

Supporting Information

Room temperature stable zinc carbonyl complex formed in zeolite ZSM-5 and its hydrogenation reactivity: A solid-state NMR study

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Experimental Methods

Materials and sample Preparation

The H-ZSM-5 zeolite (Si/Al = 21) was purchased from the Catalyst Plant of Nankai University, Tianjin, P. R. China. ^{13}CO (^{13}C -enrichment of 99.5%) was purchased from Spectra Gases, Inc. The ZnZSM-5 catalyst was prepared by reaction of metallic Zn vapor with H-form H-ZSM-5 zeolite on a vacuum line according to our previous work^{1, 2}. In general, H-ZSM-5 zeolite (Si/Al=21) was pre-dehydrated at 673 K with a pressure of 10^{-3} Pa over a period of 12 h. 1.5 g zinc foil (99.9%) was firstly placed at the bottom of a glass reactor. Then the dehydrated H-ZSM-5 zeolite was loaded into the reactor in a glovebox under dry nitrogen atmosphere and separated from zinc foil by quartz wool. The reactor was connected to the vacuum line and heated under a pressure of 10^{-3} Pa. A programmed temperature protocol was used: heating from room temperature to 773 K with a rate of 12 K/min and keeping for 2 h at 773 K, then reducing the temperature from 773 to 573 K in 15 minutes; reheating from 573 to 773 K at rate of 12 K/min and keeping for 2 h at 773 K before cool down to room temperature. The Zn content was ca. 4.8 % determined by ICP (Inductive Coupled Plasma) analysis. The Zn-exchanged ZSM-5 sample ($\text{Zn}^{2+}/\text{ZSM-5}$) was prepared by dispersing H-ZSM-5 in an aqueous solution of 1 M $\text{Zn}(\text{NO}_3)_2$ and the solution was stirred at 353 K for 4 h. This operation was repeated several times, and after washing with deionized water the $\text{Zn}^{2+}/\text{ZSM-5}$ sample was obtained³.

Zinc carbonyl complexes were generated by adsorption of a known amount of ^{13}CO (99 % ^{13}C labeled) or ^{13}C unlabeled CO (^{13}C in natural abundance) (300 μmol per

gram sample) onto the as-prepared ZnZSM-5 catalyst in a glass tube on the vacuum line and keeping for 10 min at liquid N₂ temperature; then the catalyst was warmed slowly to ambient temperature, sealed and removed from the vacuum line for further measurements.

Hydrogenation reaction

The zinc ¹³C-carbonyl complex containing ZnZSM-5 catalyst was loaded into a glass ampule in the glovebox filled with pure N₂. An excess amount of H₂ was introduced onto the catalyst on a vacuum line under liquid N₂ temperature; then the glass ampule containing catalyst was sealed off from the vacuum line. The hydrogenation reaction was performed in the sealed glass ampule at various temperatures. After the reaction was quenched at the pre-determined temperature by liquid N₂, the ampule was transferred into a 7.5 mm rotor for NMR measurements.

Solid-state NMR experiments

Solid-state NMR experiments for characterization of zinc carbonyl complexes were carried out at 14.1 T on a wide-bore Varian 600 MHz NMR spectrometer. A 7.5 mm double-resonance probe was employed to acquire ¹³C NMR spectra. The magic angle spinning rate was set to 6.154 kHz. Single-pulse ¹³C MAS experiments with ¹H decoupling were performed by using a $\pi/2$ pulse width of 5.6 μ s and a repetition time of 7 s. Since the distance between the ¹³C atoms in the multicarbonyl complex would be much longer than that between directly bonded C atoms in ordinary organic molecules, for the double quantum filtering (DQF) experiment, symmetry-based non- γ encoded recoupling sequence SR26 was used, which offers a robust approach for

long-range distance estimations even in the systems with notably large CSA interactions⁴⁻⁶. The recoupling RF nutation frequency of SR26 was adjusted to 40 kHz (equal to 6.5 times of spinning rate). The DQF build-up curve was established by the constant-time procedure ($\tau_{\text{exc}} + \tau_{\text{recon}} = \text{constant}$) to minimize the difference of relaxation or damping at each experimental point, and thus the influence of relaxation or damping can be approximately ignored when fitting the build-up curve by SIMPSON numerical simulations. τ_{exc} was increased by one-half of a super cycle (1.3 ms) and τ_{recon} was decreased by the same amount between neighboring experimental points, so as to keep the total recoupling time $T = \tau_{\text{exc}} + \tau_{\text{recon}}$ constant (23.4 ms). The number of scans for each experiment was fixed to 1800. The build-up curve was approximately symmetric with a maximum at $\tau_{\text{exc}} = \tau_{\text{recon}} = 11.7$ ms, and all points were normalized with respect to the maximum in Figure 4. For the triple quantum filtering (TQF) experiment, symmetry-based dipolar recoupling sequence $(R18^7_3)3^1$ was employed for an efficient excitation of the triple-quantum coherence⁷. The recoupling RF nutation frequency of $(R18^7_3)3^1$ was adjusted to 15 kHz (equal to 3 times of spinning rate) at the spinning rate of 5 kHz with $\tau_{\text{exc}} = \tau_{\text{recon}} = 12$ ms. The TQF spectrum was obtained with 18000 scans and recycle delay of 7 s, leading to 35 hrs experimental time.

In-situ solid-state NMR experiments for hydrogenation reaction were performed at 7.05 T on a wide-bore Varian Infinityplus-300 NMR spectrometer. For In-situ solid-state NMR experiments for hydrogenation reaction, a 7.5 mm double-resonance probe was employed to acquire ¹³C NMR spectra. Single-pulse ¹³C MAS experiments

with ^1H decoupling were performed by using a $\pi/2$ pulse width of 6.2 μs and a repetition time of 5 s. $^1\text{H}\rightarrow^{13}\text{C}$ CP MAS experiments were performed by using with a contact time of 4 ms and with a repetition time of 2 s. The magic angle spinning rate was set to 3.5 kHz. The ^{13}C chemical shift was referenced to hexamethylbenzene, as second references to tetramethylsilane (TMS).

DRIFT IR measurements

Diffuse reflectance Fourier transform infrared (DRIFT) spectra were measured at room temperature in a diffuse reflectance cell with CaF_2 windows on a BRUKER tensor 27 FTIR spectrometer. The sample was packed into the DRIFT cell in a glovebox under dry nitrogen atmosphere. The DRIFT spectra were recorded by a mercury-cadmium-telluride (MCT) detector with 128 scans at 2 cm^{-1} resolution. KBr was used for collecting the background spectrum.

Mass spectrometer (MS) analysis of decomposition of zinc carbonyl complex

The analysis of decomposition of zinc carbonyl complex was carried out in a closed system (dead volume, 10 ml) equipped with mass spectrometer (SMIMADZU), six-way-transfer valve and vacuum line system ($\square 10^{-4}$ Pa). The sample was packed into this system under dry He atmosphere in glovebox, followed by degassing at ambient temperature. The desorbed gas was analyzed with m/z ranging from 29 to 50 in full scan mode.

ESR measurements

ESR measurements were carried out on a JEOL JES-FA200 ESR spectrometer at room temperature. All the ESR spectra were recorded at a frequency of 9.072 GHz

and the microwave power was held at 0.1 mW.

Calculating IR frequencies of ^{13}C isotope shift for CO diatomic molecule^{8,9}

CO diatomic molecule was regarded two mass spherules (m_C and m_O) attached by a spring, so their vibrations can be mathematically calculated by the follow expression:

$$\nu^{CO} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Where k is the force constant determined by the chemical bond and μ is reduced mass,

for CO molecule, $\mu = \frac{m_C m_O}{m_C + m_O}$. When the C atom in CO molecule is changed to ^{13}C isotope, the value of μ changes, but k does not. This change on the reduced mass will affect the vibrational spectrum of CO molecule. The relationship between ^{12}CO and ^{13}CO vibrational frequencies is mathematically expressed by:

$$\frac{\nu^{13CO}}{\nu^{12CO}} = \sqrt{\frac{^{12}\mu}{^{13}\mu}} = 0.9778$$

The frequencies of ^{13}C isotope shift for CO diatomic molecule can be calculated by:

$$^{13}C_{Shift} = \nu^{12CO} - \nu^{13CO} = (1 - 0.9778)\nu^{12CO}$$

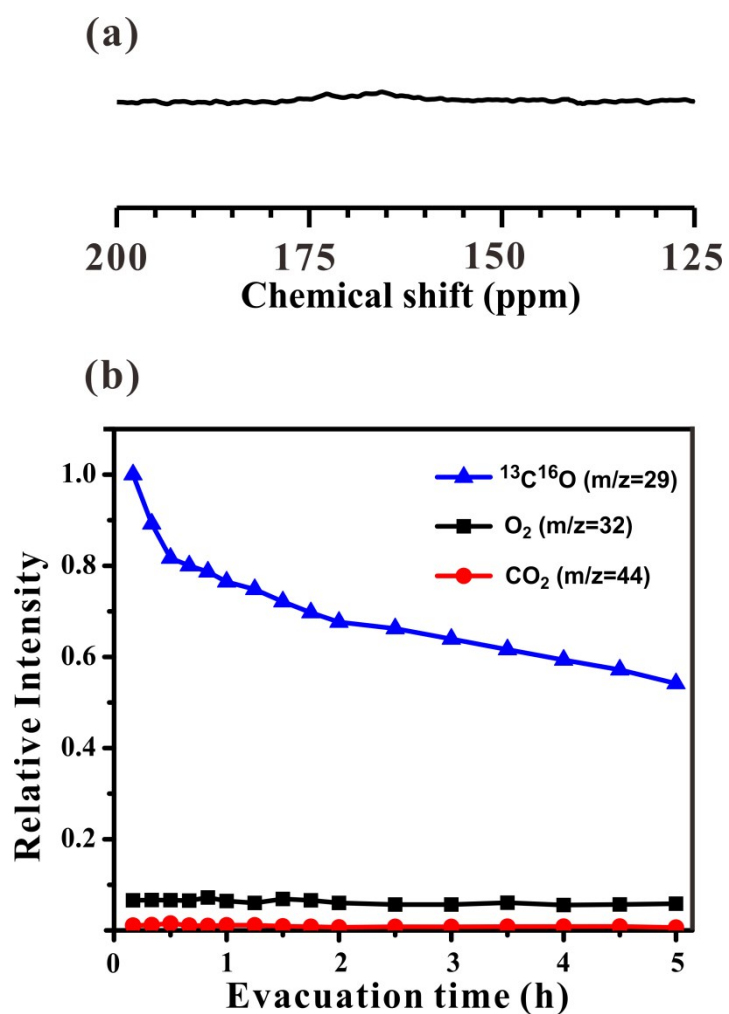


Figure S1. (a) ^{13}C MAS NMR spectrum of ^{13}CO adsorbed on ZnZSM-5 after vacuum treatment (10^{-4} Pa) for 10 h and (b) evolution of desorbed gas analyzed by QMS. No $^{13}\text{CO}_2$ ($m/z=45$) molecule is detectable, and the observed constant low level of O_2 ($m/z=32$) and CO_2 ($m/z=44$) is due to the background.

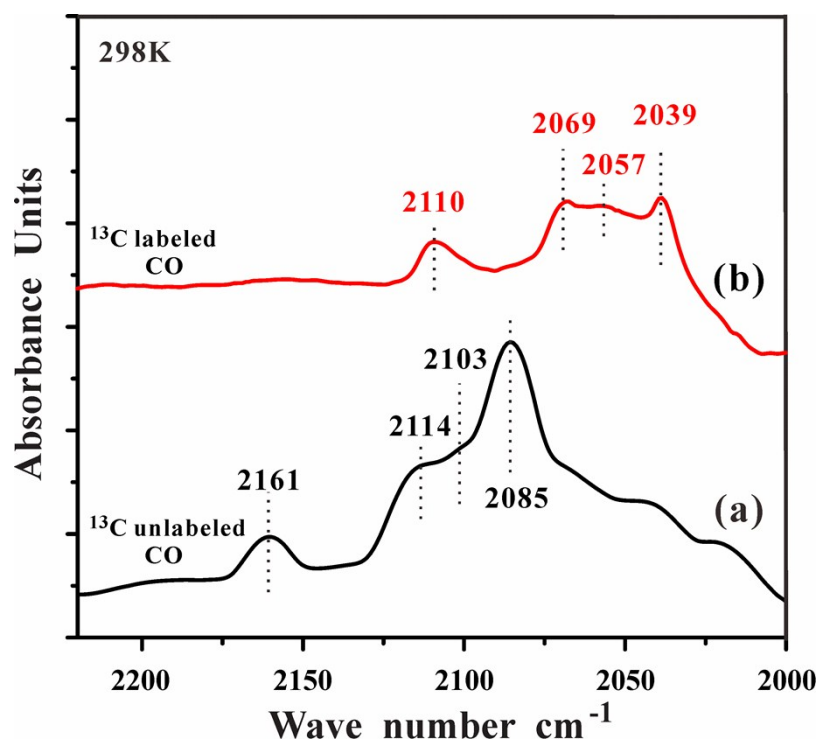


Figure S2. DRIFT IR spectra of (a) CO and (b) ^{13}C adsorbed on ZnZSM-5 at 298 K. Four ^{13}C unlabeled CO bands at 2161, 2114, 2103 and 2085 cm^{-1} are observed in the cationic metal carbonyls vibration region^{10, 11}. When ^{13}C -labeled CO was used, the frequencies shift downward to 2110, 2069, 2057 and 2039 cm^{-1} (Figure 2b). On the basis of the CO diatomic molecule model, the theoretical vibration frequency shift of ^{13}C isotope was calculated (see Table S1). A good match between the observed and predicted vibration frequency differences on ^{13}C unlabeled and labeled CO unambiguously confirms the formation of zinc carbonyls⁹. The IR bands at 2114, 2103 and 2085 cm^{-1} are assigned to multicarbonyls zinc complex with symmetric stretching, anti-symmetric stretching and bending vibration respectively, while the band at 2161 cm^{-1} to the stretching vibration of zinc monocarbonyl complex⁹.

Table S1. IR vibration frequencies of adsorbed ^{13}C O and CO on ZnZSM-5. Δv_{exp} and Δv_{cal} denote the frequency difference between adsorbed ^{13}C O and CO obtained from experimental observation and theoretical calculation respectively.

Adsorbate and frequency difference	Vibration frequency(cm^{-1})			
^{13}C -unlabeled CO	2161	2114	2103	2085
^{13}C -labeled CO	2110	2069	2057	2039
Δv_{exp}	51	45	46	46
Δv_{cal}	48	47	47	46

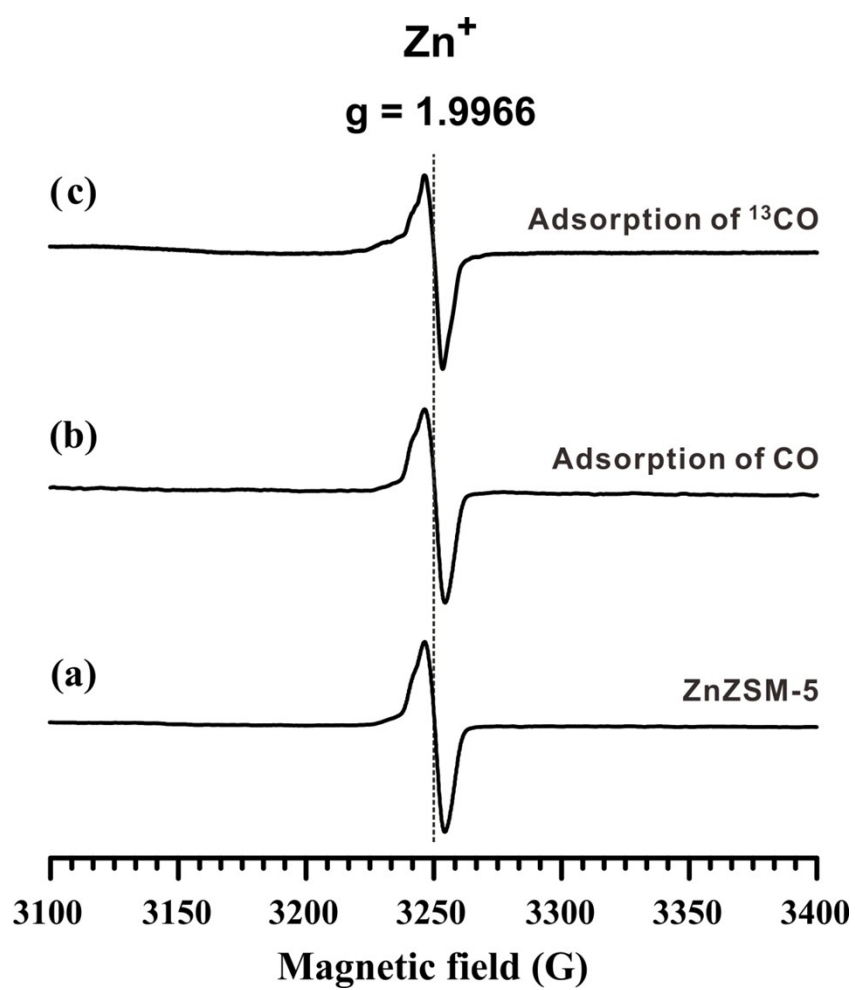


Figure S3. ESR spectra of (a) ZnZSM-5, (b) after adsorption of ¹³C-unlabeled CO and (c) after adsorption of 99% ¹³C-labeled CO, which were recorded at 298 K.

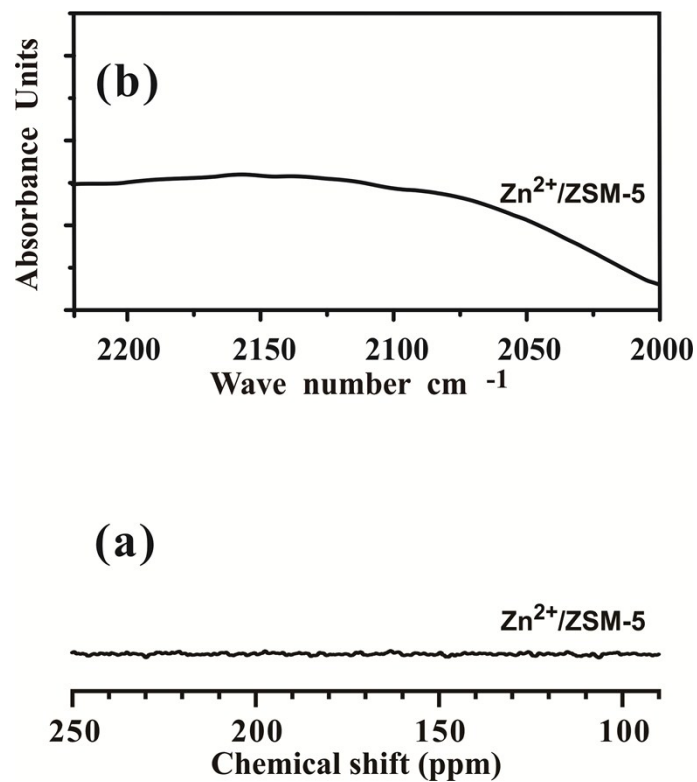


Figure S4. (a) ¹³C MAS NMR and (b) DRIFT IR spectra of ¹³CO adsorbed on Zn²⁺/ZSM-5 prepared by ion exchange method where zinc species are present as isolated Zn²⁺ ions. The spectra were recorded at 298 K.

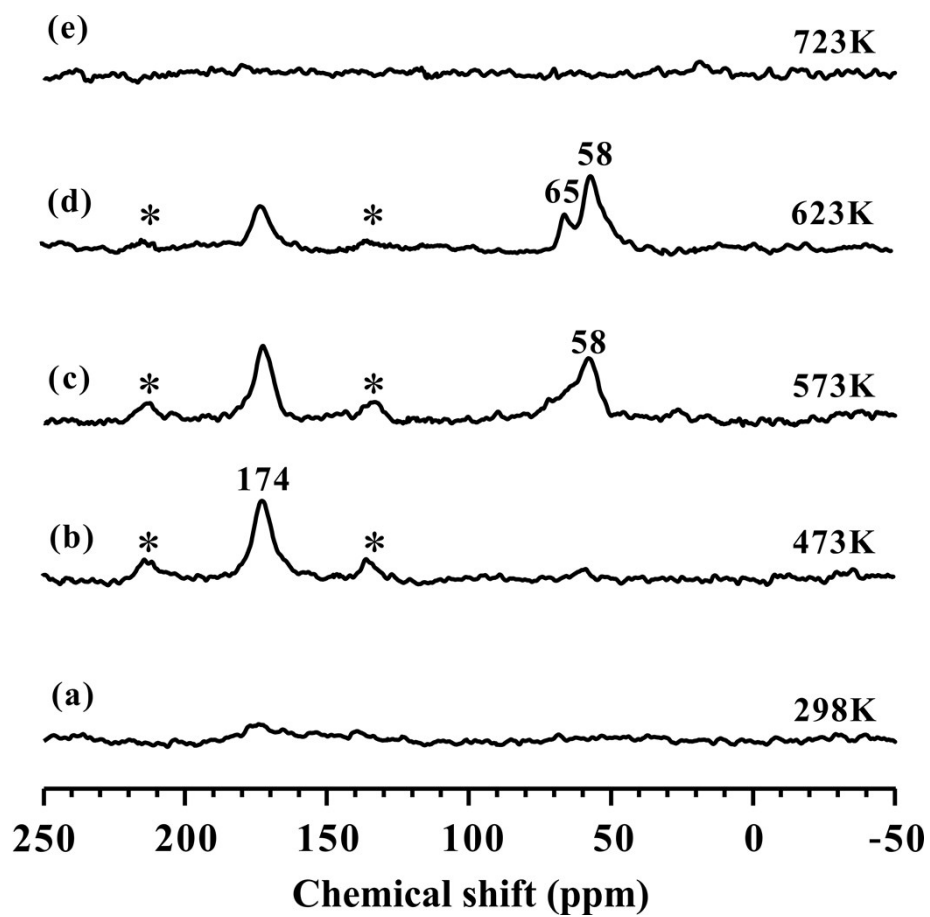


Figure S5. ^{13}C CP/MAS NMR spectra of products obtained from the reaction of zinc carbonyl complexes with H_2 at elevated temperatures.

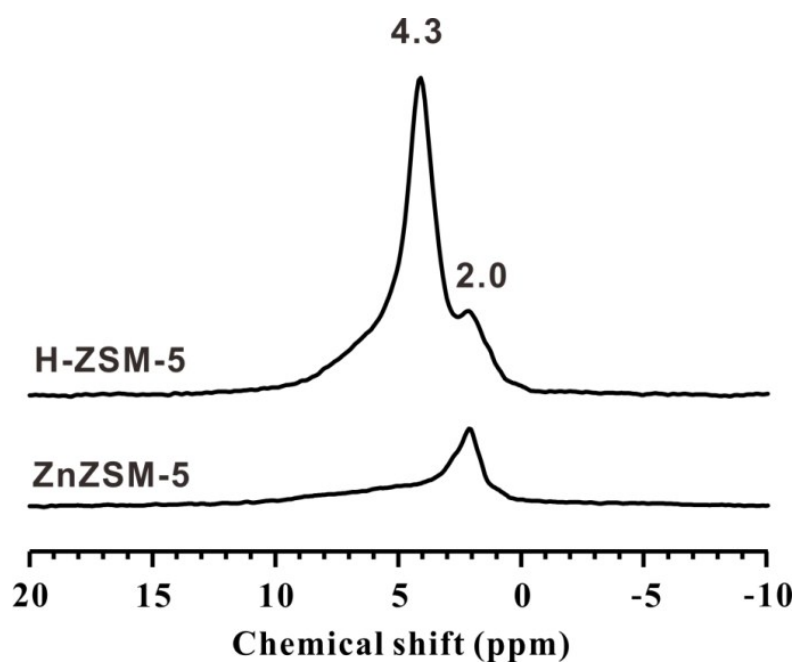


Figure S6. ^1H MAS NMR spectra of parent H-ZSM-5 and ZnZSM-5. The signals at 4.3 and 2.0 are due to bridging SiOHAl groups (Brønsted acid sites) and SiOH groups respectively.

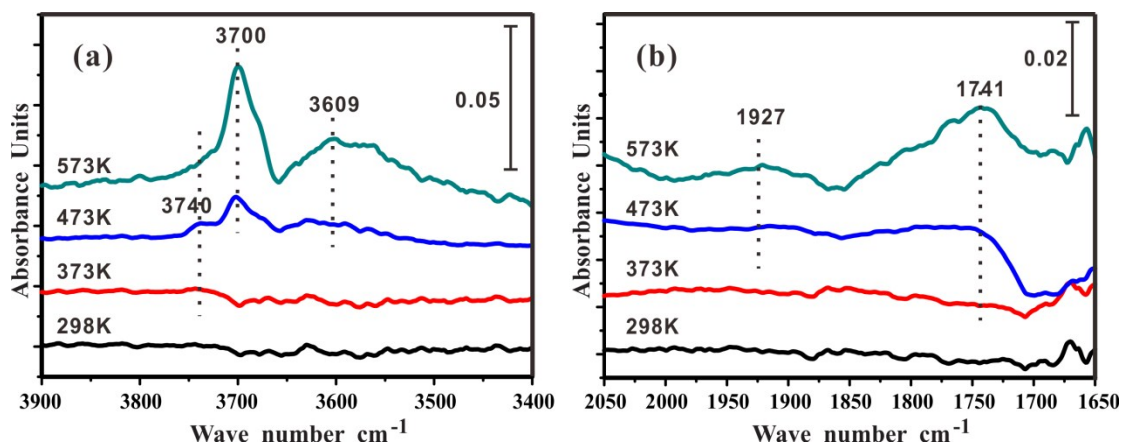
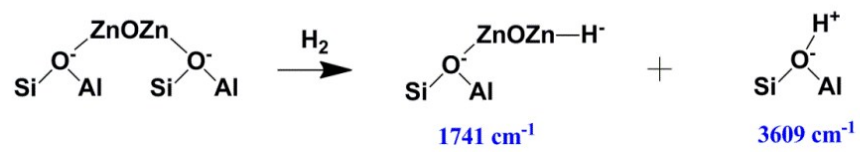


Figure S7. DRIFT IR spectrum of ZnZSM-5 obtained from the reaction of H₂ at various temperatures: 298 K, 373 K, 473 K, and 573 K. (a) the OH stretching region and (b) the Zn-H stretching region. All spectra were recorded at 298 K after evacuation of the residual H₂ gas.

In hydroxyl stretching region, IR absorptions were observed at 3740 and 3700 cm⁻¹ above 473 K; the latter band is attributed to the adsorbed water molecules generated from the reduction of dizinc (ZnOZn) cluster by H₂, and the former is due to the Si-OH group produced by slight degradation of the ZSM-5 framework. At much higher temperature of 573 K, the IR band belonging to Brønsted acid sites appeared at 3609 cm⁻¹, and new bands at 1927 and 1741 cm⁻¹ were simultaneously observed. The bands at 1927 and 1741 cm⁻¹ evidence the dissociation of H₂ on Zn²⁺ ions¹²⁻¹⁵ and ZnOZn cluster^{16, 17} respectively by the formation of Zn-H species. The simultaneously formed protons restore the Brønsted acid sites as observed at 3609 cm⁻¹. Actually, the dissociation of H₂ occurs even at 473 K, reflected by the relative weaker IR bands (3609 cm⁻¹, 1927 and 1741 cm⁻¹).



Scheme S1. H₂ disassociation on dizinc (ZnOZn) cluster in ZnZSM-5 zeolite.

References

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