

*Supporting information*

**Alkylation of benzene with carbon monoxide over Zn/H-ZSM-5 zeolite studied by in situ solid-state NMR spectroscopy**

**Xiumei Wang, Jun Xu\*, Guodong Qi, Chao Wang, Qiang wang, Feng Deng\***

State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics,  
Wuhan Center for Magnetic Resonance, Wuhan Institute of Physics and Mathematics,  
Chinese Academy of Sciences, Wuhan 430071, P. R. China; E-mail:  
xujun@wipm.ac.cn; dengf@wipm.ac.cn

## 1. Materials preparation

The Zn/H-ZSM-5 catalyst was prepared by reaction of metallic Zn vapour with HZSM-5 zeolite according to the previous report<sup>1</sup>. In brief, on a vacuum line, HZSM-5 zeolite (Si/Al=21, NanKai University) was dehydrated at a temperature of 673 K with a pressure below  $10^{-3}$  Pa over a period of 12 h, and Zn powder (99.999%, Sinopharm Chemical Reagent Co, Ltd.) was degassed at a pressure below  $10^{-3}$  Pa at room temperature. Then the dehydrated HZSM-5 and the degassed Zn powder were mixed (with a molar ratio of Zn/Al>1) and transferred into a CAVERN device<sup>2</sup> in a dry nitrogen atmosphere in a glovebox. The CAVERN device was then connected to the vacuum line, and the mixture was heated at a temperature of 773 K and a pressure of  $10^{-2}$  Pa for two hours. The excess of metallic Zn and the released hydrogen were removed by evacuation at 773 K for another 30 min. No structural changes of the zeolite framework and the extra-framework Al were found after Zn modification. The Zn content is *ca.* 3.8 wt % as determined by ICP, which results in a partial substitution of the Brønsted acid sites (Si-OH-Al) on H-ZSM-5 support and 47 % of the acid sites remaining on the Zn/H-ZSM-5 catalyst<sup>1, 3</sup>. Our previous work showed that *ca.* 1 wt % ZnO species (*i.e.*, Zn-O-Zn cluster) along with Zn<sup>+</sup> and Zn<sup>2+</sup> ions are present on the Zn/H-ZSM-5 catalyst<sup>3</sup>.

## 2. In situ Solid-State NMR experiments

<sup>13</sup>C<sub>6</sub>H<sub>6</sub> (<sup>13</sup>C, 99 %, Cambridge Isotope Laboratories, Inc.), <sup>13</sup>CO (<sup>13</sup>C, 99 %, Cambridge Isotope Laboratories, Inc.) and H<sub>2</sub> (99.99 %) were introduced onto the activated Zn/H-ZSM-5 catalyst in a glass ampule under vacuum at the temperature of

liquid N<sub>2</sub>, and then the glass ampule was sealed off from the vacuum system. The reaction was performed in the sealed ampule under elevated temperatures for a specific reaction period, quenched by liquid N<sub>2</sub>, and then the ampule was transferred into a 7.5 mm rotor for NMR measurements. All solid-state NMR experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer, equipped with a Chemagnetic triple-resonance 7.5 mm probe, with resonance frequencies of 400.13 and 100.6 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. Single-pulse <sup>13</sup>C MAS experiments with <sup>1</sup>H decoupling were performed by using a  $\pi/2$  pulse width of 4.8  $\mu$ s and a repetition time of 10 s. <sup>1</sup>H MAS experiments were carried out with a  $\pi/2$  pulse width of 5.3  $\mu$ s and a repetition time of 4 s. The magic angle spinning rate was set to 3~5 kHz. For the <sup>1</sup>H $\rightarrow$ <sup>13</sup>C CP/MAS NMR experiments, the Hartmann-Hahn condition was achieved using hexamethylbenzene (HMB), with a contact time of 2.0 ms and a repetition time of 2.0 s. The chemical shifts of <sup>13</sup>C and <sup>1</sup>H were referenced to adamantane as a second reference.

### **3. GC-MS analysis**

The catalyst with adsorbed products were dissolved in 15 wt % HF solution and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The bottom layer organic phase of the extracted solution was separated and analysed on Shimadzu GC-MS QP 2010plus gas chromatograph with aRxi™-5ms column (30 m length, 0.25 mm id., 0.25 $\mu$ m film).

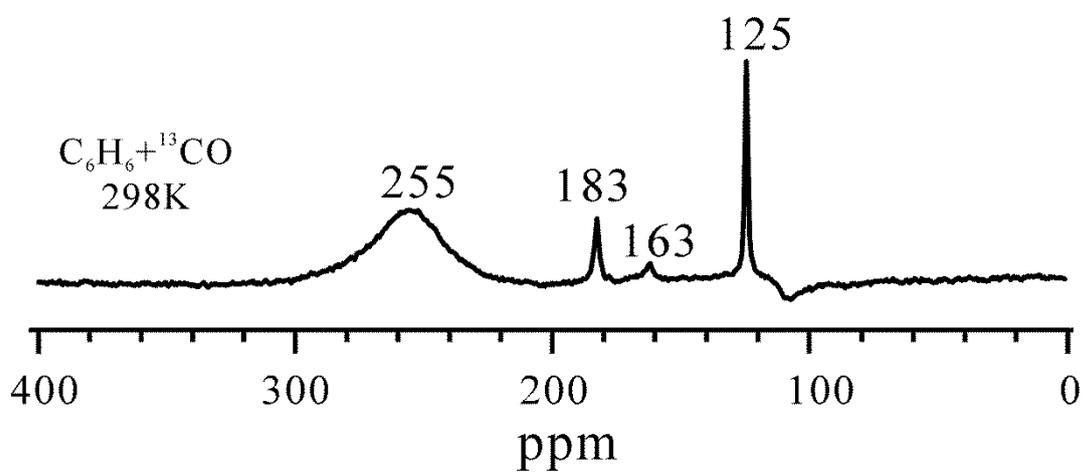


Figure S1.  $^{13}\text{C}$  MAS NMR spectrum obtained from adsorption of  $^{13}\text{CO}$  and benzene on Zn/H-ZSM-5 catalyst at 298 K for 1 h. The signals at 125, 183, 163 and 255 ppm were due to gaseous  $\text{CO}_2$ , gaseous CO, carbonate species and chemically adsorbed CO on Lewis acid site (Zn site) respectively.

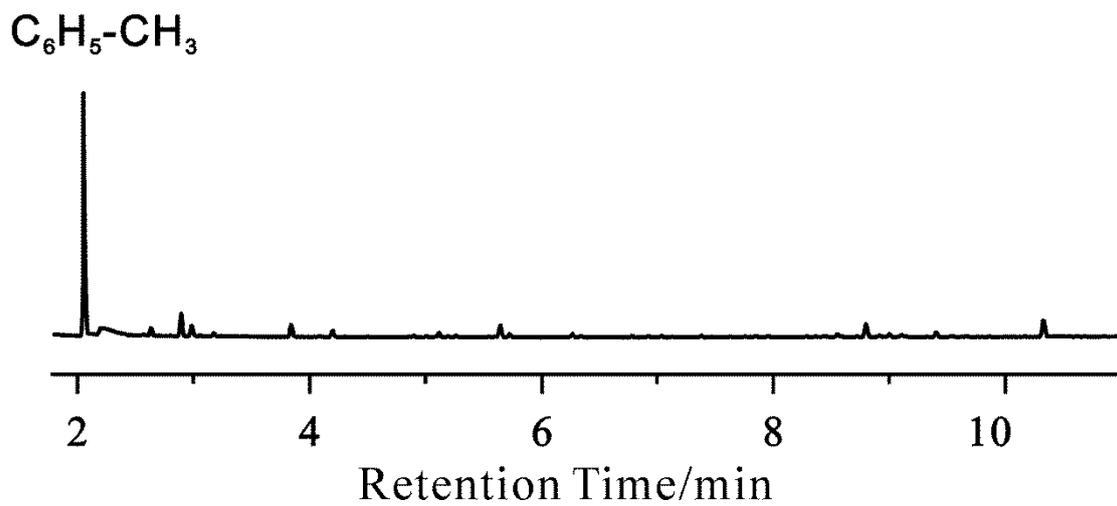


Figure S2. GC chromatogram from  $CH_2Cl_2$  extract of ZnZSM-5 sample after exposed to  $C_6H_6$  and CO for 1h at 623K.

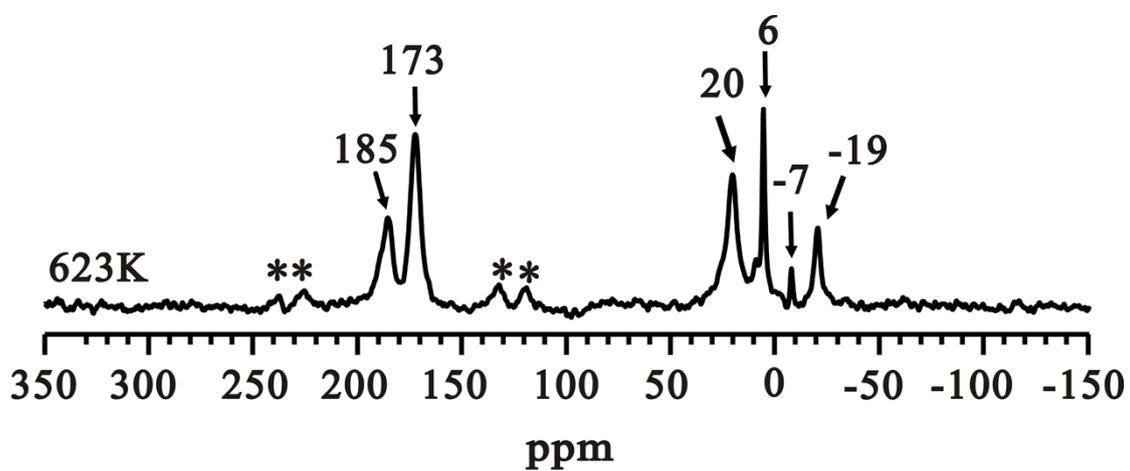


Figure S3.  $^{13}\text{C}$  CP/MAS NMR spectrum of products formed from co-adsorption of  $^{13}\text{CO}$  and  $\text{H}_2$  on Zn/H-ZSM-5 catalyst heated at 623K for 1h. Asterisks denote spinning side bands. The signals at 185 ppm and 20 ppm are due to the carbonyl carbon and the methyl group of formed acetic acid<sup>1</sup>. No alkylated benzene (toluene) is formed as no signal of the phenyl ring is observed, which is typically at *ca.* 130 ppm.

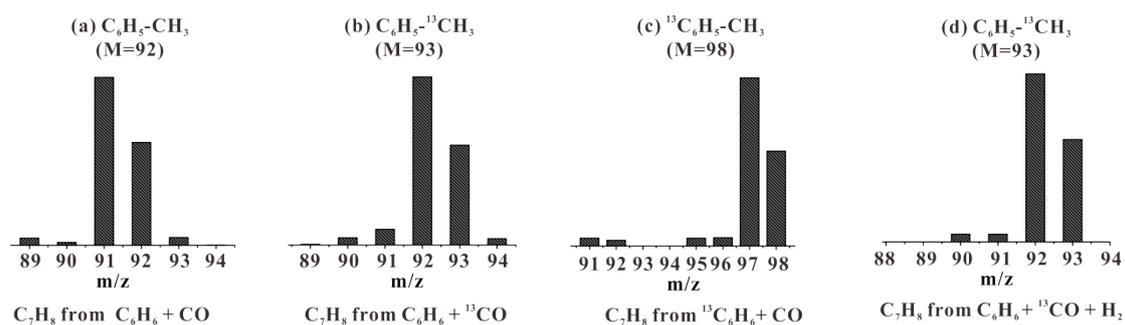


Figure S4. Mass-spectra of toluene formed from reaction of alternative  $^{13}C$  isotope labelled benzene and carbon monoxide at 623 K for 1h on zeolite Zn/H-ZSM-5: (a)  $C_6H_6$ , and CO, (b)  $C_6H_6$  and  $^{13}CO$ , (c)  $^{13}C_6H_6$  and CO and (d)  $^{13}C_6H_6$ , CO and  $H_2$ . The distribution of  $^{13}C$  label demonstrates that CO forms the methyl group of toluene while benzene provides the phenyl ring. The presence of  $H_2$  does not affect the distribution of  $^{13}C$  label of toluene.

## References

1. X. M. Wang, G. D. Qi, J. Xu, B. J. Li, C. Wang and F. Deng, *Angew. Chem. Int. Ed.*, 2012, 51, 3850-3853.
2. E. J. Munson, D. K. Murray and J. F. Haw, *J. Catal*, 1993, 141, 733-736.
3. J. Xu, A. Zheng, X. Wang, G. Qi, J. Su, J. Du, Z. Gan, J. Wu, W. Wang and F. Deng, *Chem. Sci.*, 2012, 3, 2932-2940.