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

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The structure and reactivity of room temperature stable zinc carbonyl complex in Zn-modified H-ZSM-5 zeolite was revealed by solid-state NMR spectroscopy.

Metal carbonyls is one type of important organometallic complexes involved in multidisciplinary fields from biology to chemistry¹. Synthesis and characterization of the metal carbonyls is a subject of extensive experimental and theoretical studies². Stable carbonyls can be produced on most transition metals and some main group metals in form of monocarbonyl and multicarbonyl complexes and the chemical reactivity of metal carbonyls strictly relates to their structural characteristics.

The importance of Zn-containing heterogeneous catalysts has been found in a variety of catalytic reactions³. Zn-based complex oxide for example is of great industrial importance for methanol synthesis with CO/CO₂ and H₂ as feed gas. In the proposed mechanism, chemisorption of CO and its hydrogenation step is crucial for the subsequent methanol formation⁴. In contrast to other well-documented transition metal carbonyls such as Fe, Co, and Ni carbonyls⁵, the binding of CO on Zn sites of heterogeneous catalysts is not well established. IR, photoelectron and NMR spectroscopy were frequently used for the detection of CO adsorption on zinc sites under low temperature (77-243K)⁶. Using DRIFT, Kazansky et al. reported the interaction of CO probe molecule with zinc modified zeolite to detect the zinc sites at room temperature⁷. Although chemisorption of CO was claimed to occur on the surface of ZnO or zinc substituted zeolites and formation of carbonyl complex was suggested, the speciation and reactivity characteristics of the assumed zinc carbonyl remain elusive. Recently, using matrix-isolation technique, Xu et al. reported the generation of IR

observable multicarbonyl Zn(CO)_x (x = 2-3) by reaction of laser-ablated Zn atoms with CO in solid argon under ultra-low temperature (7 or 4 K)⁸. However, the detailed structure and nature of the important cationic zinc carbonyl complex is, to date, still unknown, although there are theoretical bonding analysis on the predicted homoleptic [Zn(CO)_{1.6}]²⁺ species⁹.

Indeed, [Hg(CO)₂]²⁺ is, up to now, the only experimentally determined group 12 homoleptic carbonyl complex¹⁰. The versatile porous structure of channels and cavities endows zeolites with the capability of hosting and stabilizing metal ions or clusters. The specific anchoring site and confinement effect in zeolites allows forming highly reactive cations due to their coordinatively unsaturated property which could facilitate the adsorption and subsequent activation of reactant molecules. We recently showed that the coordinatively unsaturated Zn ions in Zn modified ZSM-5 exhibit high reactivity toward activation of methane and O₂ at low temperature¹¹. Considering the high importance of the metal carbonyl in relevance of catalysis, the stable zinc carbonyl complexes that can be well characterized would serve as ideal models not only for the group 12 metal carbonyl complexes but also for fundamental understanding of the multifaceted catalytic reaction mechanisms involving carbon monoxide over metal-containing catalysts. In this work, room temperature stable zinc monocarbonyl and dicarbonyl complexes were identified for the first time by solid-state NMR spectroscopy over a Zn modified ZSM-5 zeolite (ZnZSM-5). In addition, the hydrogenation reactivity of the carbonyl zinc complexes was demonstrated.

The adsorption of CO on the ZnZSM-5 zeolite (Si/Al=21) was firstly investigated by solid-state NMR spectroscopy. ¹³C labelled ¹³CO was used and introduced onto the catalyst surface on vacuum line. Figure 1a shows the single-pulse ¹³C magic angle spinning (MAS) NMR spectrum of ¹³CO adsorbed on ZnZSM-5 at room temperature. Two well-resolved signals at 167 and 173 ppm are observable in the up-field region of gaseous ¹³CO (ca. 180 ppm), which fall in the typical chemical shift region for homoleptic metal carbonyl cations^{2a} and surface metal (such as Ru and Rh) carbonyl complex in different configurations on zeolites¹² and Al₂O₃ support¹³. Since only the gaseous ¹³CO (physically adsorbed) signal can be observed on the

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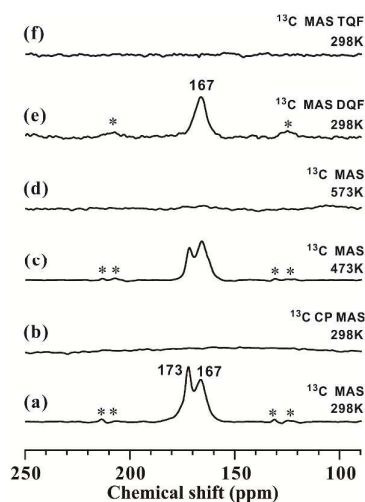


Figure 1. (a), (c), (d) single-pulse ^{13}C MAS NMR spectra of CO adsorbed on ZnZSM-5 at 298 K, 473 K and 573 K; (b) $^1\text{H}\rightarrow^{13}\text{C}$ CP MAS spectrum of sample (a) at 298 K; (e) ^{13}C MAS DQF NMR spectrum of sample (a) at 298 K; (f) ^{13}C MAS TQF NMR spectrum of sample (a) at 298 K. Asterisk indicates spinning sidebands.

parent H-ZSM-5 zeolite (not shown), the Zn ions in ZnZSM-5 might serve as the adsorption sites, leading to the formation of zinc carbonyls. However, carbonate (CO_3^{2-}), formate (COOH^-) and bicarbonate (HCO_3^-) adsorbed on the metal surface also have a similar chemical shift range (ca. 162~173 ppm)¹⁴. Previous surface analysis showed that carbonate species was readily formed by exposure of ZnO with surface defects to CO at low temperature¹⁵. Thus further experiments are needed to confirm the above assignment. The $^1\text{H}\rightarrow^{13}\text{C}$ cross polarization (CP) MAS NMR experiment was used to detect the protons in close proximity or directly bonded with the carbonyl complex. In the CP MAS spectrum (Figure 1b), the two carbonyl signals completely disappear, indicative of no protons being associated with the carbonyl complex or in close proximity. Thus the formates and bicarbonates which contain protons are not likely formed. We also found that the two carbonyl complex could be removed from the zeolite surface by thermal treatment. Heating the CO adsorbed sample at elevated temperatures leads to a decrease of the two signals and they almost disappear at 573 K (Figures 1c and 1d). Additionally, high vacuum treatment was performed on the CO adsorbed sample. After 10 h evacuation under a pressure of 10^{-4} Pa, the two NMR signals almost completely disappear as well (Figure S1a). To check the decomposition of the adsorbates, the desorbed gas derived from the thermal treatment was analyzed by mass spectroscopy. Accompanying with the disappearance of the carbonyl ^{13}C NMR signals, only ^{13}CO molecule is detectable (Figure S1b). Thus, the carbonate seems to be not present because its decomposition would generate gaseous $^{13}\text{CO}_2$. These experimental evidences suggest that the two ^{13}C NMR signals should stem from ^{13}CO directly bonded to zinc sites in ZnZSM-5 zeolite, generating thermal stable zinc carbonyl complexes. The DRIFT IR experiments of $^{13}\text{CO}/^{12}\text{CO}$ adsorption were further performed at room temperature, which also confirmed the formation of zinc carbonyl complexes¹⁶ (Figure S2 and Table S1).

It is desirable to further identify the detailed structures of zinc carbonyl complexes. For the homoleptic metal multicarbonyl complex, more than two ^{13}CO molecules can bond with the same metal site. From NMR points of view, the $^{13}\text{C}\text{-}^{13}\text{C}$ internuclear dipolar coupling is present between two ^{13}CO molecules in the multicarbonyl complex, while such kind of $^{13}\text{C}\text{-}^{13}\text{C}$ dipolar coupling is absent in the monocarbonyl complex. In order to detect the $^{13}\text{C}\text{-}^{13}\text{C}$ dipolar coupling, the double quantum filtering (DQF) NMR method was employed, in which the double-quantum coherence was realized by recoupling the homonuclear dipolar interaction¹⁷. It is presumed that the adjacent ^{13}CO molecules in the multicarbonyl complex that experience a $^{13}\text{C}\text{-}^{13}\text{C}$ dipolar interaction have an undistinguishable chemical shift. As shown in Figure 1e, the 173 ppm signal completely disappears while the 167 ppm signal remains almost unchanged in the ^{13}C DQF MAS NMR spectrum after 1800 scans. Since the DQ filtering allows removing the signals from isolated carbon atoms or carbon atoms with a long distance apart, the disappeared 173 ppm signal can thus be assigned to the zinc monocarbonyl complexes, being distantly separated on the zeolite support. In contrast, the 167 ppm signal remained in the DQF spectrum can be unambiguously attributed to multicarbonyl species such as zinc dicarbonyl complexes ($\text{CO}\text{-Zn}\text{-CO}$), in which coupled $^{13}\text{C}\text{-}^{13}\text{C}$ pairs are present.

Besides the zinc dicarbonyl complex, one may expect that other multicarbonyl complexes are probably present as well, which cannot be distinguished by the ^{13}C NMR chemical shifts. When more than two CO molecules are adsorbed on one zinc site, the $^{13}\text{C}\text{-}^{13}\text{C}$ dipolar couplings among ^{13}C spins can be detected by triple-quantum filtering (TQF) NMR experiment¹⁸. As shown in Figure 1f, no signal could be observed in the TQF spectrum even after 18000 scans, providing experimental evidence that the zinc multicarbonyl complex containing more than two CO molecules does not likely exist in our CO-adsorbed ZnZSM-5 sample.

For the zinc dicarbonyl complex, the two ^{13}C atoms can be roughly considered as an isolated coupled spin pair that makes it possible to determine the $^{13}\text{C}\text{-}^{13}\text{C}$ internuclear distance from the build-up curve of DQ coherence, which may in return provide more structural information on its adsorption mode. Figure 2 shows experimental DQF data of the 167 ppm signal and the corresponding simulated

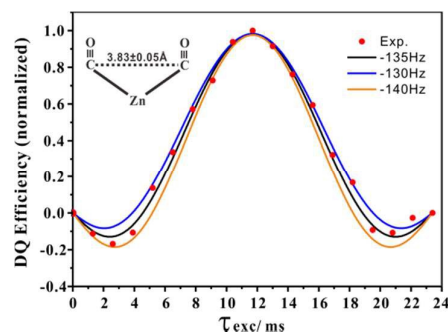


Figure 2. Normalized DQF signal amplitude at 167 ppm of CO adsorbed on ZnZSM-5, plotted against the excitation interval τ_{exc} using a constant total recoupling interval $T = 23.4$ ms. The experimental points are indicated as red dots. The black line is the best fit corresponding to a $^{13}\text{C}\text{-}^{13}\text{C}$ dipolar coupling of -135 Hz, with blue and orange lines corresponding to a deviation of ± 5 Hz.

curves as function of excitation time (τ_{exc}) obtained by constant-time procedure ($\tau_{\text{exc}} + \tau_{\text{recon}} = \text{constant}$) that is capable of minimizing the difference of relaxation or damping at each experimental point. A good fit between simulations and experimental data was achieved for a ^{13}C - ^{13}C dipolar coupling of -135 ± 5 Hz, corresponding to an internuclear distance of 3.83 ± 0.05 Å.

The room temperature observation of stable different zinc carbonyl complexes implies that distinct adsorption sites are present in ZnZSM-5, which facilitates the binding of CO molecule. Our previous detailed characterization showed that three types of Zn ions, i.e., Zn^+ ions, isolated Zn^{2+} ions and dizinc (ZnOZn) clusters were formed on the ZnZSM-5 catalyst^{11b}. In order to identify which type of Zn ions acts as the adsorption site for CO to generate the zinc carbonyl complexes, we carried out the following experiments. ESR measurement was performed on the CO adsorbed ZnZSM-5 sample (Figure S3). Compared to the bare ZnZSM-5 sample, no obvious change occurs on the Zn^+ ESR signal, indicating that CO does not adsorb on the paramagnetic Zn^+ ions. Generally, the interaction between CO and Zn^+ would result in a change of the Zn^+ ESR signal due to the variation of spin density exerted by bonded CO¹⁹. Weak adsorption of CO on Zn^{2+} ions was previously observed at low temperature on ZnY zeolite^{6c} and ZnO ^{6a}. To check the adsorption of CO on the isolated Zn^{2+} ions in ZnZSM-5, a Zn-exchanged ZSM-5 sample ($\text{Zn}^{2+}/\text{ZSM-5}$, Si/Al=21) was prepared by ion-exchange method, in which isolated Zn^{2+} ions are solely present²⁰. After CO was introduced into $\text{Zn}^{2+}/\text{ZSM-5}$ under the identical condition, no signals from zinc carbonyl complexes are observable in either solid-state NMR or DRIFT IR spectroscopy at room temperature (Figure S4). This unambiguously indicates that the carbonyl complexes observed in ZnZSM-5 (see Figure 1) do not locate on the isolated Zn^{2+} ions. The above experimental results allow us to conclude that the dizinc (Zn-O-Zn) species acts as the bonding site for CO to form the carbonyl complex. Our previous work indicates that the dizinc species contains unpaired electron density on both O p-orbital (0.86) and Zn s-orbital (0.94), existing in the form of $[\text{Zn}^+-\text{O}^--\text{Zn}^{2+}]^{2+}$ compensated by two framework Al sites on ZSM-5. This species is not a radical and would be invisible in EPR experiment^{11b}. The work of Solomon and coworkers suggested that CO adsorbed preferentially on highly polarized metal sites^{6a}. Indeed, our ^{129}Xe adsorption NMR experiments indicate the Zn^{2+} ion in the dizinc species has a strong polarizing ability^{11b}. Thus, the facile formation of zinc carbonyl complexes can be understood by considering the polarization-induced adsorption of CO on this type of Zn sites.

The stable zinc carbonyls formed at room temperature provides a good metal carbonyl model which allows us to gain insight into their chemical reactivity under a practical reaction condition. We explored the reactivity of zinc carbonyl complex in the hydrogenation reaction by using in-situ ^{13}C NMR spectroscopy. After H_2 was introduced onto ZnZSM-5 having pre-formed zinc carbonyl complexes at room temperature, the two carbonyl signals at 167 and 173 ppm become unresolved in the ^{13}C MAS spectrum (Figure 3a) probably due to the interaction between hydrogen and carbon atoms of the carbonyl complex. In the corresponding $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS spectrum (Figure S5a), however, no ^{13}C signal is observable, indicating that the formation of new C-H bond has not occurred yet. When the temperature is raised to 473 K, a new signal

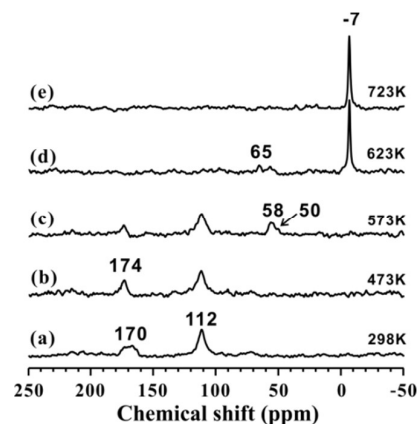
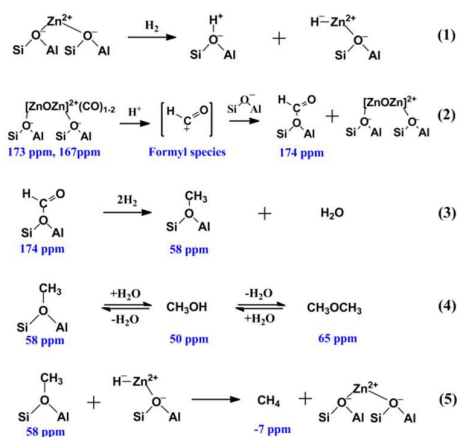


Figure 3. ^{13}C MAS NMR spectrum of the products obtained from the reaction of zinc carbonyl complex with H_2 at elevated temperatures. The signal at 112 ppm is due to the background of NMR rotor.

appears at 174 ppm (Figure 3b) and it can be notably enhanced in the corresponding $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS spectra (Figure S5b). This suggests that a new species containing C-H bond that is different from the original zinc carbonyl complex is generated by hydrogenation of CO. According to the chemical shift, it can be assigned to formate species ($-\text{COOH}$)^{11b}. Further increasing the temperature to 573 K leads to further hydrogenation, evidenced by the formation of surface methoxy species (at 58 ppm) and a small amount of methanol (at 50 ppm)²¹ (Figure 3c and Figure S5c). The formation of formate and methoxy species was also found in the hydrogenation of CO/ CO_2 with H_2 on Zn-based oxide catalysts²². Interestingly, further transformation of methoxy species and methanol into dimethyl ether (65 ppm) proceeds at higher temperature and ends up with the formation of methane (-7 ppm) (Figures 3d and 3e).

Based on the NMR experimental results, the hydrogenation reaction pathway is proposed and shown in Scheme 1. As revealed by ^1H MAS NMR spectroscopy (Figure S6), nearly all the acidic protons on ZnZSM-5 are removed by the introduced zinc species. The protons for the hydrogenation of carbonyl species should stem from the added H_2 . The dissociation of H_2 was previously reported on ZnO ²³ and Zn^{2+} ions²⁴ in zeolites. Our DRIFT experiments demonstrate that the dissociative adsorption of H_2 can occur on both isolated Zn^{2+} ions and dizinc species, restoring Brønsted acid sites for the following hydrogenation (Figure S7 and Scheme S1). Since carbonyl complexes are formed on the dizinc species, dissociation of H_2 would occur preferentially on isolated Zn^{2+} ions. The monocarbonyl and dicarbonyl complexes ($\text{ZnOZn}(\text{CO})_{1-2}$) interact with the acidic protons to form formate species and restore the ZnOZn adsorption site. The formyl species that is widely considered as a key intermediate for formation of hydrocarbons in the syngas conversion²⁵ is presumably formed in the initial stage via protons electrophilic attract on carbon atom of CO molecule^{6b}. However, the formyl species mostly involves as a transition product because of its facile interaction with the negatively charged oxygen atoms of zeolite framework to form formate species. Further hydrogenation of formate species leads to the formation of methoxy species. In the following step, the formed methoxy species interact with hydride (Zn-H) species to generate

methane product and restore the isolated Zn^{2+} ions. The derived methanol and DME also involves in hydrogenation process through reversible formation of methoxy species. It is noteworthy that the protons from dissociative H_2 may be restored on Brønsted acid sites not close to the zinc carbonyl complexes. However, the dynamic nature of the acidic protons could contribute to the hydrogenation particularly at elevated temperature²⁶. Additionally, the proton mobility can be considerably enhanced in the presence of water molecule on zeolite²⁷. Indeed, the formation of trace water is observed in the hydrogenation at temperature above 473K (Figure S7).



Scheme 1. Proposed reaction pathway for the hydrogenation of zinc carbonyls.

In summary, we report the observation of the stable surface zinc carbonyl complexes at room temperature. The geometric structure of zinc dicarbonyl complex was determined by ^{13}C DQF NMR technique. The observed zinc carbonyls shows reactivity in the hydrogenation reaction via the formation of oxygenates and hydrocarbons. The results presented herein represent an example of stable carbonyl complex with well-characterized structure and reactivity on the surface of zeolite catalysts, which might be helpful for a better understanding of the nature of zinc carbonyls in relevance to heterogeneous catalysis and enrich our knowledge in the metal carbonyls chemistry.

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