Supplementary information for

Room Temperature Activation of Methane over Zn Modified H-ZSM-5 Zeolites: Insight from Solid-state NMR and Theoretical Calculations

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NMR measurements

For ^{13}C NMR experiments of adsorbed 2-^{13}C-acetone, a measured volume of 2-^{13}C-acetone (^{13}C, 99 %, Cambridge Isotope Laboratories, Inc.) was condensed and frozen into the pre-activated sample (0.5 g) in the CAVERN device under vacuum at liquid N_2 temperature; then keeping at this temperature, the sample was transferred into a 7.5 mm zirconia NMR rotor which was sealed with a Kel-F endcap (cut with 20 grooves). The loading of adsorbed acetone is about 0.8 molecule/ Brønsted acid site.

For ^{129}Xe NMR experiments of adsorbed xenon, a known amount of catalysts (0.5 g) that had been pre-activated in the CAVERN device was transferred to an 8 mm glass tube under a dry nitrogen atmosphere in a glove box. The tube was connected to a vacuum line for degassing under a pressure below 10^{-3} Pa over a period of 2 h at room temperature. A measured volume of Xe gas (^{129}Xe 26.44%) with a known pressure was then condensed and frozen inside the sample by cooling the sample region of the glass tube with liquid N_2. Finally, the tube was flame sealed.

The activation energy of formation of methoxy species on the ZnZSM-5 catalyst was measured as follows: A known amount of methane was condensed and frozen into the pre-activated ZnZSM-5 with liquid N_2, and then the sample was transferred to NMR rotors which were sealed by Kel-F endcaps (cut with 20 grooves) in the CAVERN device. The sealed rotors were heated to a specific temperature (changing from 298 to 373 K) for a period of time, and then the reaction was quenched by liquid N_2. ^{13}C MAS NMR measurement was performed at 233 K to exclude any further reaction. The concentration of formed methoxy species was measured by ^{13}C spin counting NMR method, which was carried out by comparing the integrated intensities of the sample with that of a known amount of adamantane. Finally, the temperature dependent rate constant was obtained and the activation energy was derived from the Arrhenius equation.

Uv-visible diffuse reflectance (UV–vis DRS) **measurements**

The UV–vis DRS spectra were collected on a JASCO V-550 spectrophotometer equipped with an integrating sphere under room temperature.

Electron Paramagnetic Resonance (EPR) measurements

The *cw* EPR experiments were performed on a Bruker X-band A300-6/1 EPR spectrometer at room temperature. A microwave frequency of 9.86 GHz, a microwave power of 5 mW, and a modulation amplitude of 1.5 mT were employed for EPR settings. Prior to measurements, the ZnZSM-5 sample was prepared in the CAVERN device and transferred into a 4-mm EPR tube with valve in a glovebox. Then, the tube was connected to a vacuum line for degassing and then flame sealed.

X-ray Absorption (XAS) measurements

The Zn K-edge Extended X-ray Absorption Fine Structure (EXAFS) measurements were performed on beamline 14W (XAFS station) at the Shanghai Synchrotron Radiation Facility (SSRF), using a Si (111) double crystal monochromator. The storage ring of SSRF is operated at 3.5 GeV with a maximum current of 300 mA. All spectra were recorded in transmission mode at room temperature. The samples were loaded into a home-build airproof device under a dry nitrogen atmosphere in a glovebox for the XAS measurement. The absolute energy position was calibrated using a Zn metal foil.

GC measurements

Methanol produced by contacting water with methoxy intermediates was extracted from the ZnZSM-5 sample with acetonitrile. A Shimadzu 2010 plus gas chromatograph with a Rtx-5ms column (30 m 0.25 mm id. 0.25μm film) and a FID detector was used to identify and quantify the methanol concentration.

DFT calculations

For the adsorbed acetone calculation, acetone molecule was initially bonded to the Zn^{2+} site of the Zn^{+}–O^{-}–Zn^{2+} cluster in ZnZSM-5. The adsorption complexes of acetone with a $Al_2Si_6O_9H_{14}Zn_2O$ zeolite cluster model were optimized with the Becke's three-parameter hybrid method using the Lee-Yang-Parr correlation functional (B3LYP) and the 6-311g(d,p) basis set. The ^{13}C NMR isotropic chemical shift of the carbonyl carbon of acetone absorption complexes was calculated using the gauge independent atomic orbital (GIAO) method at B3LYP/6-311+g(d,p) level of theory and referenced to the NMR experimental value of gas-state acetone (208 ppm).

For the zinc-bound methoxy species (Zn–O–CH_3), b3lyp/6-311g(d,p) method is used for structure optimization. In order to obtain accurate ^{13}C chemical shift, we used the b3lyp/6-311+G(d,p) method to predict the NMR parameters.

In the calculations of Uv-vis spectra, the ground state geometry of Zn^{+}–O^{-}–Zn^{2+} on a ZSM-5 zeolite cluster model ($Al_2Si_6O_9H_{14}Zn_2O$) was optimized by means of density functional theory (DFT) method at the UB3LYP/6-31+G(d,p) level. In order to investigate the absorption nature of the complexes, the time dependent DFT (TD-DFT) calculations were used to determine the lowest singlet excited states based on the optimized ground-state geometry.

Table S1. Conversion and yield of methanol produced by reaction of methoxy intermediates with water. Methanol is extracted and analyzed by GC. Nearly all of the formed methanol can be extracted from the ZnZSM-5 sample.

sample	Reaction condition		Methanol	
	Temp[K]	Time [min]	selectivity[%][a]	Yield [%][b]
HZSM-5	298	120	0	0
	373	120	0	0
ZnZSM-5	298	120	100	75.2
	328	60	100	74.7
	373	30	100	75.6

[a] relative to methoxy species

[b] relative to methane

Table S2. EXAFS parameters of the reference compounds and ZnZSM-5 catalyst. ΔR: 1.8-2.8 Å for Zn foil, ZnZSM-5 and Zn^{2+}/ZSM-5, and 1.0-2.0 Å for the first shell of ZnO powder and ZnO/ZSM-5 and 2.4-3.3 Å for the second shell. K weight =3.0.

sample	Shell	R(Å)	CN	σ^2(Å^2)	R factor
Zn foil	Zn-Zn	2.64±0.01	12	0.0113±0.0015	0.011
ZnO powder	Zn-O	1.98±0.01	4	0.0051±0.0011	0.008
	Zn-Zn	3.23±0.02	12	0.0131±0.0027	0.018
ZnZSM-5	Zn-O	1.97±0.01	4.0±0.2	0.0086±0.0007	0.002
ZnO/ZSM-5	Zn-O	1.99±0.01	4.2±0.3	0.0054±0.0009	0.004
	Zn-Zn	3.22±0.02	7.4±2.8	0.0137±0.0032	0.024
Zn^{2+}/ZSM-5	Zn-O	2.00±0.01	4.0±0.6	0.0063±0.0018	0.016

CN=coordination number; R=bond distance; σ^2=Debye-Waller factor

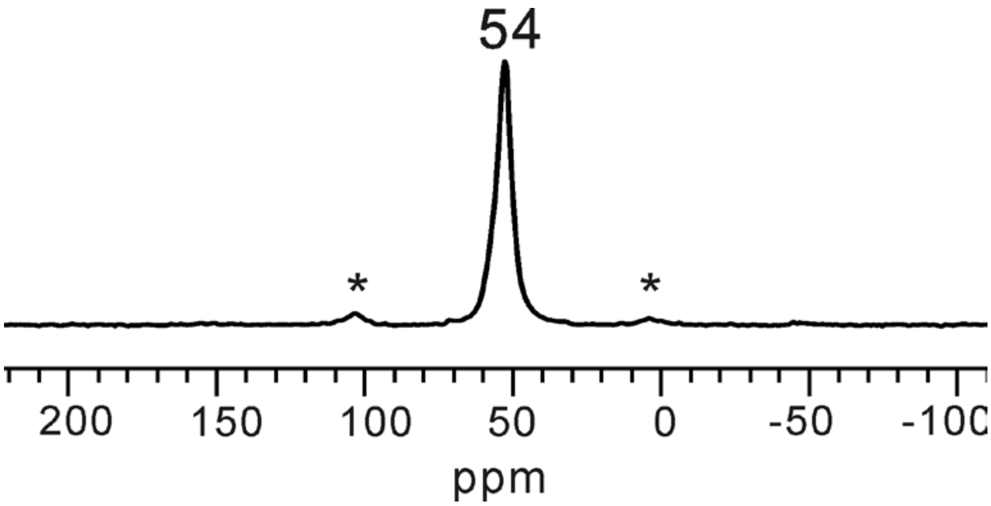

Figure S1. ^{13}C CP/MAS NMR spectrum of ^{13}C-methanol adsorbed on ZnZSM-5 catalyst at 298 K. Asterisks denote spinning sidebands.

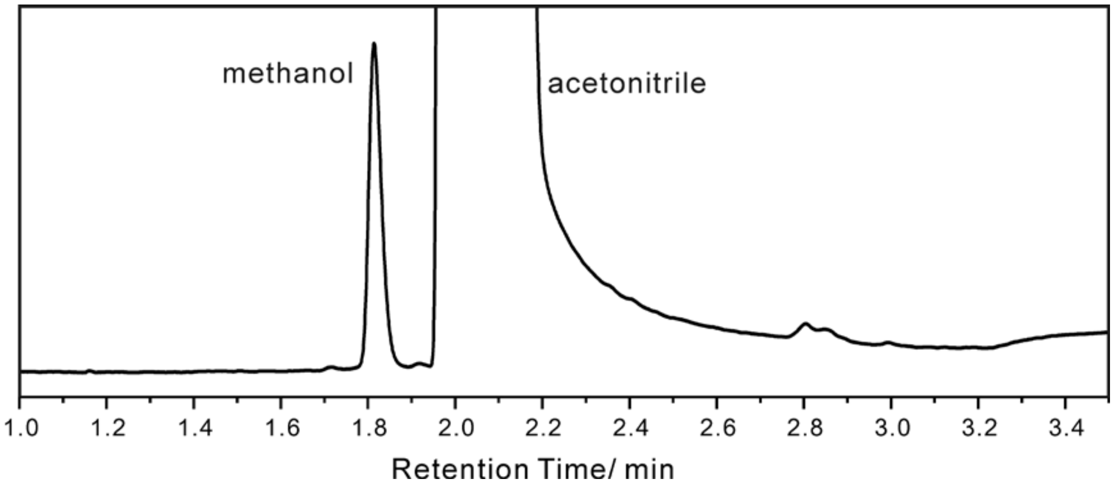

Figure S2. GC profile of methanol extracted from the ZnZSM-5 sample.

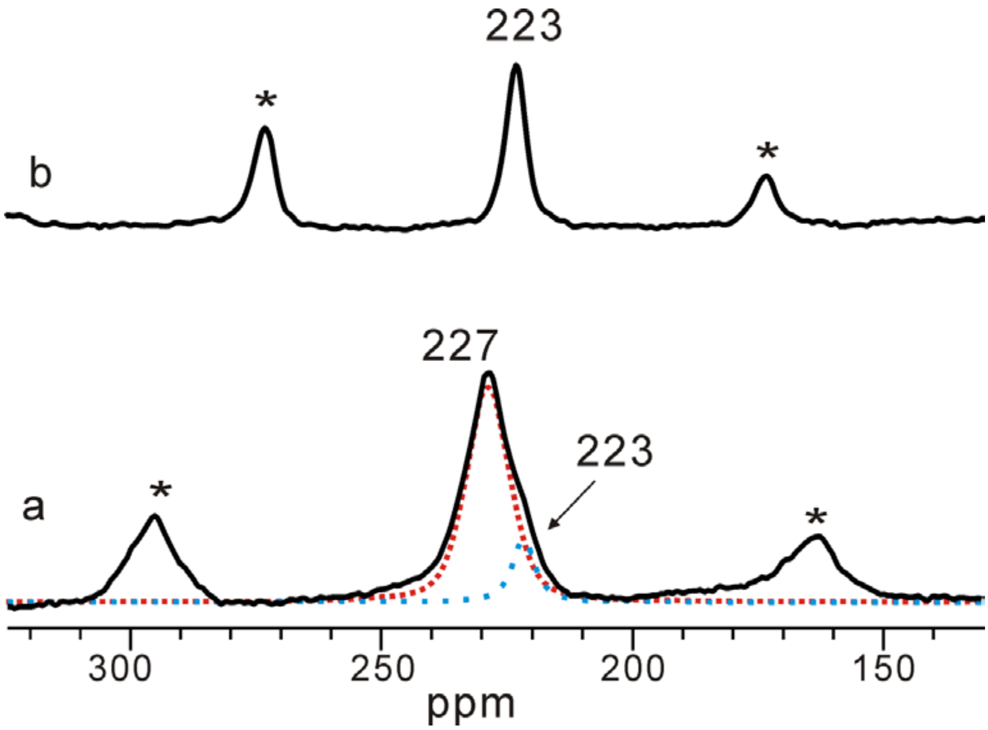

Figure S3. ^{13}C CP/MAS NMR spectra of 2-^{13}C-acetone adsorbed on (a) Zn^{2+}/ZSM-5 and (b) HZSM-5. One type of Zn ions as Lewis acid site (227 ppm) and one type of Brönsted acid site (223 ppm) are resolved on Zn^{2+}/ZSM-5. Asterisks denote spinning sidebands.

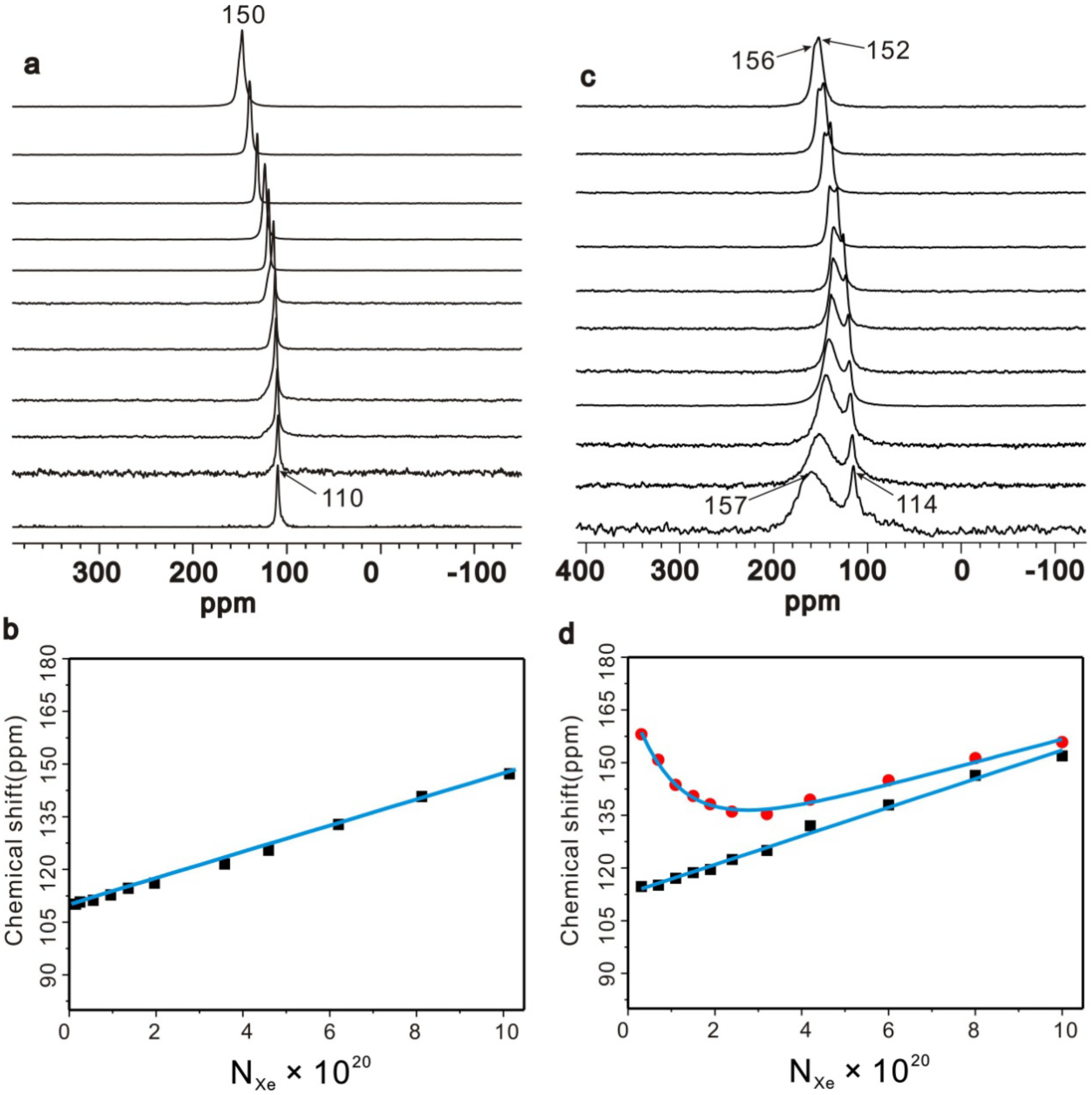

Figure S4. ^{129}Xe NMR spectra as a function of xenon density and the corresponding ^{129}Xe chemical shifts as a function of xenon density. (a, b) HZSM-5 and (c, d) Zn^{2+}/ZSM-5. For the Zn^{2+}/ZSM-5 sample, two xenon adsorption sties at 157 and 114 ppm are identified at low xenon pressure, corresponding to xenon atoms adsorbed on Zn^{2+} ions and in the channel of ZSM-5 zeolite, respectively.

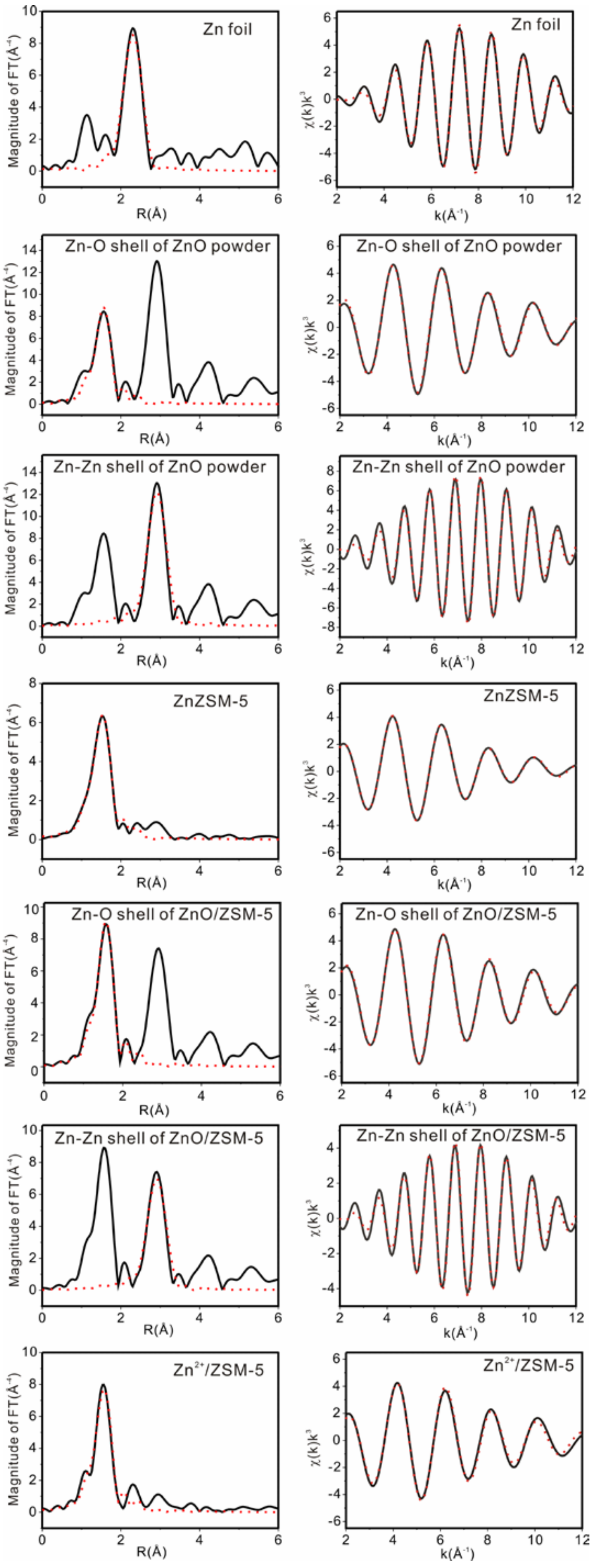

Figure S5. Experimental (solid line) and theoretical (dotted line) EXAFS spectra of reference compounds and ZnZSM-5 catalyst.

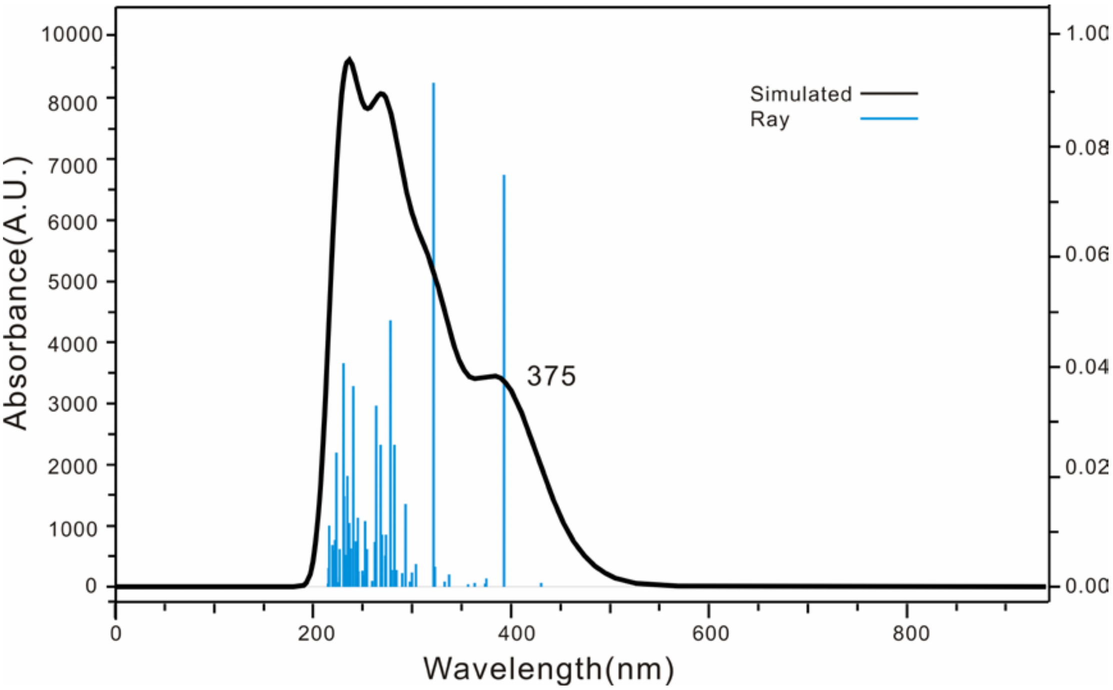

Figure S6. Calculated ray and simulated Uv–Vis spectra of the Zn^{+}–O^{-}–Zn^{2+}cluster in ZnZSM-5.

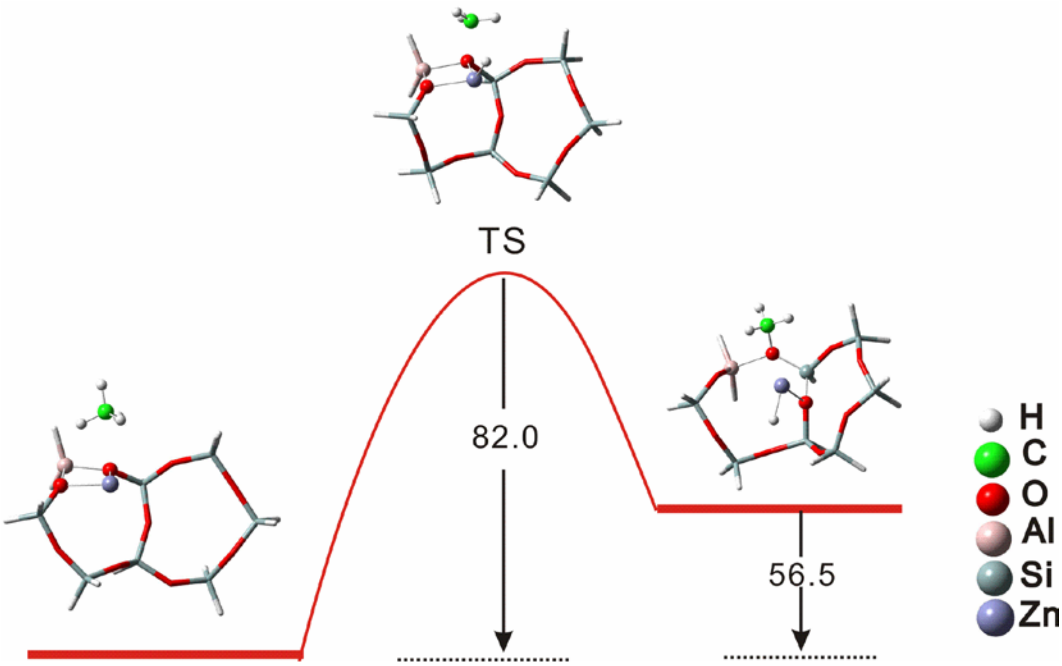

Figure S7. Proposed pathway for the formation of surface methoxy species (CH_3O–) on isolated Zn^+ ion. Calculated energies (kcal/mol) are indicated.

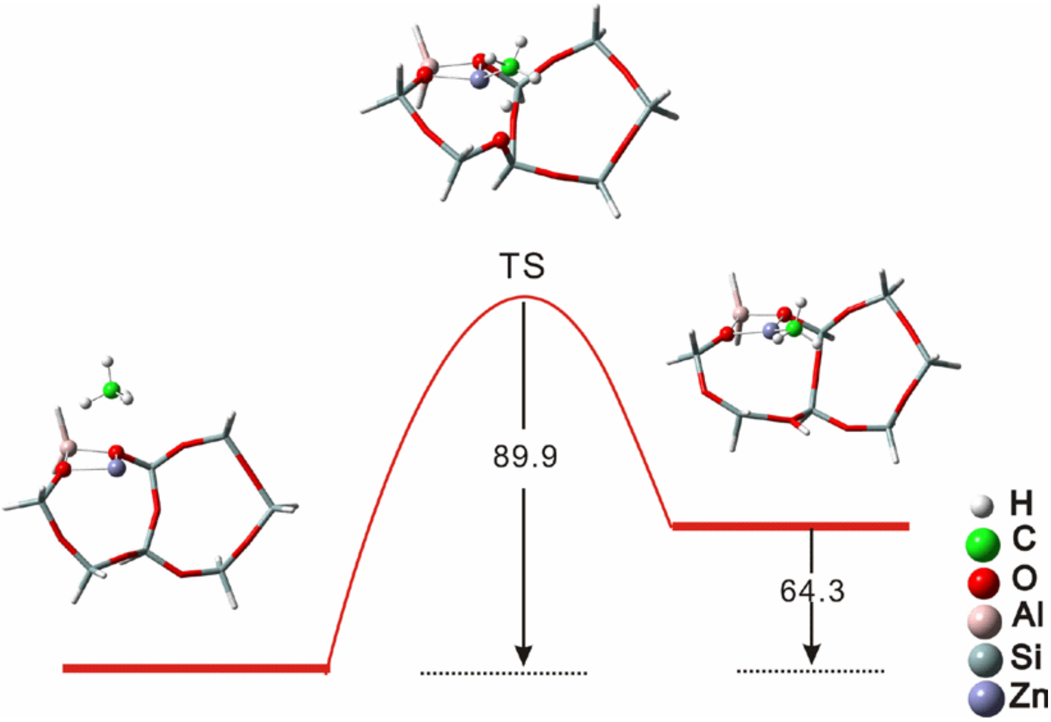

Figure S8. Proposed pathway for the formation of zinc methyl species (Zn–CH_3) on isolated Zn^+ ion. Calculated energies (kcal/mol) are indicated.