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Surface Chemistry of Iron Carbonyls Grafted on a Hydrated Sodium–Y Zeolite

Sir:

A large number of metal carbonyl support systems[1] have so far been reported in zeolites[2,3] as well as on oxides[4,5] to study the relationships among homogeneous catalysis, organometallic chemistry, and heterogeneous catalysis. However, all of these works have been carried out on rigorously dehydrated zeolites, as far as we are aware. We wish here to report on the remarkable difference between the behaviors of iron carbonyls in hydrated and dehydrated zeolites. In the hydrated zeolite iron carbonyls yielded an anionic hydride $HFe_3(CO)_{11}^-$ grafted by ionic interaction with an Al^{3+} cation on the zeolite lattice in a way similar to the behavior observed in solution,[6] while the carbonyls were weakly adsorbed in the dehydrated zeolite. This observation will provide new insights into the chemistry of metal carbonyls in the zeolite.

Iron carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$,[7] were selected as model carbonyls, since the behavior of the iron carbonyls in solution has been well investigated. When $Fe(CO)_5$ was sublimed onto a hydrated Na–Y zeolite,[8] the zeolite became pale yellow. The IR absorption bands of CO were observed at 2098, 2013, and 1987 cm^{-1}, which were slightly shifted to lower frequencies compared to those of free $Fe(CO)_5$[9] and may indicate some interaction between the carbonyl ligands and the zeolite framework. Treatment under vacuum at 298 K, however, produced a solid that showed no $\nu(CO)$ bands in the infrared spectrum and the white color of the mother zeolite. This indicates the low reactivity of the surface hydroxyl groups of the zeolite toward the carbonyl ligands of $Fe(CO)_5$, which is quite consistent with the weak interaction of $Fe(CO)_5$ with silanol groups of silica.[5,10]

The Na–Y/$Fe_2(CO)_9$ system was warmed at 333 K in order to get a sufficient vapor pressure, and then the sample was evacuated at the same temperature for 30 min. The Na–Y became pink, and the generation of the anionic hydride species $HFe_3(CO)_{11}^-$ grafted on the aluminum cation by ionic interaction was confirmed as follows. The adsorbed species showed an absorption maximum at 540 nm in the diffuse-reflectance UV–vis spectrum, which is characteristic of $HFe_3(CO)_{11}^-$.[11] The IR spectrum of the species gave a shoulder of medium intensity at 2040 cm^{-1}, two broad and intense bands at 1987 and 1950 cm^{-1} for the linear carbonyls, and a broad band of smaller intensity at 1600 cm^{-1} in the bridging region. The values are in agreement with those for $[NR_4][HFe_3(CO)_{11}]$[12] and $HFe_3(CO)_{11}^-$ supported on alumina.[5] The shift of about 100 cm^{-1} to lower frequency of the $\nu(CO)$ band of the bridging carbonyl is due to the interaction between the aluminum cation and the oxygen lone pair of a coordinated CO.[5,13] The small red shifts of the $\nu(CO)$ bands corresponding to the linear carbonyls are presumably attributable to the inner electrostatic fields of the zeolites.[14]

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(1) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109.

(2) Ballivet-Tkatchenko, D.; Coudurier, G. *Inorg. Chem.* **1979**, *18*, 558.

(3) Gelin, P.; Coudurier, G.; Ben Taarit, Y.; Naccache, C. *J. Catal.* **1981**, *70*, 32. Goodwin, G. D., Jr.; Naccache, C. *J. Mol. Catal.* **1982**, *14*, 259. Namba, S.; Komatsu, T.; Yashima, T. *Chem. Lett.* **1982**, 115. Blackmond, D. G.; Goodwin, J. G., Jr. *J. Chem. Soc., Chem. Commun.* **1981**, 125. Huang, T.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 5244. Ballivet-Tkatchenko, D.; Coudurier, G.; Mozzanega, H. "Catalysis by Zeolites"; Imelik, B. et al., Eds.; Elsevier: New York, 1980; p 309. Gelin, P.; Ben Taarit, Y.; Naccache, C. "Proceedings of the 7th International Congress on Catalysis"; Elsevier: New York, 1981; p 898. Tanaka, K.; Watters, K. L.; Howe, R. F.; Andersson, S. L. T. *J. Catal.* **1983**, *79*, 251. Schneider, R. L.; Howe, R. F.; Watters, K. L. *Ibid.* **1983**, *79*, 298. Abdo, S.; Howe, R. F. *J. Phys. Chem.* **1983**, *87*, 1713, 1722.

(4) Smith, A. K.; Hugues, F.; Theolier, A.; Basset, J. M.; Ugo, R.; Zanderighi, G. M.; Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F. *Inorg. Chem.* **1979**, *18*, 3104. Ichikawa, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2268, 2273. Watters, K. L.; Howe, R. F.; Chojnacki, T. P.; Fu, C.; Schneider, R. L.; Wong, N. B. *J. Catal.* **1980**, *66*, 424. Kuznetsov, V. L.; Bell, A. T. *Ibid.* **1980**, *65*, 374. Correa, F.; Nakamura, R.; Stimson, R. E.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 5114. Beeba, M.; Streusand, B. J.; Schrader, G. L.; Gates, B. C. *J. Catal.* **1981**, *69*, 218. Deeba, M.; Gates, B. C. *Ibid.* **1981**, *67*, 303. Goodwin, J. G., Jr.; Naccache, C. *Appl. Catal.* **1982**, *4*, 145. Tanaka, K.; Watters, K. L.; Howe, R. F. *J. Catal.* **1982**, *75*, 23. Zecchina, A.; Guglielminotti, E.; Bossi, A.; Camia, M. *Ibid.* **1982**, *74*, 225, 240, 252. Ferkul, H. E.; Stanton, D. J.; McCowan, J. D.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1982**, 955. Hucul, D. A.; Brenner, A. *Ibid.* **1982**, 830. Nakamura, R.; Oomura, A.; Okada, N.; Echigoya, E. *Chem. Lett.* **1982**, 1463. Hugues, F.; Dalmon, J. A.; Bussiere, P.; Smith, A. K.; Basset, J. M.; Olivier, D. *J. Phys. Chem.* **1982**, *86*, 5136. Collier, G.; Hunt, D. J.; Jackson, S. D.; Moyes, R. B.; Pickering, I. A.; Wells, P. B.; Simpson, A. F.; Whyman, R. *J. Catal.* **1983**, *80*, 154.

(5) Hugues, F.; Basset, J. M.; Ben Taarit, Y.; Choplin, A.; Primet, M.; Rojas, D.; Smith, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 7020.

(6) Hieber, W.; Brendel, G. *Z. Anorg. Allg. Chem.* **1957**, *289*, 324. McFarlane, W.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 181.

(7) $Fe(CO)_5$ was obtained from Strem Chemicals and used as received. $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ were prepared by the conventional methods and purified before use by sublimation.

(8) Before the adsorption of the iron complex, Na–Y (UCC, SK-40) was treated in the following way: Na–Y was heated slowly under vacuum (1.3×10^{-2} Pa) up to 673 K, exposed to oxygen (13.3 kPa, 1 h), and evacuated (1.3×10^{-2} Pa, 1 h) at the same temperature. The support was then rehydrated by introduction of water vapor (2.4 kPa) at 298 K for 1 h and evacuated at 298 K (1.3×10^{-2} Pa).

(9) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; Wiley-Interscience: New York, 1978; p 280.

(10) Jackson, R. L.; Trusheim, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6590.

(11) Heiber, W.; Beutner, H. *Z. Naturforsch.* **1962**, *17B*, 211.

(12) Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1976**, *118*, 199. Hodali, H. A.; Arcus, C.; Shriver, D. F. *Inorg. Synth.* **1980**, *20*, 218. The $[NEt_4][HFe_3(CO)_{11}]$ complex gives $\nu(CO)$ bands at 2073 (w), 2008 (s), 2000 (s), and 1709 (m) cm^{-1} in C_6H_6 solvent.

(13) For example: Alich, A.; Nelson, N. J.; Strope, D.; Shriver, D. F. *Inorg. Chem.* **1972**, *11*, 2976. Kristoff, J. S.; Shriver, D. F. *Inorg. Chem.* **1974**, *13*, 499. Shriver, D. F.; Onaka, S.; Strope, D. *J. Organomet. Chem.* **1976**, *117*, 277.

(14) Jacobs, P. A. *Catal. Rev.-Sci. Eng.* **1982**, *24*, 415 and references therein.

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An analysis of the gas phase during the adsorption showed the presence of 0.93 mol of CO, 0.04 mol of CO_2, and 0.03 mol of H_2 per $Fe_2(CO)_9$ adsorbed. The basic character of the hydroxyl groups on alumina[15,16] and on alkali-metal cation-exchanged zeolites[17] has been shown. Reaction 1, similar to

$$3Fe_2(CO)_9 + 2OH^- \rightarrow 2HFe_3(CO)_{11}^- + 3CO + 2CO_2 \tag{1}$$

the formation of $HFe_3(CO)_{11}^-$ from $Fe_3(CO)_{12}$ in basic solution,[6] was concluded for the grafting of $Fe_2(CO)_9$ on the zeolite lattice. The appearance of IR bands at 1405 and 1350 cm^{-1} during the adsorption indicates that most of CO_2 remains adsorbed on zeolite as a hydrogen carbonate anion (eq 2). The

$$CO_2 + OH^- \rightarrow HCO_3^- \tag{2}$$

small amount of H_2 produced has been concluded to result from the water-gas shift reaction (WGSR), since the $HFe_3(CO)_{11}^-$/Na–Y system has been confirmed in a separate experiment to be active for the WGSR.[18]

The hydroxyl groups in reaction 1 are presumably generated through reaction 3, which has been generally proposed in water

$$O^{2-}(\text{lattice oxygen}) + H_2O \rightleftarrows 2OH^- \tag{3}$$

adsorption on an oxide surface. Although there is no report for such high reactivity of zeolite oxygen as that suggested in reaction 1, the experimental findings mentioned above strongly suggest reaction 1 to be reasonable. The framework oxygen atoms in zeolite have indeed been found to participate in the reversible exchange with the oxygen of water,[19] adsorbed oxygen,[20] and carbon dioxide,[21] though the reactions have been observed at 473 K or above. Furthermore, it is widely accepted that the hydrothermal treatment of zeolite causes easy transformation of the zeolite structure.[22] These facts suggest the relatively high reactivity of zeolite oxygen and support reaction 1.

In attempt to detect a precursor in the course of the grafting, ESR spectra of $g_I = 2.0545$, $g_{II} = 2.0395$, and $g_{III} = 2.0013$ were observed upon evacuation of the $Fe_2(CO)_9$/Na–Y system at room temperature. With progress of the reaction between $Fe_2(CO)_9$ and Na–Y, the spectrum at $g_{II} = 2.0395$ first developed and then the species with $g_{III} = 2.0013$ appeared. Further reaction of the samples resulted in a decrease in intensity of the spectrum at $g_{III} = 2.0013$ and the appearance of a third small spectrum at $g_I = 2.0545$. All of these spectra substantially disappeared when the sample was warmed to 333 K. The species with g_I, g_{II}, and g_{III} were assigned to $Fe_3(CO)_{11}^-$, $Fe_2(CO)_8^-$, and $Fe_3(CO)_{12}^-$, respectively, from the comparison with ESR spectra of iron carbonyl radicals in THF solution[23] or in CH_2Cl_2 solution.[24] These anions indicate the presence of electron-donating sites in the Na–Y zeolite and might be precursors for the $HFe_3(CO)_{11}^-$ species.

When $Fe_3(CO)_{12}$ was adsorbed on the hydrated Na–Y, the IR, UV, and volumetric studies indicated the formation of $HFe_3(CO)_{11}^-$ interacting via the bridging carbonyl with an acidic center (eq 4). The adsorption of $Fe_3(CO)_{12}$ was much

$$Fe_3(CO)_{12} + OH^- \rightarrow HFe_3(CO)_{11}^- + CO_2 \tag{4}$$

slower than that of $Fe_2(CO)_9$. This is due to the molecular size of $Fe_3(CO)_{12}$ (ca. 1.05 nm × 0.75 nm)[25] being close to the diameter of the zeolite window (approximately 1.0 nm).[26] This observation indicates that the hydride anion was generated inside the zeolite supercages. The $HFe_3(CO)_{11}^-$ species grafted on the hydrated zeolite was stable at 433 K under a dynamic vacuum and up to 473 K in the presence of CO.

When $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ was introduced on Na–Y zeolites dehydrated at 773 K, the carbonyl was adsorbed as it was and no hydride anion was observed. The adsorbed $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ was unstable under a static vacuum at temperatures higher than 373 K. Ballivet-Tkatchenko and Coudurier[2] have reported that $Fe_3(CO)_{12}$ or $Fe(CO)_4$ bonded to the zeolite was obtained as a stable species in a dehydrated H–Y zeolite matrix upon the admission of $Fe_3(CO)_{12}$, $Fe_2(CO)_9$, or $Fe(CO)_5$. It was further reported that treating $Fe_3(CO)_{12}$/zeolite under a CO atmosphere restored the IR spectra of the $Fe(CO)_5$- or $Fe_2(CO)_9$/zeolite system. The same research group has also presented that when the $Fe_3(CO)_{12}$/H–Y zeolite system was heated to 333 K, $H_2Fe_3(CO)_{11}$ was formed within the supercage and interacted with the zeolite through hydrogen bonding.[27] The difference among the behaviors of the iron carbonyls in hydrated and dehydrated Na–Y and dehydrated H–Y indicates the importance of the degrees of hydration of the zeolites and the acid–base properties of the zeolites used.

Registry No. $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; $HFe_3(CO)_{11}^-$, 55188-22-2.

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[15] Knözinger, H.; Stubner, B. *J. Phys. Chem.* **1978**, *82*, 1526.

[16] Che, M.; Naccache, C.; Imelik, B. *J. Catal.* **1972**, *24*, 328.

[17] Ono, Y. "Catalysis by Zeolites"; Imelik, B. et al., Eds.; Elsevier: New York, 1980; p 19.

[18] Iwamoto, M.; Kusano, H.; Kagawa, S. *Chem. Lett.* **1983**, 1483.

[19] Iwamoto, M.; Morita, S.; Kagawa, S. *J. Phys. Chem.* **1981**, *85*, 3955.

[20] Antoshin, G. V.; Minachev, Kh. M.; Sevastjanov, E. N.; Kodratjev, D. A.; Newy, C. Z. *Adv. Chem. Ser.* **1971**, *No. 101*, 514. Iwamoto, M.; Morita, S.; Kagawa, S. *J. Chem. Soc., Chem. Commun.* **1980**, 842.

[21] Peri, J. B. *J. Phys. Chem.* **1975**, *79*, 1582. Gensse, C.; Anderson, T. F.; Fripiat, J. J. *Ibid.* **1980**, *84*, 3562.

[22] Barrer, R. M. "Hydrothermal Chemistry of Zeolites"; Academic Press: New York, 1982.

[23] Krusic, P. J.; Filippo, J. S., Jr.; Hutchinson, H.; Hance, R. L.; Daniels, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2129. Krusic, P. J. *Ibid.* **1981**, *103*, 2131. Krusic, P. J.; Filippo, J. S., Jr. *Ibid.* **1982**, *104*, 2045.

[24] El Murr, N.; Chaloyard, A. *Inorg. Chem.* **1982**, *21*, 2206.

[25] Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351.

[26] Rabo, J. A. *ACS Monogr.* **1976**, *No. 171*, 1.

[27] Ballivet-Tkatchenko, D.; Coudurier, G.; Mozzanega, H.; Tkatchenko, I. *Fundam. Res. Homogeneous Catal.* **1979**, *3*, 257.

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Sulfide Bronzes: Preparation and Characterization of (RE)Pd_3S_4 (RE = Rare Earth)

Sir:

The platinum-group bronzes, $M_xPt_3O_4$ and $M_xPd_3O_4$ where M = Li, Na, Ni, Cd, etc. and $0 < x \leq 1$, are a widely studied class of materials of considerable technological interest. The platinum bronzes have been used as chlor-alkali anodes[1] and as H_2–O_2 fuel-cell electrocatalysts.[2] Moreover, $Na_xPt_3O_4$ is the active component of Adam's catalyst, a mixture of Pt, α-PtO_2, and $Na_xPt_3O_4$ used for the reduction of organic compounds.[3]

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[1] (a) Thiele, G.; Zöllner, G.; Koziol, K. British Patent 1328270, 1973. (b) Thiele, G.; Zöllner, G.; Koziol, K. U.S. Patent 4042484, 1977. (c) Koziol, K.; Sieberer, H.-H.; Rathjen, H. C. U.S. Patent 3948752, 1976. (d) Zöllner, D.; Zöllner, C.; Koziol, K. U.S. Patent 3962068, 1976. (e) Zöllner, C.; Zöllner, D.; Koziol, K. U.S. Patent 3992280, 1976. (f) Fukuda, M.; Asai, K. German Patent 1671455, 1975. (g) Thiele, G.; Zöllner, D.; Koziol, K. German Patent 1813944, 1975.

[2] Shannon, R. D.; Gier, T. E.; Carcia, P. F.; Bierstedt, P. E.; Flippen, R. B.; Vega, A. J. *Inorg. Chem.* **1982**, *21*, 3372.

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