Supporting Information

Probing the active sites for methane activation on Ga/ZSM-5 zeolites with solid-state NMR spectroscopy

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Experimental Methods

Materials and sample Preparation

Ammonium form ZSM-5 (SiO_2/Al_2O_3 = 23, Zeolyst) was calcined in air at 823 K for 6 h to obtain the proton form H-ZSM-5. H-ZSM-5 and $Ga(NO_3)_3 \cdot xH_2O$ (99.99 % metal basis, purchased from Aladdin Reagent Co., Ltd.) were used as starting materials. Ga-zeolites were prepared by incipient wetness impregnation according to the previously reported procedure[1]. In general, 2 g of H-ZSM-5 was added into 3 mL of $Ga(NO_3)_3$ solution containing 0.3668 g $Ga(NO_3)_3 \cdot xH_2O$. The resulting mixture was stirred at room temperature for 5 h. Then the sample was dried at 383 K for 10 h and calcined at 773 K under flowing air for 6 h. The obtained catalyst was denoted as Ga/ZSM-5. The Ga/ZSM-5 sample was then subjected to a reduction-oxidation cycle under a H_2-O_2 flow at different temperature (523~773K). 1g of Ga/ZSM-5 was pressed and crushed into pellets between 40~60 mesh and then placed into a stainless tubular fixed-bed reactor (6 mm ID, 26 cm length). The sample was gradually heated at a temperature ramp rate of 2 K/min under N_2 atmosphere until reaching the target temperature and treated with 10% H_2/N_2 mixture for 2 h, then the flowing gas was switched to dry air and kept for 2 h. The sample was then cooled down to room temperature in dry air. All the gas flow rates were 60 sccm. The resultant sample was denoted as Ga/ZSM-5-X (X denotes the treating temperature). All Ga/ZSM-5 samples contain ca. 5 wt % of gallium.

Methane activation

The activation of ^{13}C-enriched methane (^{13}C, 99 %, Cambridge Isotope Laboratories, Inc.) was carried out in a sealed glass tube (6 mm ID, 5 cm length) according to the previously reported procedure[1b]. Typically, a controlled amount of ^{13}CH$_4$ was introduced onto the pre-activated Ga-modified ZSM-5 catalyst in a glass tube under vacuum at the temperature of liquid N$_2$, and then the glass tube was sealed off from the vacuum system with flam. The reaction was performed in the sealed glass tube at 573 K for 1 h and then quenched by liquid N$_2$. Prior to NMR measurements, the reacted sample was degassed on a vacuum line to remove the physically adsorbed methane, and then transferred to NMR rotor under dry nitrogen atmosphere in a glovebox. The reacted Ga/ZSM-5-X sample was denoted as Ga/ZSM-5-X-^{13}CH$_4$.

X-ray power diffraction (XRD) measurement

The structure and crystalline nature of H-ZSM-5 and different Ga/ZSM-5 were examined by X-ray diffractometer (X'Pert^3 Powder) using a CuKα radiation with a step of 0.02° at a respective voltage of 40 kV and a current of 40 mA.

Transmission electron microscopy (TEM) measurement

TEM imaging experiments were carried out by using a FEI Tecnai G2 f20 microscope equipped with a Schottky gun operating at 200 kV.

Solid-state NMR experiments

^{27}Al MAS and ^{13}C CP/MAS solid-state NMR experiments were carried out at 9.4 T on a Bruker Avance III 400 spectrometer with resonance frequencies of 399.33, 104.05 and 100.42 MHz for ^{1}H, ^{27}Al and ^{13}C, respectively. All the NMR spectra were

acquired on a 4 mm double-resonance probe with a spinning rate of 10 kHz. [7]Al MAS NMR spectra were recorded using small-flip angle technique with a pulse length of 0.36 μs (<π/12) and a recycle delay of 1s. The [27]Al chemical shifts were referenced to 1M Al(NO$_3$)$_3$ aqueous solution (0 ppm). For the [1]H→^{13}C CP/MAS NMR experiments, the Hartmann-Hahn conditions was achieved using hexamethylbenzene (HMB), with a contact time of 4 ms and a repetition time of 2 s. The ^{13}C chemical shifts were referenced to adamantine.

[31]P MAS, [71]Ga QCPMG, [1]H-[71]Ga S-RESPDOR, [13]C-^{27}Al S-RESPDOR solid-state NMR experiments were carried out at 11.7 T on a Bruker Avance III 500 spectrometer with resonance frequencies of 500.57, 202.64, 152.66, 125.87 and 130.44 MHz for ^{1}H, ^{31}P, [71]Ga, ^{13}C and [27] Al, respectively. Single-pulse ^{31}P MAS experiments with high power proton decoupling were performed on a 4 mm probe, using a π/2 pulse of 3.95 μs and a spinning rate of 10 kHz. 420 scans were collected for each spectrum with a recycle delay of 80 s.

[71]Ga WURST-QCPMG[2] experiments were performed using a 1.9 mm probe at a spinning rate of 40 kHz. The central transition (CT) signal was enhanced by irradiating a single satellite transition (ST) sideband using WURST pulse before the CT-selective pulse. Rotor-synchronized inter-pulses and inter-acquisition delays were employed in the QCPMG scheme. The acquisition time for each full echo was 0.56 ms and the number of Meiboom-Gill loops was 12. [71]Ga WURST-QCPMG spectra of Ga/ZSM-5 were acquired by averaging about 96,000 transients with a recycle delay of

1 s. The ^{71}Ga chemical shifts were referenced to 1 M Ga(NO$_3$)$_3$ aqueous solution (0 ppm).

In ^{1}H-{^{71}Ga} S-RESPDOR experiments, the duration of ^{71}Ga saturation pulse was set to 1.5 rotor periods with $\nu_1(71Ga) = 110$ kHz. The ^{1}H *rf* nutation frequency of the $\pi/2$ and π pulses was $\nu_{1H} = 62.5$ kHz, which yields $\pi/2$ and π pulse lengths of 4 and 8 μs, respectively. The ^{1}H-^{71}Ga dipolar couplings were reintroduced by applying SR42 1 heteronuclear recoupling pulse sequence on the ^{1}H channel with $\nu_{1H} = 2\nu_R = 25$ kHz. 2000 scans were collected for each spectrum with a recycle delay of 2 s. The scan-to-scan alternation of the collection of S and S_0 spectra was used to reduce the effect of spinning speed fluctuation [1a, 3].

^{13}C-^{27}Al S-RESPDOR experiments were performed on a 4 mm HX double-resonance probe with a frequency splitter (REDOR-BOX) attached to X channel, which enables tuning and matching to both ^{13}C and ^{27}Al Larmor frequencies on the X channel. ^{1}H→^{13}C cross polarization (CP) with a contact time of 3 ms was employed to prepare the initial ^{13}C signal. SR4 dipolar recoupling[4] was used on the ^{13}C channel with $\nu_{13C} = 20$ kHz. Continuous-wave ^{1}H decoupling with an amplitude of 71.4 kHz was used during SR4, while a TPPM (two pulse phase modulation) ^{1}H decoupling with an amplitude of 71.4 kHz was used during acquisition. A π pulse length of 8 μs was used on the ^{13}C channel. The saturation pulse on the ^{27}Al channel with an amplitude of 53.4 kHz and the length of 100 μs = TR was utilized to transfer ^{13}C-^{27}Al interactions. The number of scans for each experiment was determined according to the strength of ^{13}C signal with recycle delay of 3 s. The magic angle spinning rate was set to 10 kHz.

Analytical simulation of the ^{13}C-^{27}Al dephasing curve

The simulation of ^{13}C-^{27}Al dephasing curve was performed according to previous report[3]. For an ideal case in which the heteronuclear dipolar dephasing is only induced by an isolated nuclear spin pair, the analytical formula of S-RESPDOR is expressed as:

$$\frac{\Delta S}{S_0} = \frac{f}{2I+1}\left\{2I - \frac{\pi\sqrt{2}}{4(2I+1)}\sum_{k=1}^{2I}[4I-2(k-1)]J_{1/4}\left(\frac{k\pi\lambda}{4}\right)J_{-1/4}\left(\frac{k\pi\lambda}{4}\right)\right\}$$

where I is the spin quantum number of the quadrupolar nucleus and $J_{\pm 1/4}$ denotes $\pm 1/4$–order Bessel function of the first kind. The dimensionless parameter $\lambda = \tau * |D_{IS}|$, where the I and S nuclei are the non-observed (^{27}Al) and the observed (^{13}C) nuclei respectively, is equal to the product of the dephasing period and the dipolar coupling constant in rad s^{-1}. The formula depends on the dimensionless parameter λ and the pre-factor parameter f. Note that the parameter f represents the fraction of sample in which the spin states of quadrupolar nucleus are saturated by the saturation pulse, and is equal to 1 only for 100 %-abundant I nuclei experiencing a complete saturation. Meanwhile, the $D_{IS} = \frac{\mu_0 \gamma_I \gamma_S h}{4\pi^2 r_{IS}^3}$ is the heteronuclear dipolar interaction between two spins, reflecting the distance, r_{IS}, between two interactive nuclei. In present case, the ^{13}C-^{27}Al dipolar dephasing curves were fitted by the above analytical formula. The parameter f and D_{IS} were determined by best fitting the experimental dephasing curves, and the ^{13}C-^{27}Al distances were accordingly obtained.

Computational method

The H-ZSM-5 zeolite is represented by 72T cluster models, which was extracted from their crystallographic structural data [http://www.iza-structure.org/databases/]. It contains the complete double 10-MR intersection pores of ZSM-5 zeolite. The terminal Si-H was fixed at a bond length of 1.47 Å, oriented along the direction of the corresponding Si-O bond. The extra-framework Ga-CH$_3$ species was coordinated to zeolite framework oxygen, and two framework Al atoms located at T12 and T7 sites were used to maintain the electric neutralization of calculated models. In this work, the 24T active site atoms and the Ga-CH$_3$ species were treated as the high-layer, while the rest of the frameworks were treated as the low-layer. To retain the structural integrity of the modeled zeolite, partial structure optimizations of the 72T cluster were performed by relaxing the atoms in the high-level layer while keeping the rest of atoms fixed at their crystallographic positions. A combined theoretical approach, namely ONIOM (ωb97xd/6-31G(d,p): hf/3-21g) was used for the geometry optimization. The ωB97XD hybrid density function was developed to consider long-range-corrected hybrid functional[5], which implicitly accounted for empirical dispersion and could describe long-range dispersion interactions well with respect to the traditional density functional theory methods. This functional was also recently found to perform very well for the description of zeolite structures.
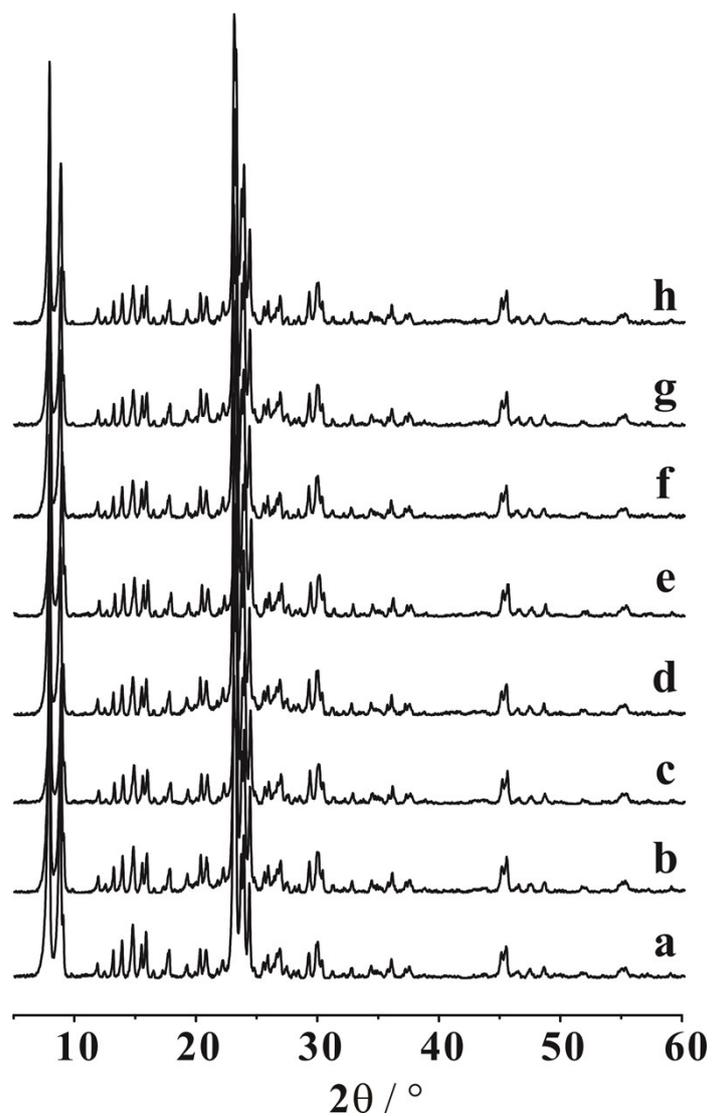
Figure S1. XRD patterns of H-ZSM-5 and Ga/ZSM-5 zeolites: (a) H-ZSM-5, (b) Ga/ZSM-5, (c) Ga/ZSM-5-250, (d) Ga/ZSM-5-300, (e) Ga/ZSM-5-350, (f) Ga/ZSM-5-400, (g) Ga/ZSM-5-450 and (h) Ga/ZSM-5-500.
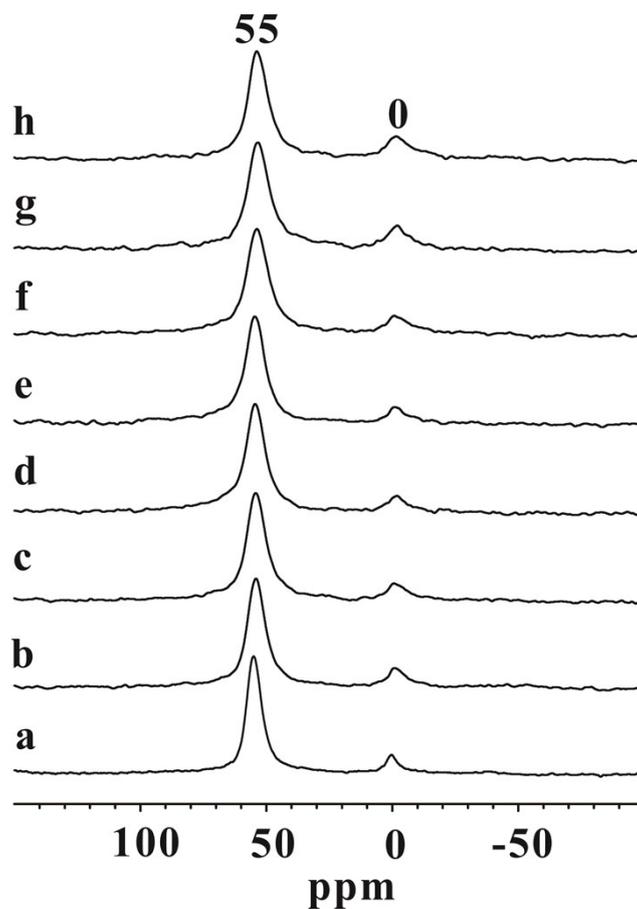
Figure S2. ^{27}Al MAS NMR spectra of H-ZSM-5 and Ga/ZSM-5 zeolites. (a) H-ZSM-5, (b) Ga/ZSM-5, (c) Ga/ZSM-5-250, (d) Ga/ZSM-5-300, (e) Ga/ZSM-5-350, (f) Ga/ZSM-5-400, (g) Ga/ZSM-5-450, and (h) Ga/ZSM-5-500. Tetrahedral framework Al site at 55 ppm is observable on all the Ga/ZSM-5 zeolites. The weak signal at 0 ppm is assigned to octahedral extra-framework Al arising from dealumination during catalyst preparation or post-treatment.
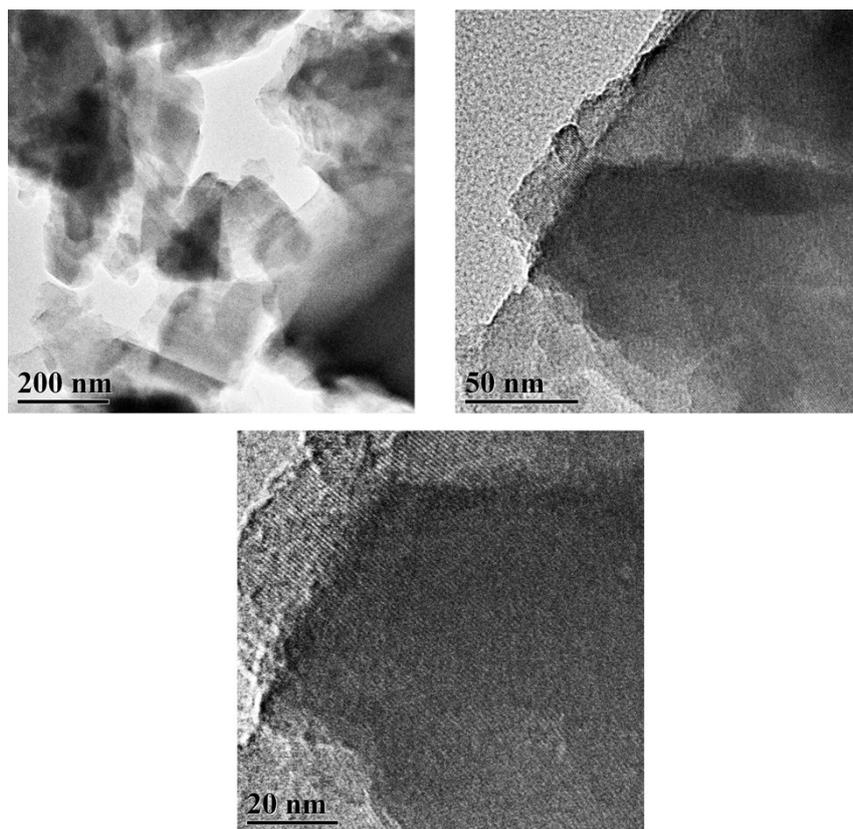
Figure S3. TEM images of Ga/ZSM-5-450 zeolite.
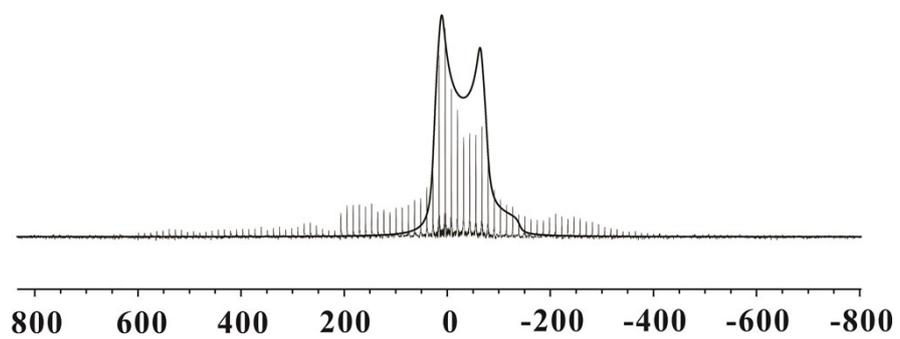
Figure S4. [71]Ga QCPMG MAS NMR spectra of bulk Ga_2O_3 powder.

Table S1. NMR parameters extracted from [71]Ga QCPMG NMR spectra and the relative content of Ga species on Ga/ZSM-5 corresponding to the signal at 58 and 190 ppm, respectively.

Sample	δ_{iso} (ppm)	C_Q (MHz)	relative content (%)
Ga/ZSM-5	58	8.3	64.9
	190	7.6	35.1
Ga/ZSM-5-250	58	8.3	62.5
	190	7.6	37.5
Ga/ZSM-5-300	58	8.3	60.1
	190	7.6	39.9
Ga/ZSM-5-350	58	8.3	55.4
	190	7.6	44.6
Ga/ZSM-5-400	58	8.3	52.2
	190	7.6	47.8
Ga/ZSM-5-450	58	8.3	49.7
	190	7.6	50.3
Ga/ZSM-5-500	58	8.3	47.6
	190	7.6	52.4
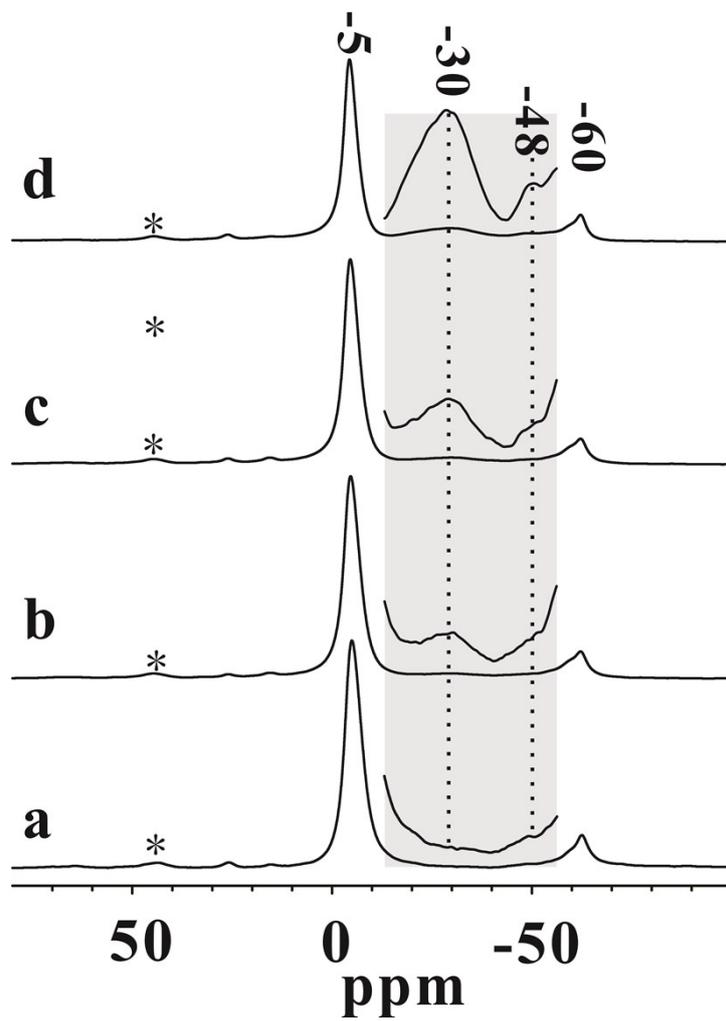
Figure S5. ^{31}P MAS NMR spectra of TMP adsorbed on H-ZSM-5 and Ga/ZSM-5: (a) H-ZSM-5, (b) Ga/ZSM-5-250, (c) Ga/ZSM-5-350, and (d) Ga/ZSM-5-450.
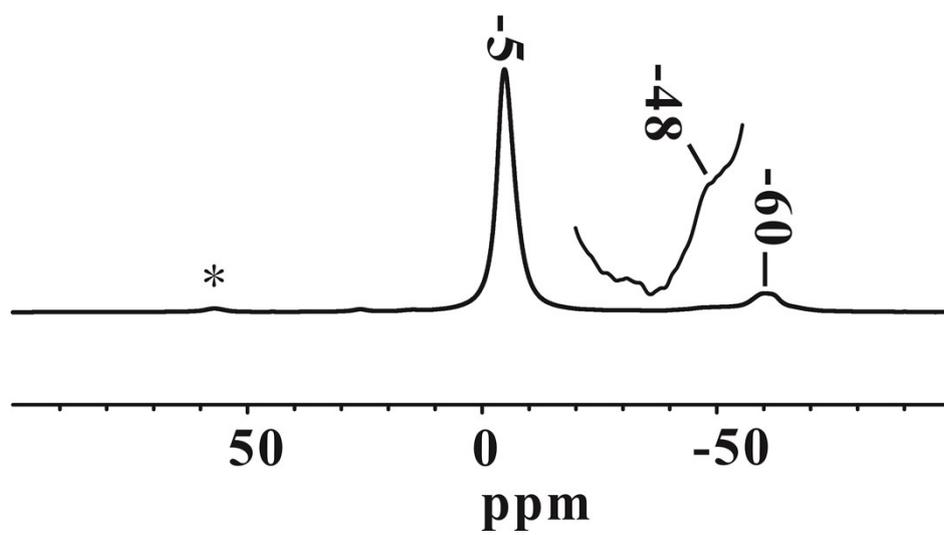
Figure S6. ^{31}P MAS NMR spectra of TMP adsorbed on Ga_2O_3/ZSM-5.
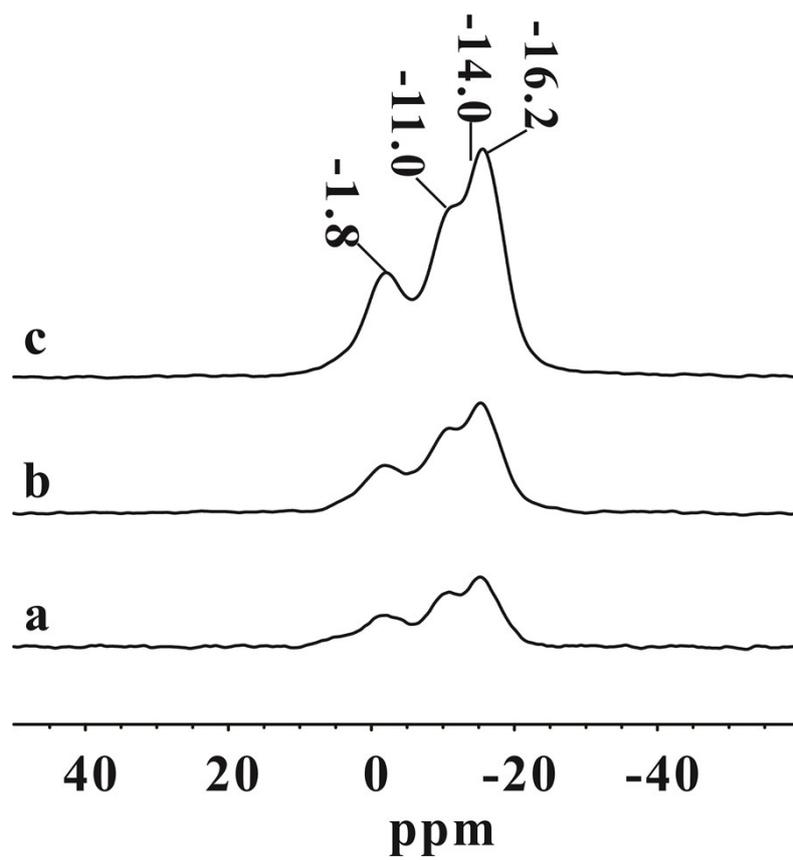
Figure S7. ^{13}C CP/MAS spectra of Ga/ZSM-5-250 (a), Ga/ZSM-5-350 (b), and Ga/ZSM-5-450 (c) reacted with $^{13}CH_4$ at 573 K for 1h.
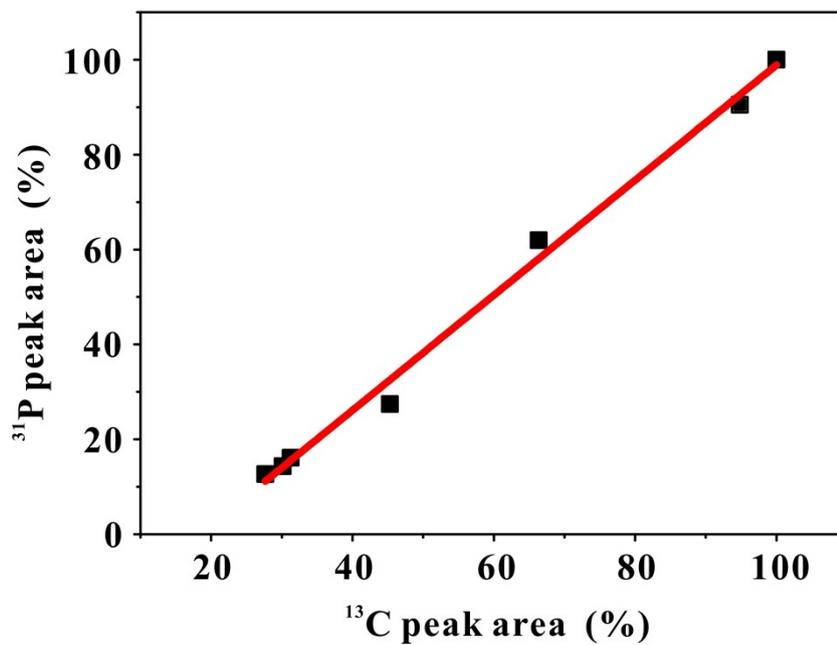
Figure S8. Normalized ^{31}P peak integration (-30 ppm) as a function of normalized ^{13}C peak integration of the Ga-CH$_3$ groups on Ga/ZSM-5, Ga/ZSM-5-250, Ga/ZSM-5-300, Ga/ZSM-5-350, Ga/ZSM-5-400, Ga/ZSM-5-450 and   Ga/ZSM-5-500.

References

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