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Interaction of $Cr(CO)_6$ with Na-Y Zeolite: Effect of Co-Adsorbed Ammonia

Zeolites are often used as supports for catalytically active transition metal complexes and dispersed metals. In favorable cases, the pore structure of the support allows stabilization of the active species and prevents aggregation, leading to a decrease of catalytic activity (*1*). A further advantage of zeolite-supported catalysts is the shape-selectivity which they often manifest (*2, 3*). This arises from either steric hindrance of some transition states or from diffusional selectivity toward reactant or product molecules.

Many catalytic processes are mediated by transition metal carbonyls and their decomposition products, which include well-dispersed metal particles. The large pores and cages of faujasite-type zeolites allow accommodation of carbonyls such as $Fe(CO)_5$, $Mo(CO)_6$, or $Co_2(CO)_8$ (*4, 5*). The interaction between the support and the metal carbonyl, about which much remains to be known, is a major factor which influences the type of catalyst formed and catalytic behavior. We report here a study of the interaction between $Cr(CO)_6$ and an Na-Y zeolite; the effect of co-adsorbed ammonia is also considered. FTIR spectroscopy and molecular modeling have been used to characterize and visualize the zeolite-metal carbonyl adduct formed.

Na-Y (Linde: LZ-Y52) was pressed into a self-supporting disk and activated at 625 K (1 h under a dynamic vacuum of 10^{-5} Torr: 1 Torr = 133.3 N m^{-2}) in a suitable cell for IR measurements. $Cr(CO)_6$ (Strem Chemical Co.) was admitted into the cell by vacuum sublimation at room temperature. FTIR spectra were obtained using a Bruker IFS 48 instrument, and computer modeling was carried out with Chem-X.

Time-resolved spectra of $Cr(CO)_6$ on Na-Y are shown in Fig. 1. The spectrum obtained immediately after admission of the metal carbonyl into the IR cell is dominated by a strong absorption band centered at 1980 cm^{-1}. This is the frequency to be expected for the strongest IR active mode (T_{1u}) of a slightly disturbed (physisorbed) $Cr(CO)_6$ molecule. Weaker bands are expected at ca. 2010 (E_g) and 2115 cm^{-1} (A_{1g}) (*6, 7*) and are also experimentally observed in Fig. 1. Upon standing, the original spectrum develops more complex features *without substantive change in the overall integral intensity*. The prominent 1980-cm^{-1} band progressively decreases while new bands are formed. This can be explained in terms of a diffusion-controlled penetration of the metal carbonyl into the zeolite pellet. Heavy $Cr(CO)_6$ vapor impinging on both sides of the pellet forms a penetration front which saturates the exposed surface of the sample. Thus, most of the metal carbonyl remains simply physisorbed. As the penetration front advances through the pellet, $Cr(CO)_6$ molecules fill the faujasite cages (supercages) where they interact with Na^+ ions forming bonded species with substantially altered CO stretching frequencies.

The simplest interaction between $Cr(CO)_6$ and an Na^+ ion leads to formation of $(CO)_5CrCO\ .\ .\ .\ Na^+$ species (adduct I). This would give a stretching frequency of the Na^+-bonded CO ligand lower than 1980 cm^{-1}, and three IR active modes at higher frequency; two of them higher than the above E_g and A_{1g} frequencies (*6, 8*).

Computer modeling (data not shown for the sake of brevity) demonstrates that octahedral $Cr(CO)_6$ molecules and Na^+ ions are of the right size to form also double-bonded

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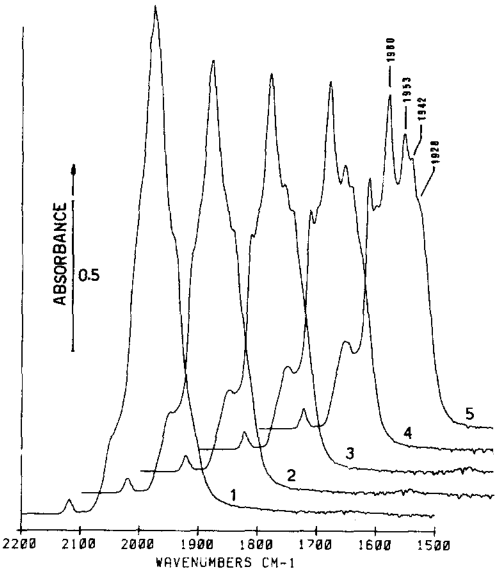

FIG. 1. Time-dependent spectra of $Cr(CO)_6$ on Na-Y zeolite. Spectrum 1 was obtained immediately after admission of $Cr(CO)_6$ into the IR cell. Spectra 2–5 were obtained successively after the respective times: (2) 15, (3) 30, (4) 50, and (5) 100 min. The wavenumber scale refers to spectrum 1, with peak maximum at 1980 cm^{-1}: for clarity of presentation, Spectra 2–5 are each displaced by 100 cm^{-1} with respect to the previous spectrum. The maximum absorbance is at 1980 cm^{-1} in each spectrum.

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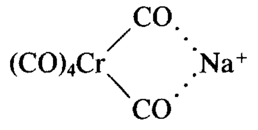
$(CO)_4Cr(CO)_2\cdots Na^+$
(adduct II). These species would give two IR active modes lower than 1980 cm^{-1} (symmetric and antisymmetric stretching vibrations of the Na^+-bonded CO ligands) and four bands at higher frequency (*9*).

Adducts I and II, along with some remaining slightly perturbed $Cr(CO)_6$ molecules, can explain the main features of the final spectrum in Fig. 1. In fact, three low-frequency bands are seen at 1953, 1942, and 1928 cm^{-1}, together with several bands at higher frequencies: 2130–2110, 2070–2045, and 2012–2000 cm^{-1}. It is relevant to point out that up to three $Fe(CO)_5$ molecules were recently shown (*4*) to be accommodated into the supercage of Y-type zeolites. On account of its similar size, $Cr(CO)_6$ is probably in an analogous situation. In addition to adducts I and II, other anchored $Cr(CO)_6$ species (e.g., $Cr(CO)_6$ O-bonded to two Na^+ ions via *trans*-CO ligands) cannot be excluded on the basis of the present IR spectra. Experimental work to clarify this point is currently in progress.

After the final spectrum of Fig. 1 was taken, 5 Torr (final equilibrium pressure) of NH_3 was dosed into the IR cell. The observed effect (Fig. 2, spectrum 1) was (i) the appearance of the modes of adsorbed NH_3, (ii) the total disappearance of the complex spectrum of Fig. 1, curve 5, and (iii) reappearance of the original spectrum corresponding to slightly perturbed $Cr(CO)_6$ mol-

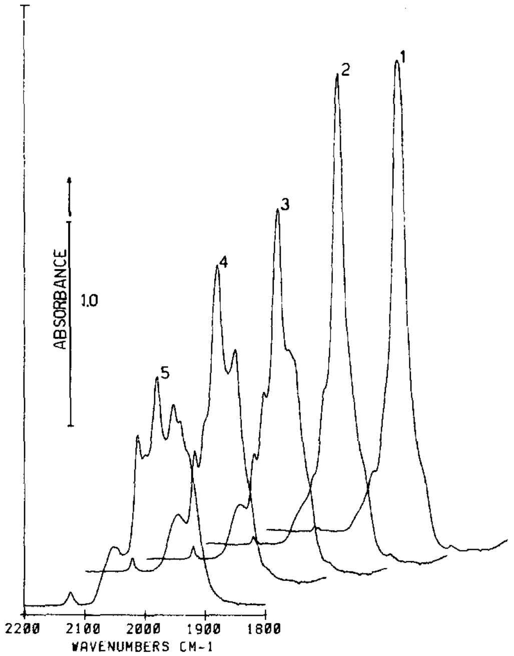

FIG. 2. Spectrum 1 shows the effect of dosing with NH_3 (5 Torr) after the final spectrum of Fig. 1 had been obtained. Spectra 2–5 show the effect of outgassing NH_3 for increasing times. The wavenumber scale refers to spectrum 5, and other spectra are displaced for clarity as in Fig. 1. The maximum absorbance is at 1980 cm^{-1} in each spectrum.

ecules. This effect is interpreted in terms of solvation of the Na^+ ions in the supercage by NH_3 and consequent detachment of $Cr(CO)_6$ due to competitive interaction. On outgassing NH_3 for increasing time at room temperature, the final spectrum in Fig. 1 was regenerated (spectrum 5). It is thus shown that NH_3 and $Cr(CO)_6$ are in competition for the coordination to the same Na^+ ions. During this NH_3 desorption experiment the integrated intensity of the spectrum remains constant. This can be readily explained in terms of a greater difficulty of $Cr(CO)_6$ to diffuse out of the faujasite cage. Contrary to the effect shown by NH_3, dosing with 25 Torr of CO (spectra not shown) did not modify the final spectrum in Fig. 1.

The observed competitive interaction can be relevant for further studies on the chemistry of transition metal carbonyls in the presence of oxophilic acceptors and on the ion-pairing effects between carbonyl anions and alkali metal cations (*10*).

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