



Cite this: *Chem. Commun.*, 2015, 51, 9177

Received 30th March 2015,
Accepted 24th April 2015

DOI: 10.1039/c5cc02601f

www.rsc.org/chemcomm

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 a room temperature stable zinc carbonyl complex in Zn-modified H-ZSM-5 zeolite were revealed by solid-state NMR spectroscopy.

Metal carbonyls are one type of important organometallic complexes involved in multidisciplinary fields from biology to chemistry.¹ Synthesis and characterization of metal carbonyls is a subject of extensive experimental and theoretical studies.² Stable carbonyls can be produced on most transition metals and some main group metals in the 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 reactions.³ 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 are crucial for the subsequent methanol formation.⁴ In contrast to other well-documented transition metal carbonyls such as Fe, Co, and Ni carbonyls,⁵ 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 at low temperature (77–243 K).⁶ Using DRIFT, Kazansky *et al.* reported the interaction of CO probe molecules with zinc modified zeolite to detect the zinc sites at room temperature.⁷ Although chemisorption of CO was claimed to occur on the surface of ZnO or zinc substituted zeolites and

formation of a carbonyl complex was suggested, the speciation and reactivity characteristics of the assumed zinc carbonyl remain elusive. Recently, using the matrix-isolation technique, Xu *et al.* reported the generation of IR observable multicarbonyl Zn(CO)_x (*x* = 2–3) by the reaction of laser-ablated Zn atoms with CO in solid argon at ultra-low temperature (7 or 4 K).⁸ However, the detailed structure and nature of the important cationic zinc carbonyl complex are, to date, still unknown, although there are reports on theoretical bonding analysis of the predicted homoleptic [Zn(CO)_{1–6}]²⁺ species.⁹

Indeed, [Hg(CO)₂]²⁺ is, up to now, the only experimentally determined group 12 homoleptic carbonyl complex.¹⁰ 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 allow formation of 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 temperature.¹¹ Considering the high importance of the metal carbonyl in relevance to 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 a vacuum line. Fig. 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

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† Electronic supplementary information (ESI) available: Experimental details regarding sample preparation and the applied analytical techniques. See DOI: 10.1039/c5cc02601f

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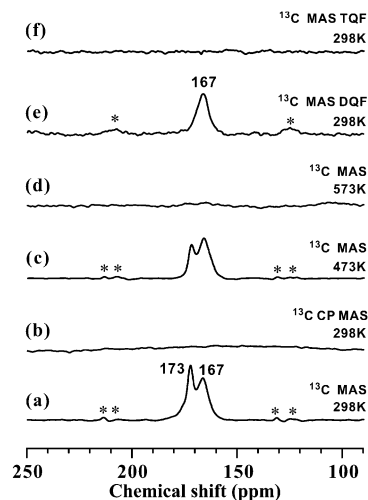


Fig. 1 (a), (c), (d) Single-pulse ^{13}C MAS NMR spectra of CO adsorbed on ZnZSM-5 at 298 K, 473 K and 573 K; (b) $^1\text{H} \rightarrow ^{13}\text{C}$ CP MAS spectrum of sample (a) at 298 K; (e) ^{13}C MAS DQF NMR spectrum of sample (a) at 298 K; (f) ^{13}C MAS TQF NMR spectrum of sample (a) at 298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

metal carbonyl cations^{2a} and the surface metal (such as Ru and Rh) carbonyl complex in different configurations on zeolites¹² and Al_2O_3 support.¹³ Since only the gaseous ^{13}CO (physically adsorbed) signal can be observed on the parent H-ZSM-5 zeolite (not shown), the Zn ions in ZnZSM-5 might serve as 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 were readily formed by exposure of ZnO with surface defects to CO at low temperature.¹⁵

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 (Fig. 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 complexes 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 (Fig. 1c and d). 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 (Fig. S1a, ESI†). To check the decomposition of the adsorbates, the desorbed gas derived from vacuum treatment was analyzed by mass spectroscopy. Accompanying the disappearance of the carbonyl ^{13}C NMR signals, only ^{13}CO molecules are detectable (Fig. S1b, ESI†). Thus, the carbonate seems to be not present because its decomposition would generate gaseous $^{13}\text{CO}_2$. These experimental results suggest that the two ^{13}C NMR signals should stem from ^{13}CO directly bonded to zinc sites in ZnZSM-5 zeolite, generating thermally

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 (Fig. S2 and Table S1, ESI†).

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}C – ^{13}C internuclear dipolar coupling is present between two ^{13}CO molecules in the multicarbonyl complex, while such kind of ^{13}C – ^{13}C dipolar coupling is absent in the monocarbonyl complex. In order to detect the ^{13}C – ^{13}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 interaction.¹⁷ It is presumed that the adjacent ^{13}CO molecules in the multicarbonyl complex that experience a ^{13}C – ^{13}C dipolar interaction have an undistinguishable chemical shift. As shown in Fig. 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 removal of the signals from isolated carbon atoms or carbon atoms that are far apart, the 173 ppm signal that disappeared can thus be assigned to the zinc monocarbonyl complexes, being distantly separated on the zeolite support. In contrast, the 167 ppm signal that remained in the DQF spectrum can be unambiguously attributed to multicarbonyl species such as zinc dicarbonyl complexes (CO-Zn-CO), in which coupled ^{13}C – ^{13}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}C – ^{13}C dipolar coupling among ^{13}C spins can be detected by triple-quantum filtering (TQF) NMR experiments.¹⁸ As shown in Fig. 1f, no signal could be observed in the TQF spectrum even after 18 000 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 which makes it possible to determine the ^{13}C – ^{13}C internuclear distance from the build-up curve of DQ coherence, which may in return provide more structural information on its adsorption mode. Fig. 2 shows experimental DQF data of the 167 ppm signal and the corresponding simulated curves as a function of excitation time (τ_{exc}) obtained by using the constant-time procedure ($\tau_{\text{exc}} + \tau_{\text{recon}} = \text{constant}$) which 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 molecules. 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 act as the adsorption site for CO to generate the

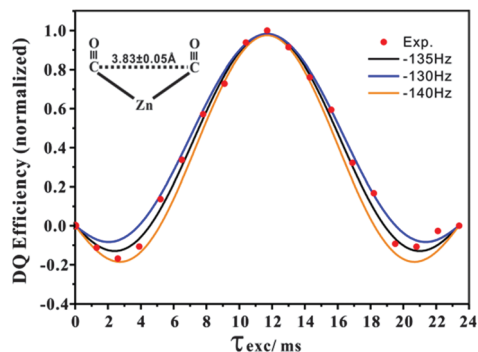


Fig. 2 Normalized DQF signal amplitude at 167 ppm of CO adsorbed on ZnZSM-5, plotted against the excitation interval τ_{exc} , using a constant total recoupling interval $T = 23.4$ ms. The experimental points are indicated as red dots. The black line is the best fit corresponding to a ^{13}C – ^{13}C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

zinc carbonyl complexes, we carried out the following experiments. ESR measurements were performed on the CO adsorbed ZnZSM-5 sample (Fig. S3, ESI†). Compared to the bare ZnZSM-5 sample, no obvious change occurs in the Zn^{2+} ESR signal, indicating that CO does not adsorb on the paramagnetic Zn^{2+} ions. Generally, the interaction between CO and Zn^{2+} would result in a change of the Zn^{2+} ESR signal due to the variation of spin density exerted by bonded CO.¹⁹ 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 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 the ion-exchange method, in which isolated Zn^{2+} ions are solely present.²⁰ After CO was introduced into $\text{Zn}^{2+}/\text{ZSM-5}$ under identical conditions, no signals from zinc carbonyl complexes were observed by either solid-state NMR or DRIFT IR spectroscopy at room temperature (Fig. S4, ESI†). This unambiguously indicates that the carbonyl complexes observed in ZnZSM-5 (see Fig. 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 ESR experiments.^{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 that 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 provide a good metal carbonyl model which allows us to gain insight into their chemical reactivity under practical reaction conditions. We explored the reactivity of the zinc carbonyl complexes in the hydrogenation reaction by using *in situ* ^{13}C NMR spectroscopy. After H_2 was introduced onto ZnZSM-5 having pre-formed zinc

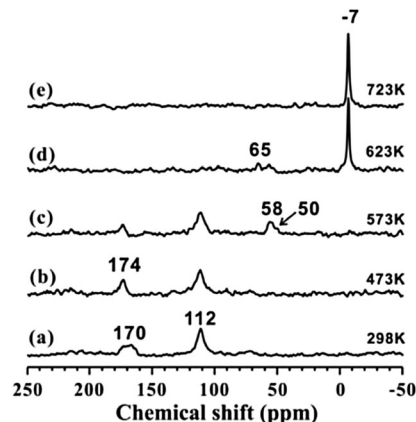
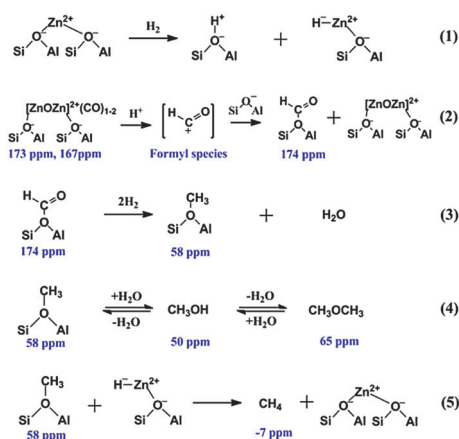


Fig. 3 ^{13}C MAS NMR spectra of the products obtained from the reaction of the zinc carbonyl complex with H_2 at elevated temperatures. The signal at 112 ppm is due to the background of the NMR rotor.

carbonyl complexes at room temperature, the two carbonyl signals at 167 and 173 ppm become unresolved in the ^{13}C MAS spectrum (Fig. 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 (Fig. S5a, ESI†), however, no ^{13}C signal is observable, indicating that the formation of new C–H bonds has not occurred yet. When the temperature is raised to 473 K, a new signal appears at 174 ppm (Fig. 3b) and it can be notably enhanced in the corresponding $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS spectra (Fig. S5b, ESI†). This suggests that a new species containing C–H bonds 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 (Fig. 3c and Fig. S5c, ESI†). The formation of formate and methoxy species was also found in the hydrogenation of CO/ CO_2 with H_2 on Zn-based oxide catalysts.²² 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) (Fig. 3d and e).

Based on the NMR experimental results, the hydrogenation reaction pathway is proposed and shown in Scheme 1. As revealed by ^1H MAS NMR spectroscopy (Fig. S6, ESI†), 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 disassociation 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 (Fig. S7 and Scheme S1, ESI†). 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 in the formation



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

of hydrocarbons in syngas conversion²⁵ is presumably formed in the initial stage *via* electrophilic attraction of protons to the carbon atom of the CO molecule.^{6b} However, the formyl species is mostly involved as a transition product because of its facile interaction with the negatively charged oxygen atoms of the zeolite framework to form formate species. Further hydrogenation of formate species leads to the formation of methoxy species. In the following step, the methoxy species thus formed interact with hydride (Zn-H) species to generate the methane product and restore the isolated Zn²⁺ ions. The derived methanol and DME are also involved in the hydrogenation process through reversible formation of methoxy species. It is noteworthy that the protons from dissociative H₂ 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 temperature.²⁶ Additionally, the proton mobility can be considerably enhanced in the presence of water molecule on zeolite.²⁷ Indeed, the formation of trace water is observed in the hydrogenation at temperature above 473 K (Fig. S7, ESI†).

In summary, we report the observation of the stable surface zinc carbonyl complexes at room temperature. The geometric structure of the zinc dicarbonyl complex was determined by the ¹³C DQF NMR technique. The observed zinc carbonyls show reactivity in the hydrogenation reaction *via* the formation of oxygenates and hydrocarbons. The results presented herein represent an example of a 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 with relevance to heterogeneous catalysis and enrich our knowledge in the area of metal carbonyl chemistry.

This work was supported by the National Natural Science Foundation of China (Grants 21210005, 21173254, 21221064 and 20113223).

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