[*Supporting Information*]

Mechanistic Insight into the Formation of Acetic Acid from the Direct Conversion of Methane and Carbon Dioxide on Zinc-Modified H–ZSM-5 Zeolite

Jian-Feng Wu,[†] Si-Min Yu,[†] Wei David Wang,[†] Yan-Xin Fan,[†] Shi Bai,[†] Chuan-Wei Zhang,[‡] Qiang Gao,[‡] Jun Huang,[□] and Wei Wang[†]*

[†]State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, P. R. China

[‡]National Engineering Research Center for Fine Petrochemical Intermediates, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, Gansu 730000, P. R. China

[□]Laboratory for Catalysis Engineering, School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia

wang_wei@lzu.edu.cn

Contents

A. Experimental section

Materials. As-synthesized zeolite Na–ZSM-5 (n_{Si}/n_{Al} = 15) were purchased from the Catalyst Plant of Nankai University, Tianjin. ^{13}C-labeled methane (^{13}C-enrichment of 99%) and carbon dioxide (^{13}C-enrichment of 99%) were purchased from Spectra Gases and Cambridge Isotopes, respectively.

Sample preparation. H–ZSM-5 (n_{Si}/n_{Al} = 15) and Zn/H–ZSM-5 zeolites (n_{Si}/n_{Al} = 15, Zn content of 5.9 ± 0.1 wt%) were prepared[1] and characterized by spectroscopic methods, such as PXRD and solid-state NMR spectroscopy. Zn/H–ZSM-5 zeolite was obtained by impregnation of zeolite H–ZSM-5 with $Zn(NO_3)_2$. Typically, $Zn(NO_3)_2$•$6H_2O$ (0.292 g) was dissolved in deionized water (1.21 mL), into which zeolite H–ZSM-5 (1.00 g) was added under stirring. The impregnated zeolite was dried in a rotary evaporator at 333 K for 0.5 h and treated in a muffle furnace at 673 K for 6 h. The Zn/H–ZSM-5 samples were then obtained after further calcination in glass tubes in vacuum (< 10^{-2} mbar) at 693 K for 20 h.

Co-conversion of CH_4 and CO_2 on Zn/H–ZSM-5 catalyst. Methane (*ca.* 50 mbar, ^{13}C-enriched or non-labeled) and carbon dioxide (*ca.* 50 mbar, ^{13}C-enriched or non-labeled) were co-adsorbed on the activated Zn/H–ZSM-5 catalyst (*ca.* 0.15 g) on a vacuum line and then flame-fused in a glass tube (the outer diameter of about 6 mm and the length of about 180 mm). After the reaction at 473–773 K for 20 min, the glass tube was cooled down with liquid nitrogen and opened in a glove box; and the catalyst was quickly transferred into a 4 mm MAS NMR rotor for solid-state NMR analysis.

Activation of $^{13}CH_4$ on Zn/H–ZSM-5 catalyst. The reaction was conducted on a Zn/H–ZSM-5 catalyst with $^{13}CH_4$ (51 mbar) at 453 K for 45 min and then the working catalyst was evacuated for 20 min to remove unreacted $^{13}CH_4$.

Activation of zinc acetate [$Zn(CH_3COO)_2$]. Zinc acetate dihydrate [$Zn(CH_3COO)_2$•$2H_2O$] was loaded into a glass tube and activated at 373 K in vacuum (< 10^{-2} mbar) for 5 h. The glass tube was then flame-fused for further use.

Reaction of zinc acetate [$Zn(CH_3COO)_2$] on H–ZSM-5 zeolite. Activated H–ZSM-5 zeolite (0.27 g) and anhydrous zinc acetate [$Zn(CH_3COO)_2$] (0.19 g) were mixed in a glove box and the sample was transferred into a 4 mm MAS NMR rotor. The rotor without a cap was placed into a glass tube (inner diameter of about 4.4 mm and length of about 180 mm) which was then flame-fused. Upon the reaction at a given temperature, the fused glass tube was cooled in liquid nitrogen, opened in a glove box, and the rotor was capped for the solid-state NMR measurements.

Glass insert experiment. $^{13}CH_4$ (5 mbar) and $^{13}CO_2$ (5 mbar) were co-adsorbed on Zn/H–ZSM-5 catalyst (0.068 g) on a vacuum line in a glass insert (*ca.* 0.17 cm^3) which was then flame-fused symmetrically. After the reaction at 673 K for 20 min, the sealed glass insert was fitted into a 7 mm rotor for the solid-state NMR measurements.

Solid-State NMR experiments.

Experiments with the 4 mm NMR probe. The ^{1}H MAS NMR and the ^{13}C MAS NMR [^{13}C high-power proton decoupling (HPDEC) or ^{13}C cross-polarization (CP)] investigations were performed with a 4 mm Bruker MAS NMR probe on a Bruker Avance II WB 400 MHz NMR spectrometer under magic-angle-spinning (MAS), and with the spinning rate of 10.0 kHz. ^{13}C HPDEC MAS NMR spectra were recorded with a $\pi/2$ excitation of 4.0 μs and a repetition time of

5 s. ^{13}C CP/MAS NMR experiments were performed with a contact time of 3.0 ms and a repetition time of 3 s. ^{1}H MAS experiments were carried out with a $\pi/2$ excitation of 4.0 μs and a repetition time of 5 s. The ^{1}H and ^{13}C chemical shifts were referenced to tetramethylsilane (TMS) and the precision of the ^{1}H and ^{13}C chemical shift is of ±0.1 and ±1.0 ppm, respectively.

Experiment with the 7 mm NMR probe. Some of the ^{13}C HPDEC MAS NMR investigations (indicated accordingly in the text) were performed with a 7 mm Bruker MAS NMR probe on a Bruker Avance II WB 400 MHz NMR spectrometer with the spinning rate of 3.5 kHz. The ^{13}C HPDEC MAS NMR spectra were recorded with a $\pi/2$ excitation of 8.4 μs and a repetition time of 15 s. The ^{13}C chemical shifts were referenced to adamantane and the precision of the ^{13}C chemical shift is of ±1.0 ppm.

B. Structural characterization of Zn/H–ZSM-5 zeolite

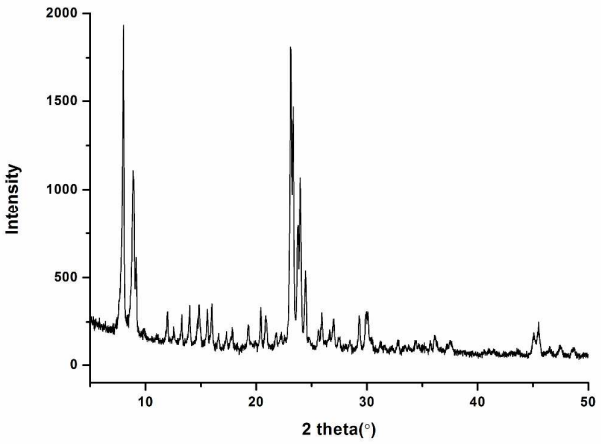

Figure S1. PXRD pattern of the synthesized Zn/H–ZSM-5 catalyst, which is in accordance with those[2] previously reported.

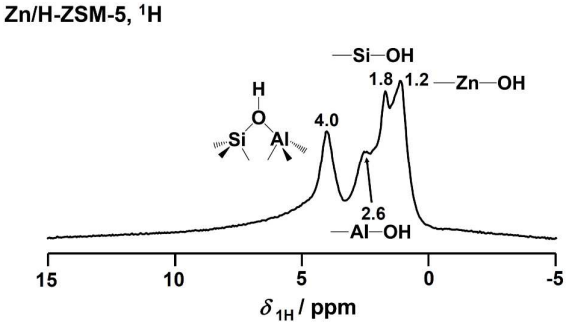

Figure S2. ^{1}H MAS NMR spectrum of the synthesized Zn/H–ZSM-5 zeolite recorded with a 4 mm NMR probe. The ^{1}H NMR signals at 4.0, 2.6, 1.8 and 1.2 ppm are attributed[3] to hydrogen atoms at Brönsted acid site, –Al–OH, –Si–OH, and –Zn–OH groups, respectively.

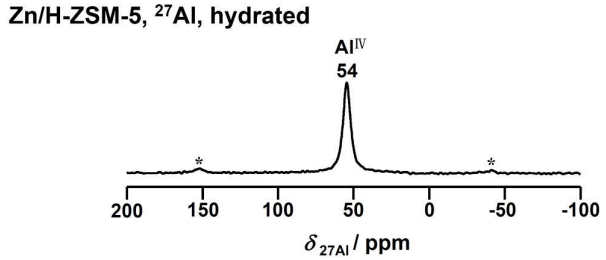

Figure S3. ^{27}Al MAS NMR spectrum of the Zn/H–ZSM-5 zeolite recorded after sample hydration. The ^{27}Al NMR signal at 54 ppm is due to the 4-coordinated framework aluminum atoms (Al^{IV})[1]. The ^{27}Al MAS NMR spectrum was obtained with a 4 mm NMR probe.

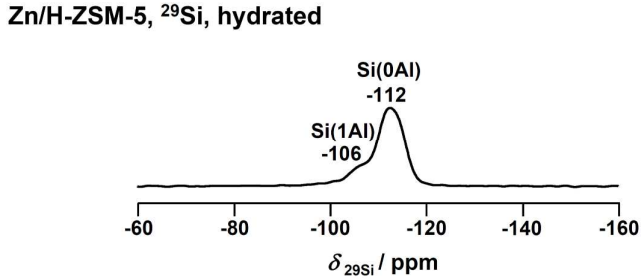

Figure S4. ^{29}Si MAS NMR spectrum of the Zn/H–ZSM-5 zeolite after sample hydration. The ^{29}Si NMR signals at −106 and −112 ppm are assigned to Si(1Al) and Si(0Al) atoms[4], respectively. The ^{29}Si MAS NMR spectrum was obtained with a 4 mm NMR probe.

C. Decomposition of acetic acid into CH_4 and CO_2 on Zn/H–ZSM-5 catalyst

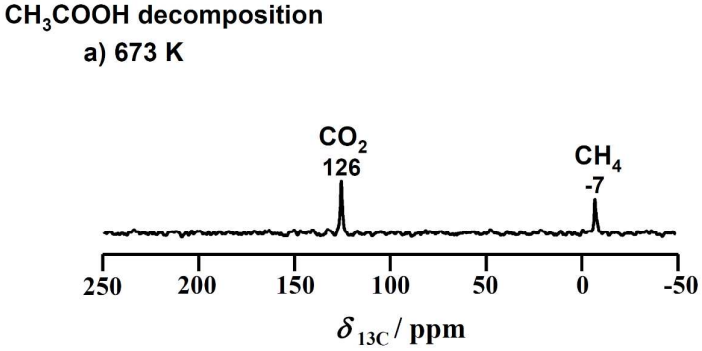

Figure S5. Solid-state NMR investigation on the decomposition of acetic acid into CH_4 and CO_2 on Zn/H–ZSM-5 catalyst. The ^{13}C HPDEC MAS NMR spectrum was recorded with a 4 mm NMR probe after the reaction of acetic acid on Zn/H–ZSM-5 catalyst at 673 K for 20 min.

D. Co-conversion of CH_4 and CO_2 on Zn/H–ZSM-5 catalyst

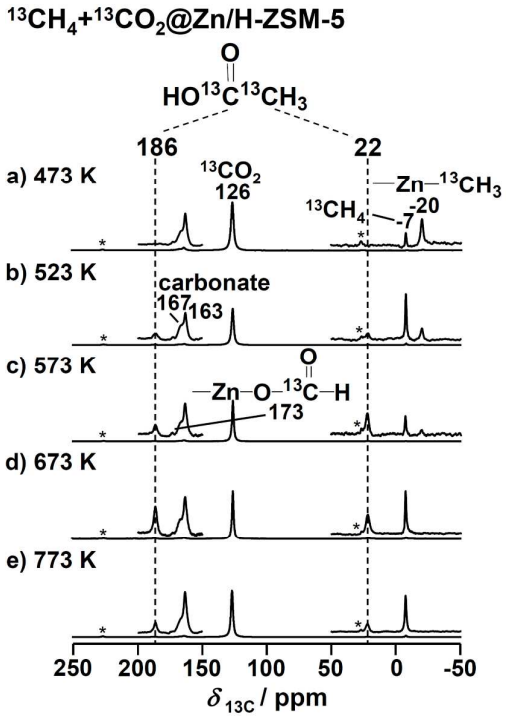

Figure S7. Solid-state NMR investigation on the co-conversion of methane and carbon dioxide over Zn/H–ZSM-5 zeolite. The ^{13}C HPDEC MAS NMR spectra were recorded after the reaction of $^{13}CH_4$ and $^{13}CO_2$ on Zn/H–ZSM-5 zeolite at a) 473 K, b) 523 K, c) 573 K, d) 673 K, and e) 773 K. The asterisks denote the spinning sidebands. The spectra were recorded with a 4 mm probe.

E. Sealed glass insert experiment

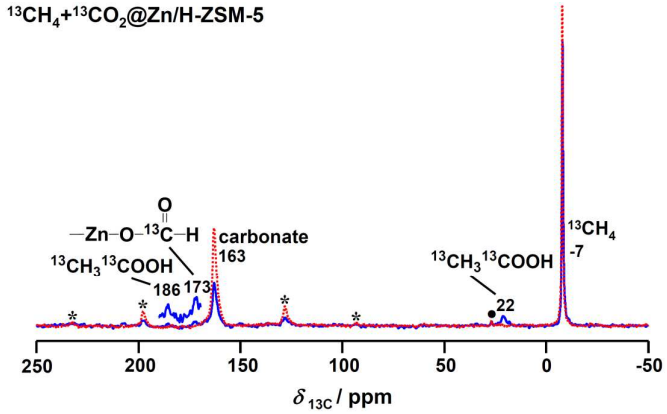

Figure S6. Investigation on the reaction of CH_4 and CO_2 on Zn/H–ZSM-5 catalyst performed in a glass insert. The ^{13}C HPDEC MAS NMR spectra were recorded before (dotted line) and after (solid line) the reaction of $^{13}CH_4$ and $^{13}CO_2$ on Zn/H–ZSM-5 catalyst at 673 K for 20 min. The asterisks and the black dot denote the spinning sidebands. The spectra were recorded with a 7 mm NMR probe.

F. Investigation on the origin of carbon atoms of acetic acid

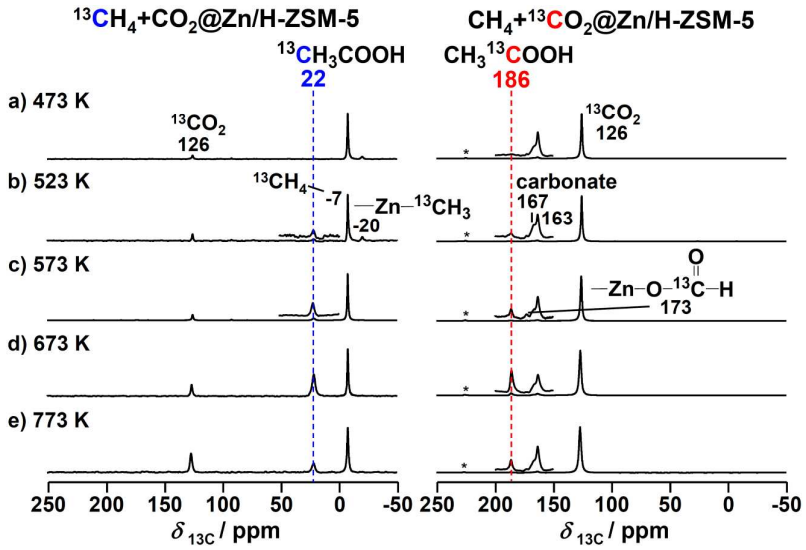

Figure S8. Solid-state NMR investigation on the origin of carbon atoms of acetic acid. The ^{13}C HPDEC MAS NMR spectra were recorded after the reaction of ^{13}C-labled methane ($^{13}CH_4$) with non-labeled carbon dioxide (CO_2) (left) and of non-labeled methane (CH_4) with ^{13}C-labled carbon dioxide ($^{13}CO_2$) (right) on Zn/H–ZSM-5 zeolite at a) 473K, b) 523K, c) 573K, d) 673K, and e) 773 K. The asterisks denote the spinning sidebands. The spectra were recorded with a 4 mm probe.

G. Evidence for the ^{1}H MAS NMR assignment of zinc methyl species (–Zn–$^{13}CH_3$)

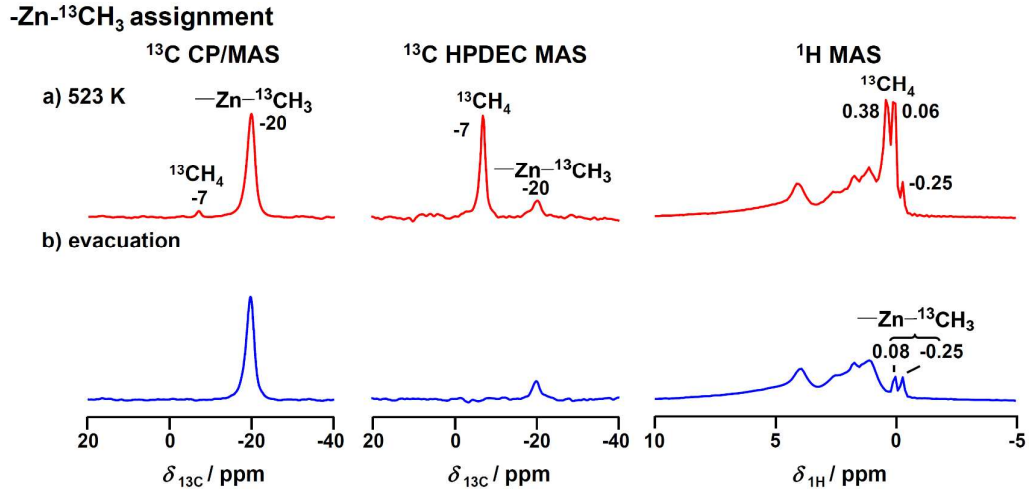

Figure S9. The ^{13}C CP/MAS NMR (left), ^{13}C HPDEC NMR (middle), and ^{1}H MAS NMR (right) spectra were recorded, a) upon the activation of $^{13}CH_4$ on Zn/H–ZSM-5 zeolite at 523 K for 20 min; and b) after the evacuation of sample a) for 20 min. After evacuation, no $^{13}CH_4$ signal could be observed at –7 ppm (for adsorbed methane) or –10 ppm (for gaseous methane) in the corresponding ^{13}C CP/MAS (bottom, left) and ^{13}C HPDEC MAS (bottom, middle) NMR spectra. These results indicated that unreacted $^{13}CH_4$ in a) had been totally removed after evacuation in b). Thus, only the zinc methyl species (–Zn–$^{13}CH_3$, ^{13}C NMR chemical shift of –20 ppm) was remained on Zn/H–ZSM-5 zeolite after evacuation. Accordingly, the ^{1}H NMR doublets at 0.08 and –0.25 ppm in the corresponding ^{1}H MAS NMR spectrum (bottom, right) should be assigned exclusively as zinc methyl species (–Zn–$^{13}CH_3$). All the spectra were recorded with a 4 mm NMR probe.

H. Activation of methane on Zn/H–ZSM-5 catalyst

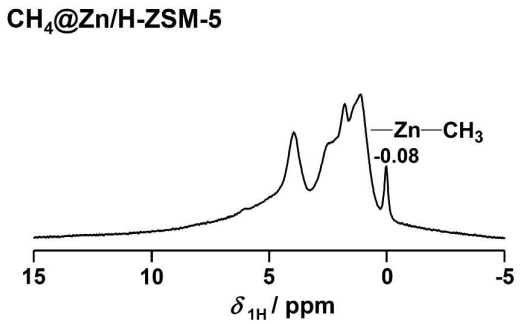

Figure S10. Solid-state NMR investigation on the activation of methane alone on Zn/H–ZSM-5 catalyst. The ^{1}H MAS NMR spectrum was recorded after the activation of non-labeled CH_4 (52 mbar) on Zn/H–ZSM-5 catalyst at 453 K for 45 min (unreacted CH_4 was removed upon evacuation thereafter). The spectrum was recorded with a 4 mm NMR probe.

I. References

1. Stepanov, A. G.; Arzumanov, S. S.; Gabrienko, A. A.; Toktarev, A. V.; Parmon, V. N.; Freude, D. *J. Catal.* **2008**, *253*, 11−21.
2. Chen, J.; Feng, Z.; Ying, P.; Li, C. *J. Phys. Chem. B* **2004**, *108*, 12669−12676.
3. a) Kolyagin, Y. G.; Ordomsky, V. V.; Khimyak, Y. Z.; Rebrov, A. I.; Fajula, F.; Ivanova, I. I. *J. Catal.* **2006**, *238*, 122−133. b) Berndt, H.; Lietz, G.; Völter, J. *Appl. Catal. A* **1996**, *146*, 365-379. c) Noei, H.; Qiu, H.; Wang, Y.; Löffler, E.; Wöll, C.; Muhler, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7092−7097.
4. Hunger, M.; Brunner, E., Characterization I–NMR Spectroscopy. In *Molecular Sieves–Science and Technology*, Vol. 4 (Eds: Karge, H. G. J. and Weitkamp, J.), Springer–Verlag: Berlin, **2004**, pp. 201−293.