl cation, and the surface tert-butoxy is totally presented as tert-butyl cation even at 273 K. Compared to SMS, the more feasible transition of C-O bond on other bulky alkoxy group or alkyl cation has also rationalized their role as important intermediates, either in cracking, dehydration, isomerization, alkylation, etc. over acid catalysts. The generation and transition procedure of alkoxy groups or carbocations would be of great significance to the hydrocarbon-related reactions catalyzed by acid zeolites.

Scheme S 1. Chemical formula of surface methoxy, ethoxy, isopropoxy, and tert-butoxy species over zeolite materials.
Figure S 9. The dynamic evolution of C-O distance in (a) ethoxy, (b) isopropoxy, (c) tert-butoxy along with the temperature increasing from 273 K to 673 K in ZSM-5 zeolite.

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