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NMR Observation of a Zinc Carbonyl in Zeolite ZnY

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We report the first NMR observation of a zinc carbonyl, which was formed at 148 K inside the pore system of a zinc-exchanged Y type zeolite. The isotropic ^{13}C shift, 165 ppm, was measured with magic angle spinning (MAS), and this was also observed for CO on ZnO at 98 K.

The preparation and characterization of organometallic complexes on zeolite and metal oxide supports is of great interest.[1−3] Examples of processes in which surface and zeolite-supported organometallic complexes have roles in catalysis include hydrogenolysis,[4] reforming,[5] and olefin polymerization.[6] Previous MAS NMR studies of carbon monoxide in zeolites have included studies of weak interactions with Brønsted sites and alkali metal cations by Pfeifer[7,8] and studies of more stable metal carbonyls formed on Rh and Ru by Takahashi[9] and Apple.[10,11]

Stable organometallic compounds containing zinc are typically of the dialkylzinc, alkylzinc halide, and alkyl(alkoxy)-zinc classes.[12] There are no reports of the isolation of a zinc carbonyl, and the only suggestions of such species have come from infrared[13,14] or photoelectron[15] studies of CO weakly bound to ZnO. Since metal cations in zeolites are coordinated by several framework oxygen sites, we view the species in the zeolite to be structurally analogous to the alkyl(alkoxy) compounds[16] with CO bound through the carbon end.

Figure 1 shows ^{13}C MAS NMR spectra from representative studies of ^{13}CO on zeolite ZnY and polycrystalline ZnO.[17] A single isotropic peak was observed at 165 ppm on ZnO at 98 K, and this value, ca. 17 ppm upfield of the gas phase shift, suggests chemisorption. Even at this relatively low temperature, the CO was weakly bound to sites on ZnO as implied by dynamical averaging of the chemical shift anisotropy. An identical isotropic shift was seen for CO on metal sites in ZnY zeolite, but a complex, static on the millisecond time scale, was implied by the extensive sideband pattern at 148 K. Analysis of sideband intensities by the method of Herzfeld and Berger[18] gave principal components of the ^{13}C chemical shift tensor of $\delta_{11} = 302$ ppm, $\delta_{22} = 265$ ppm, and $\delta_{33} = -72$ ppm; these values are in the range of those reported for terminal carbonyls in well-characterized transition metal complexes.[19] Following Apple's work on other zeolites,[11] we carried out a CPMG experiment at 148 K, but we saw no dipolar oscillation. This shows that the low-temperature species on ZnY is a monocarbonyl. Raising the temperature of the CO on ZnY samples resulted in reversible reorientational and chemical exchange dynamics for the CO ligands[20] and, at higher temperatures, an irreversible water−gas shift reaction to make some CO_2 (126 ppm at 498 K).[21] We also used manometry to demonstrate that the adsorption of CO is completely reversible at 398 K.

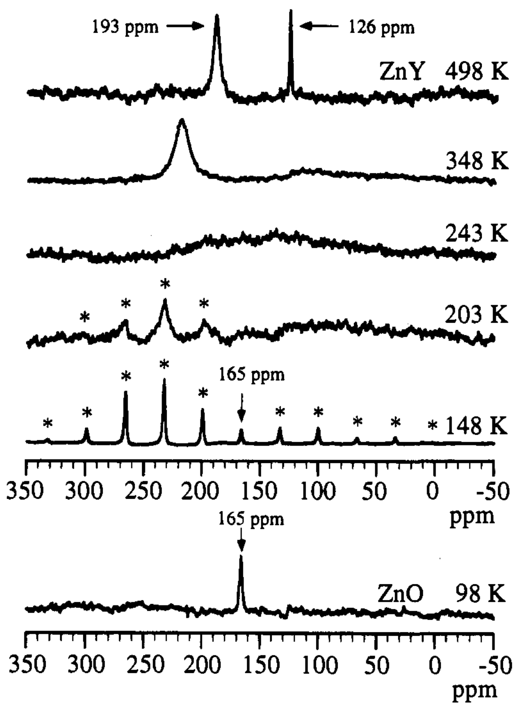

Figure 1. 75.3 MHz ^{13}C MAS NMR spectra of carbon monoxide-^{13}C on zeolite ZnY and polycrystalline ZnO. At 98 K on ZnO, the adsorbate formed a zinc carbonyl with an isotropic chemical shift of 165 ppm. In a similar study on zeolite ZnY, carbon monoxide also formed a zinc carbonyl at 148 K, which at higher temperatures reverted to a weakly adsorbed CO species in fast exchange with free CO. CO_2 formed at 498 K. Asterisks denote spinning sidebands.

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(1) Gates, B. C. *Chem. Rev.* **1995**, *95*, 511−522.

(2) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57−65.

(3) Reven, L. *J. Mol. Catal.* **1994**, *86*, 447−477.

(4) Kawi, S.; Chang, J.-R.; Gates, B. C. *J. Phys. Chem.* **1994**, *98*, 12978−12988.

(5) Hughs, T. R.; Buss, W. C.; Tamm, P. W.; Jacobson, R. L. In *New Developments in Zeolite Science and Technology*; Murakami, Y., Iijima, A., Ward, J. W., Eds.; Elsevier: Amsterdam, 1986; pp 725-732.

(6) Eisen, M. S.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10358−10368.

(7) Michael, A.; Wolfgang, M.; Michel, D.; Pfeifer, H. *Chem. Phys. Lett.* **1981**, *84*, 30−32.

(8) Koch, M.; Brunner, E.; Pfeifer, H.; Zscherpel, D. *Chem. Phys. Lett.* **1994**, *228*, 501−505.

(9) Takahashi, N.; Miura, K.; Fukui, H. *J. Phys. Chem.* **1986**, *90*, 2797−2800.

(10) Shoemaker, R. K.; Apple, T. M. *J. Phys. Chem.* **1985**, *89*, 3185−3188.

(11) Molitor, P. F.; Shoemaker, R. K.; Apple, T. M. *J. Phys. Chem.* **1989**, *93*, 2891−2893.

(12) *Organometallic Compounds of Zinc, Cadmium, and Mercury*; Wardell, J. L., Ed.; Chapman and Hall: New York, 1985; pp 135−156.

(13) Ghiotti, G.; Boccuzzi, F.; Scala, R. *J. Catal.* **1985**, *92*, 79−97.

(14) Lavalley, J.; Saussey, J.; Raïs, T. *J. Mol. Catal.* **1982**, *17*, 289−298.

(15) Gay, R. R.; Nodine, M. H.; Henrich, V. E.; Zeiger, H. J.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 6752−6761.

(16) Coates, G. E.; Ridley, D. *J. Chem. Soc.* **1965**, 1870−1877.

(17) The spectra reported here were obtained with low loadings of CO: 0.97 mmol/g or ca. 0.23 CO per Zn for ZnY (Si/Al = 2.6) and 0.03 mmol/g for ZnO. Studies at higher CO loadings indicated that up to 30% of the zinc in ZnY formed the carbonyl species while higher loadings of CO also formed a physisorbed species with a single ^{13}C peak near the gas phase shift of 182 ppm. Similar results were also obtained for a second ZnY sample prepared from a material with Si/Al = 6.4. The source and preparation of the ZnO were described previously (Kheir, A. A.; Howard, T.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 10839−10840).

(18) Herzfeld, J.; Berger, A. *J. Chem. Phys.* **1980**, *73*, 6021−6030.

(19) Walter, T. H.; Reven, L.; Oldfield, E. *J. Phys. Chem.* **1989**, *93*, 1320−1326.

(20) The coalescence of the ^{13}C sideband pattern was studied on a number of samples and at 90.4 MHz in addition to 75.3 MHz (shown). The effect is almost certainly due to the conflict of incoherent motional averaging and coherent averaging by MAS (Suwelack, D.; Rothwell, W. P.; Waugh, J. S. *J. Chem. Phys.* **1980**, *73*, 2559−2569). At temperatures above coalescence, the nonspinning spectra were very similar to the MAS spectra. The feature at ca. 219 ppm at 348 K could be a peak due to CO in a Lewis acid−base complex with zinc, but the reproducible observation of an accompanying tail to high field also suggests that this feature is the downfield edge of a CSA line shape collapsing in an as-yet uncharacterized dynamical process. A reviewer also raised the possibility of a bridged carbonyl species.

(21) The source of water for this reaction was hydroxyl groups and Brønsted sites in the ZnY zeolite (Murray, D. K.; Howard, T.; Goguen, P. W.; Krawietz, T. R.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 6354−6360).

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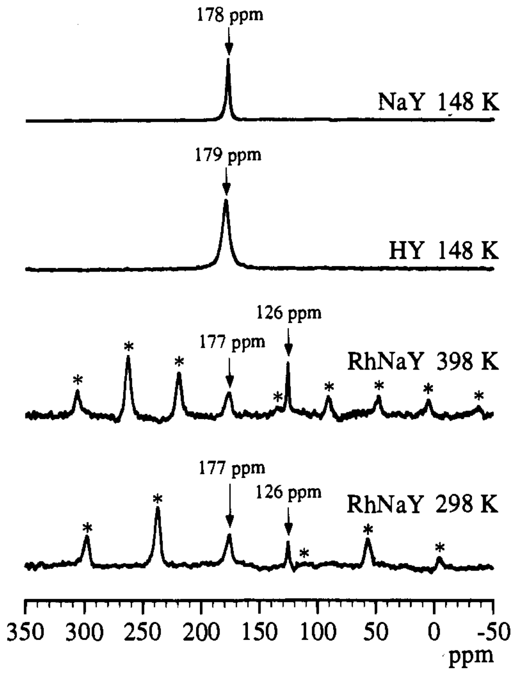

Figure 2. 90.4 MHz ^{13}C MAS NMR spectra of carbon monoxide-^{13}C on zeolites NaY, HY, and RhNaY. ^{13}CO loadings were approximately 0.1 equiv per framework aluminum. Small upfield shifts of the CO resonances and facile reorientation were indicative of weak interaction of CO with zeolites NaY and HY. RhNaY formed a rigid metal carbonyl upon adsorption at 298 K, which persisted at higher temperatures. Asterisks denote spinning sidebands.

The nature of the zeolite zinc carbonyl species can best be appreciated in the context of control experiments replicating observations reported on other materials (Figure 2).[7,8,22] CO yielded only an isotropic peak at a chemical shift several parts per million upfield of the gas phase value on either NaY or HY, even at temperatures of 148 K (shown) or as low as 123 K. The modest change in isotropic shift and rapid dynamics indicate little, if any, bonding. RhNaY,[23] in contrast, forms a tightly bound carbonyl, and this was reflected in the absence of ligand reorientation even at 398 K. The species formed at low temperature in ZnY is thus clearly a metal carbonyl like that on the Rh zeolite, except that the CO is far more weakly bound to the Zn.

Previous IR studies[13,14] have reported a peak at 2187 cm^{-1} upon adsorption of CO on ZnO and assigned this to a Zn$-$CO species; we repeated this observation for our material.[24] The diffuse reflectance infrared spectrum of CO on ZnY was more complex, but also showed intensity in that region. The identical isotropic ^{13}C NMR shift observed for CO on ZnY and ZnO suggests that these are similar surface carbonyls, but they differ in the ease of ligand dissociation. This may reflect zinc's poorer coordination by lattice oxygens in the zeolite compared to ZnO.

This study suggests the possibility of identifying other weakly bound organometallic surface complexes through NMR investigations at suitably low temperatures.

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(22) Neutron activation analysis and ^{29}Si MAS NMR showed cation exchange efficiency and zeolite framework composition as follows: NaY (91% Na, Si/Al = 2.6), dealuminated HY (99% H, Si/Al = 5.5), and RhNaY (Si/Al = 2.6, wt % Rh = 2.2, or 5% of framework sites).

(23) RhNaY was prepared from NaY (Strem Chemicals). The exchange was performed with 0.014 M RhCl$_3$ solution and followed a procedure discussed by Murray et al.: Murray, D. K.; Chang, J.-W.; Haw, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 4732–4741.

(24) Diffuse reflectance infrared spectroscopy was performed on a Nicolet 510P spectrometer equipped with a Spectra-Tech diffuse reflectance cell utilizing ZnSe windows. Typically, 0.01 g of catalyst was heated over several hours to a maximum temperature of 673 K for Y type zeolites and 773 K for ZnO under a stream of dry nitrogen gas.