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NMR and Visible Spectroscopic Study of Chromium Carbonyl Supported on Na-X Zeolite and Alumina

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Solid-state ^{13}C NMR spectroscopy and diffuse-reflectance visible spectroscopy (DRS) have been used to study samples prepared from $\text{Cr}(\text{CO})_6$ and Na-X zeolite or γ -alumina. A rose-colored surface carbonyl with $\text{Cr}(\text{CO})_3$ stoichiometry is formed when $\text{Cr}(\text{CO})_6$ reacts with the zeolite at 393 K. The ^{13}C chemical shift of 247 ppm found by using NMR with magic-angle spinning indicates an anionic tricarbonyl. DRS absorption bands at 460 and 540 nm are from this surface species. With the addition of CO, the 540-nm band is removed and a 460-nm band from an intermediate carbonyl, $\text{Cr}(\text{CO})_4$ or $\text{Cr}(\text{CO})_5$, appears. The addition of oxygen was monitored with NMR spectroscopy and DRS and showed that the CO liberated when chromium is oxidized reacts with the remaining $\text{Cr}(\text{CO})_3$ to form the intermediate carbonyl and finally physisorbed $\text{Cr}(\text{CO})_6$. Samples prepared from $\text{Cr}(\text{CO})_6$ and alumina at 393 K produce small ^{13}C NMR peaks at 225, 216, and 207 ppm although some of the chromium is oxidized.

Introduction

A considerable literature has developed regarding the reaction of group VI metal carbonyls with oxide supports.^{1,2} The relationship between supported inorganic carbonyls and heterogeneous catalysts of industrial interest has been the main driving force for this work.³⁻⁵ Occasionally, the reactions produce surface carbonyls with very reproducible metal-to-carbonyl ratios rather than surface mixtures with the metal in various states of oxidation. The molybdenum tricarbonyl surface compound formed when $\text{Mo}(\text{CO})_6$ reacts with γ -alumina is an example that has been studied extensively.⁶⁻⁸ Recent studies have employed solid-state NMR spectroscopy to characterize samples made from both $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ on alumina.⁹⁻¹¹

The reaction of $\text{Cr}(\text{CO})_6$ with a support depends greatly on the support used. With silica¹² and alumina,¹³ the oxidation of the chromium by surface hydrogens occurs in the same temperature range as decarbonylation even though the reaction mixture is rigorously kept free of oxygen. The decomposition of $\text{Cr}(\text{CO})_6$ on calcium oxide,¹⁴ magnesia,¹⁴ or H-Y zeolite¹⁵ apparently also produces an assortment of supported chromium carbonyl and oxidized species. However, when Na-X zeolite is used as a support at 393 K, a chromium tricarbonyl compound forms that is stoichiometrically well-defined.¹⁶ The temperature-programmed decomposition of $\text{Cr}(\text{CO})_6$ on Na-X zeolite shows two well-separated peaks at 395 and 550 K representing the carbon monoxide molecules evolved.¹⁶ The use of solid-state NMR spectroscopy and diffuse-reflectance visible spectroscopy (DRS) in the characterization of samples prepared from $\text{Cr}(\text{CO})_6$ on Na-X zeolite as well as γ -alumina is reported here.

Experimental Section

Samples were prepared in a quartz reactor connected to a stainless-steel manifold that provides access to an oil-diffusion vacuum pump, a pressure transducer, purified gases, and ^{13}C -enriched carbon monoxide. Helium and carbon monoxide were passed through a Cr/SiO_2 oxygen scavenger before use. The supports were Na-X zeolite (Davison Type 13X, Grade 542) and γ -alumina (Catapal extrudate from Vista Chemical Co.). The NMR samples were prepared from 0.5 g of a 60-80-mesh support, and 1.2 g of a 100-140-mesh support was used for DRS samples. Both supports were calcined for 1 h at 773 K in an O_2 flow (30 mL/min) and for 0.5 h under vacuum at the same temperature.

To prepare samples with the zeolite support, $\text{Cr}(\text{CO})_6$ (typically 10 mg for the DRS samples and 20 mg for the NMR samples) was dissolved in a few milliliters of freshly distilled pentane. The solution and pentane washings were then added to the calcined zeolite in the reactor against a 100 mL/min helium flow, which was used to evaporate the pentane and to protect the sample from oxygen. After the sample temperature was cautiously increased in several increments, the sample was heated for over 1 h at 393 K in a flow of helium (30 mL/min). CO flushed from the reactor was trapped on silica at 77 K before the amount was determined by gas chromatography. Heating was stopped when the rate of CO evolution became small. $\text{Cr}(\text{CO})_6$ and alumina were dry-mixed in the reactor instead of using the pentane impregnation technique, but other

aspects of the preparation of $\text{Cr}(\text{CO})_6$ supported on alumina were similar to those just described for the zeolite support.

The NMR samples were enriched by adding a known amount of ^{13}C O (95 ± 5 isotope %) to the evacuated reactor containing the supported carbonyl sample and heating the closed reactor for 0.5 h at 373 K. The NMR samples were flushed with helium at either room temperature or 393 K and placed in a glass tube attached to the side of the reactor without opening the reactor. The glass tube was sealed in a flame and sent to the CSU Regional NMR Center. There the sample was opened under a nitrogen atmosphere and placed in a Kel-F rotor that was sealed with a Teflon plug. The NMR spectra were obtained at 37.74 MHz on a modified Nicolet NT-150 spectrometer with home-built magic-angle spinning (MAS) and cross-polarization (CP) accessories. The ^1H and ^{13}C 90° pulse lengths were 5 μs .

A cylindrical quartz cuvette (Wilmad WG-37) with a 1.4-mL sample volume and a 5-mm sample thickness was used for the DRS. The 3-mm-o.d. stem was modified so that the cuvette could be attached to the reactor and also fitted with a valve (Nupro B-4J). The DRS samples were placed in the cuvette without opening the reactor, and this connection was sealed in a flame. The spectra were obtained on a Varian Cary 219 spectrophotometer with an 11-cm integrating sphere. The reflectance spectra are difference spectra with the calcined support subtracted by using the "auto base line" accessory of the spectrophotometer. No attempt was made to obtain absolute absorbance values for these spectra. The background absorbance of the zeolite support made it difficult to obtain reliable spectra below 400 nm, but the spectra of samples with alumina as the support could be extended to 260 nm. For further additions of CO or O_2 gas, the sealed cuvette was attached directly to the manifold through the Nupro valve. The amount of gas added was calculated from the pressure measured in the 9.0-mL manifold, and the transfer of gas was carried out with the cuvette in liquid nitrogen.

Results

A description of samples A-I is presented in Table I. The CO/Cr ratios for the zeolite samples agree with previous work¹⁶ that found an overall stoichiometry of $\text{Cr}(\text{CO})_3$ on the surface. The pentane evaporation method was used for the Na-X samples,

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Table I. Samples Prepared from $\text{Cr}(\text{CO})_6$ and either Na-X Zeolite or Alumina

sample	support	loading, ^a $10^4(\text{g of Cr/g of support})$	initial CO/Cr ratio on surface ^a	final CO/Cr ratio on surface ^{a,b}	^{13}C isotope % ^a	method
A	NaX	18.7 ± 0.4	3.05 ± 0.07		1	DRS
B	NaX	20.7 ± 0.5	3.19 ± 0.07		1	DRS
C	NaX	82 ± 2	3.0^c		61 ± 2	NMR
D	NaX	93 ± 2	2.99 ± 0.07	3.5 ± 0.1	61 ± 2	NMR
E	NaX	113 ± 2	3.18 ± 0.06	4.4 ± 0.1	59 ± 5	NMR
F	NaX	89 ± 2	2.94 ± 0.07	4.9 ± 0.1	45 ± 2	NMR
G	Al_2O_3	13.3 ± 0.3	2.01 ± 0.11		1	DRS
H	Al_2O_3	62 ± 1	3.21 ± 0.06		66 ± 2	NMR
I	Al_2O_3	76 ± 2	3.76 ± 0.05	4.2 ± 0.1	41 ± 1	NMR

^aUncertainties quoted are standard deviations estimated from propagation-of-error treatments. ^bA "final" CO/Cr mole ratio is reported for samples that have had their mole ratio increased by the addition of CO after their initial decomposition at 393 K. ^cAssigned value based on ratios found with similar samples.

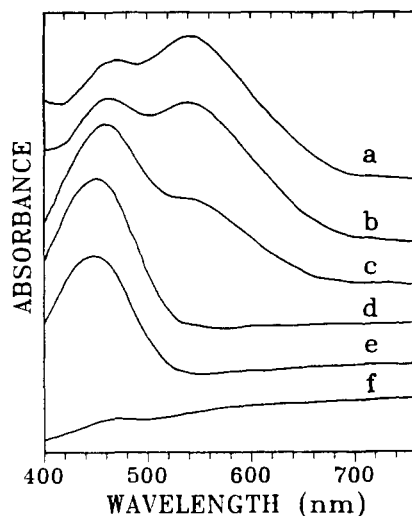


Figure 1. Diffuse-reflectance visible spectra showing the effects of carbon monoxide additions to chromium tricarbonyl on Na-X zeolite. The Na-X zeolite absorbance has been subtracted. CO added to tricarbonyl sample A: (a) 0; (b) 0.00778 ± 0.00005 mmol; (c) 0.0240 ± 0.0001 mmol; (d) 0.121 ± 0.001 mmol; (e) 0.317 ± 0.002 mmol. There is 0.0469 ± 0.0004 mmol of Cr in the sample. The sample was evacuated and pressurized with oxygen (<200 kPa) to give spectrum f. The spectra have been vertically offset, and all originally had the same absorbance at 760 nm.

since the dry-mix method tended to produce zeolite samples with an inhomogeneous appearance and a low loading. The color of the samples is an interesting aspect of this chemistry. When a rose-colored $\text{Cr}(\text{CO})_3/\text{Na-X}$ sample is exposed to air through a narrow opening (such as the cuvette stem), three bands of color develop in a few minutes: the original rose band, a bright yellow middle band, and the beige band of the zeolite. Eventually, the whole sample returns to the light color of the zeolite. The CO/Cr ratios for the alumina samples in Table I increase as the loading is increased. The alumina samples were brownish green.

Figure 1 shows the diffuse-reflectance spectra of $\text{Cr}(\text{CO})_3/\text{Na-X}$ sample A before and after exposure to carbon monoxide. The spectrum of the original sample (A) has absorption bands at 460 and 540 nm. In addition, a smaller 380-nm band outside the spectral range shown in the figure is present. With the incremental addition of CO, the band at 540 nm disappears and the absorbance at 460 nm increases as the sample turns bright yellow. The addition of a small amount of oxygen to $\text{Cr}(\text{CO})_3/\text{Na-X}$ sample B decreases the 540-nm absorbance and slightly increases the absorbance at 460 nm. Further addition of O_2 removes the 540-nm band completely while the 460-nm absorbance becomes smaller. The 460-nm band disappears when the number of moles of O_2 added is about twice the number of moles of Cr in the sample. The spectra in Figure 1 were recorded under identical conditions, apart from the vertical offset.

Figure 2 shows ^{13}C NMR spectra of $\text{Cr}(\text{CO})_3/\text{Na-X}$ (sample C) (a) with and (b) without magic-angle spinning. The isotropic

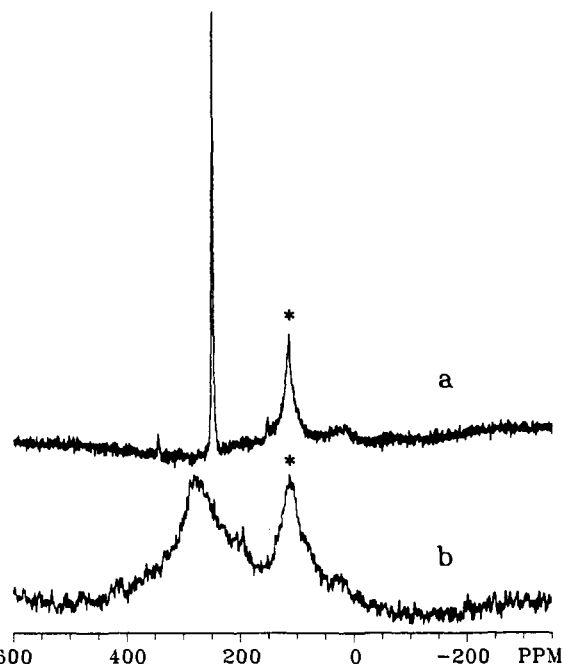


Figure 2. ^{13}C NMR spectra of sample C, chromium tricarbonyl on Na-X zeolite with a repetition time of 4 s. The Kel-F and Teflon rotor materials give the peaks at 110 (*) and 20 ppm. Spectrum a is the MAS spectrum with 1400 scans and no line-broadening factor. Spectrum b was taken without MAS and used 788 scans and a 30-Hz line-broadening factor.

chemical shift for the tricarbonyl is 247 ppm, as indicated in the MAS spectrum of Figure 2a. All chemical shifts are reported relative to TMS and have an uncertainty of ± 1 ppm. A repetition rate of 4 s was appropriate since T_1 for the ^{13}C resonance at 247 ppm was found to be 0.95 ± 0.06 s by using the progressive saturation method¹⁷ with six τ values. The amplitudes of the sidebands at 343 and 150 ppm (spinning rate 3.6 kHz) are consistent with the chemical shift anisotropy manifested in the powder spectrum of Figure 2b. The resonance at 110 ppm in each spectrum (marked with *) as well as a smaller peak near 20 ppm is from Kel-F and Teflon carbons in the rotor. Cross polarization would suppress these background signals, but an attempt to use CP and MAS on sample C with a contact time of 15 ms produced a very small signal at 247 ppm after 3000 scans.

NMR spectra were also obtained for samples D-F, in which the CO/Cr ratios were between 3 and 6 (Table I). Sample F, with an overall stoichiometry of $\text{Cr}(\text{CO})_{4.9}$ on the zeolite, gave a single peak at 213 ppm, which is undoubtedly physisorbed $\text{Cr}(\text{CO})_6$. The resonance line width is 100 Hz with MAS and 350 Hz without spinning (± 10 Hz). An MAS spectrum of sample D, $\text{Cr}(\text{CO})_{3.5}$ on zeolite, showed a tricarbonyl peak at 247 ppm, which was less intense than the signal from the rotor carbons, but

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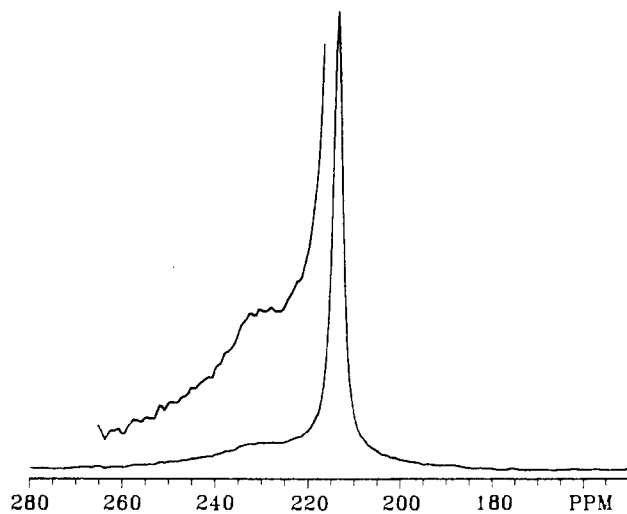


Figure 3. ^{13}C NMR MAS spectra of $\text{Cr}(\text{CO})_{4.4}/\text{Na-X}$ zeolite, sample E. A 5-fold expansion is given above 220 ppm. The spectrum used 6000 scans with a repetition time of 1 s and a line-broadening factor of 30 Hz.

no new resonances could be clearly identified. Figure 3 is the MAS spectrum for sample E, $\text{Cr}(\text{CO})_{4.4}$ on zeolite. The large resonance at 213 ppm is again physisorbed $\text{Cr}(\text{CO})_6$. However, a small broad peak is seen at 230 ppm in the expanded part of the spectrum.

The spectra given in Figure 4 show the effect of exposing the sample to air. The NMR rotor containing tricarbonyl sample C was opened to air and then resealed within a few seconds. An MAS spectrum (Figure 2a) had been obtained for this sample before the exposure. Thus, the sample had been compressed against the outer wall of the rotor and the void in the center of the sample provided easy access for the air. By the time data collection for the first spectrum of Figure 4 was complete, the 247 ppm resonance had already been reduced significantly. Data were then collected continuously over 36 h with a new spectrum produced every 1.1 h. The $\text{Cr}(\text{CO})_6$ resonance begins to appear after 7 h, and the height of this resonance becomes constant after about 30 h. In this experiment the Kel-F/Teflon background peak at 110 ppm provides a convenient internal intensity reference.

Attempts to obtain ^{13}C NMR signals from the $\text{Cr}(\text{CO})_{3.21}/\text{Al}_2\text{O}_3$ sample (H) were unsuccessful with and without CP. NMR spectra (a) without and (b) with CP are shown in Figure 5 for the $\text{Cr}(\text{CO})_{4.2}/\text{Al}_2\text{O}_3$ sample (I) for a contact time of 15 ms. When a contact time of 5 ms was used to obtain a CP/MAS spectrum of this sample, no signal was observed. By a change in the spinning rate, it was demonstrated that the broad resonance at 225 ppm in Figure 5a is not a sideband of the rotor signal at 110 ppm. A resonance at 207 ppm is seen with and without CP. The resonance at 216 ppm in the spectrum using CP/MAS is a barely visible shoulder on the 225 ppm peak in the spectrum taken without CP.

The diffuse-reflectance spectrum of sample G, $\text{Cr}(\text{CO})_6$ decomposed on γ -alumina, has an intense, broad band at 420 nm with a broad shoulder centered at 600 nm. With the addition of CO, the main band decreases and the shoulder disappears completely. A band at 280 nm becomes distinct after the sample is exposed to excess CO overnight.

Discussion

Samples prepared from $\text{Cr}(\text{CO})_6$ and Na-X zeolite by heating at 393 K are referred to as chromium tricarbonyls because 3.07 ± 0.11 is the average initial ratio of CO/Cr left on the zeolite. However, this overall ratio does not differentiate among mononuclear $\text{Cr}(\text{CO})_3$, binuclear $\text{Cr}_2(\text{CO})_6$, and polynuclear carbonyls. Even a mixture of different surface species is not ruled out. The three diffuse-reflectance bands at 380, 460, and 540 nm for tricarbonyl sample A give some indication of the species involved. Similar visible bands are not found in spectra for tricarbonyl-(arene)chromium compounds. A wavelength of 376 nm reported for the lowest energy band of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ is typical for these compounds.¹⁸ Spectra for binuclear complexes correspond

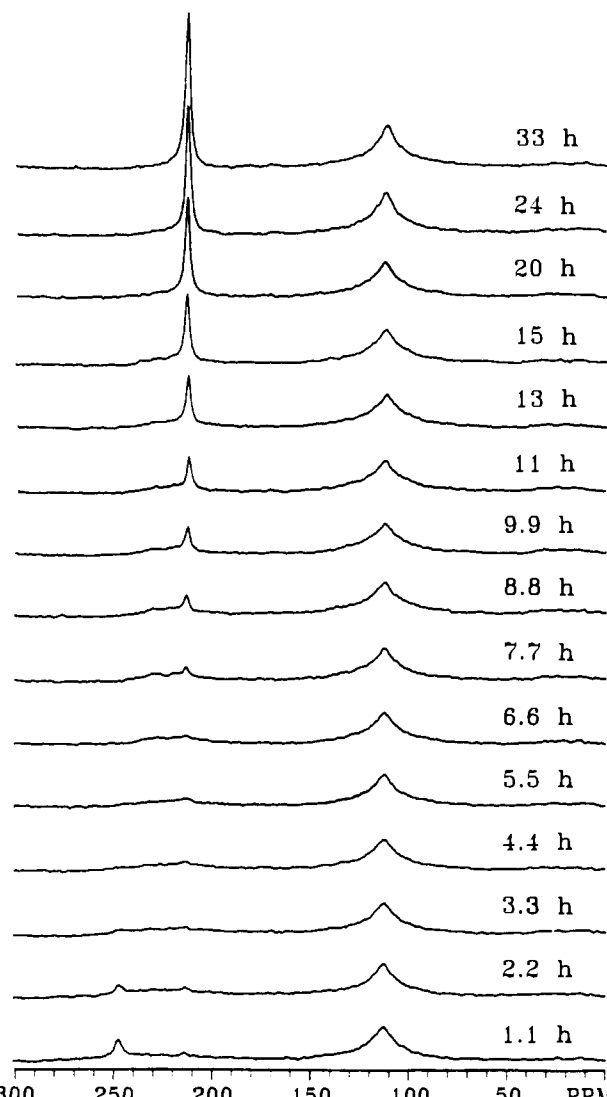


Figure 4. ^{13}C NMR MAS spectra of sample C, chromium tricarbonyl on Na-X zeolite after a brief exposure of the sample to air. Each spectrum used 1000 scans with a repetition time of 4 s and a line-broadening factor of 30 Hz.

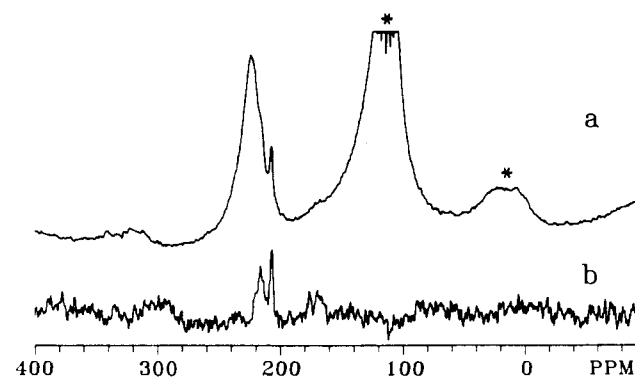


Figure 5. ^{13}C NMR MAS spectra of the $\text{Cr}(\text{CO})_{4.2}/\text{Al}_2\text{O}_3$ sample (I). Spectrum a (single-pulse mode, no CP) represents 90 000 scans with a repetition time of 1 s and a line-broadening factor of 30 Hz. Spectrum b (CP, 15-ms contact time) represents 60 000 scans with a repetition time of 1 s and a line-broadening factor of 30 Hz. Peaks from the Kel-F and Teflon rotor materials are marked *.

to the sample A spectrum better because $\sigma \rightarrow \sigma^*$ and $d\pi \rightarrow \sigma^*$ transitions associated with a group VI metal-metal bond are in the near-UV or visible region.¹⁸ The binuclear complex (η^5 -

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$C_5H_5)_2Cr_2(CO)_6$ has absorption bands at 488 and 590 nm.¹⁸

The isotropic ^{13}C NMR chemical shift of 247 ppm for the zeolite-supported tricarbonyl represents a carbonyl carbon substantially deshielded compared to those in tricarbonyl(arene)-chromium compounds. While the normal range for these compounds is from 232 to 236 ppm,¹⁹ the anionic tricarbonyl $Na-[(\eta^5-C_5H_5)Cr(CO)_3]$ dissolved in THF has a chemical shift of 246.7 ppm.²⁰ Deshielding in anionic carbonyls is fairly general, and deshielding due to electron donation to the chromium in a tricarbonyl has been demonstrated.²⁰ Since the zeolite framework is negatively charged, it is reasonable to suppose that the tricarbonyl species is an anionic surface carbonyl with zeolite oxygens (O_2) acting as ligands. A surface compound analogous to $[Cr_2(CO)_{10}]^{2-}$ can be formulated as $[(O_2)_4Cr_2(CO)_6]^{x-}$. While this compound is consistent with DRS and NMR indications of a binuclear, anionic species, it is premature to rule out a mononuclear species, $[(O_2)_3Cr(CO)_3]^{x-}$, or a mixture, since the details of bonding to the surface are not clear. Yong and Howe have recently suggested that a molybdenum carbonyl species supported on Na-Y zeolite is binuclear and anionic.²¹

Whereas $^1H-^{13}C$ CP involving surface protons has been found to be useful in enhancing the ^{13}C NMR spectrum of the $Mo(CO)_3$ surface complex on a partially dehydroxylated γ -alumina,¹⁰ CP does not work well on the Na-X zeolite. This presumably results from the limited number of surface hydroxyl groups in the zeolite.²² The openings in the zeolite framework do not exclude $Cr(CO)_6$ (diameter 0.91 nm, calculated from van der Waals radii and bond lengths).²³ The "effective pore size" in the Na-X zeolite is between 0.8 and 0.9 nm with "supercage" diameters of about 1.3 nm.²² A binuclear complex with a structure similar to that of $[Cr_2(CO)_{10}]^{2-}$ would be approximately 1.2 nm in length (including van der Waals radii) and could fit into the supercage.²⁴ Since the sample with the highest loading (E) averages only 0.36 chromium atom per supercage, the chromium complexes are probably well dispersed among the zeolite cavities.

The NMR spectra also give information about motion involving the surface compound. The chemical shift anisotropy (CSA) of the chromium tricarbonyl in Figure 2 is less than half the anisotropy observed for $Mo(CO)_3$ /alumina.¹⁰ As expected for a static carbonyl, the $Mo(CO)_3$ /alumina CP/MAS spectra show a sideband pattern consistent with a CSA powder pattern width of 400 ppm. Thus, for the chromium tricarbonyl on Na-X, rapid motion involving the surface complex causes the partial collapse of the powder pattern at room temperature.

The increase of the DRS absorbance at 460 nm when CO is added to tricarbonyl sample A is assumed to signal the formation of an intermediate surface carbonyl, $Cr(CO)_4$ or $Cr(CO)_5$. The identification of the band at 460 nm for a tetracarbonyl or a pentacarbonyl complex is reasonably consistent with assignments for model compounds in solution. The low-energy transitions of $Cr(CO)_5$ (piperidine) and $Cr(CO)_4$ (ethylenediamine) are "d-d" transitions at 420 and 424 nm, respectively.¹⁸ The yellow color observed as the high-wavelength band disappears when either CO or O_2 is added to the tricarbonyl thus indicates the presence of one or more intermediate carbonyls. Our interpretation considers the band at 460 nm from the intermediate carbonyl to coincidentally occur at the same frequency as a band from the tricarbonyl sample.

Although the 460-nm DRS band thought to come from an intermediate carbonyl is readily observed, the ^{13}C NMR spectra with MAS for the corresponding species proved difficult to obtain. Three samples prepared by adding CO to the tricarbonyl showed either the 247 ppm or the 213 ppm peaks but only minor reso-

nances between these shifts. The small peak at 230 ppm in Figure 3 may be due to a $Cr(CO)_4$ or $Cr(CO)_5$ species. Although the shift seems appropriate for a nonionic tricarbonyl,¹⁹ the negative zeolite framework could result in a downfield shift to 230 ppm for the tetra- or pentacarbonyl.

The 213 ppm resonance attributed to physisorbed $Cr(CO)_6$ is within the range of shifts reported for $Cr(CO)_6$ in various solvents.¹⁹ Its presence has been observed previously in Na-Y zeolite.¹⁵ Since the resonance remains relatively narrow without MAS, the 0.91-nm-diameter complex must be undergoing rapid rotation within the 1.3-nm-diameter supercage of the zeolite. Physisorbed $Mo(CO)_6$ and $W(CO)_6$ on alumina have also been found to give relatively narrow lines without MAS.¹⁰

The oxidation of the chromium tricarbonyl on Na-X can be explained in a way consistent with the NMR and DRS spectra. Oxygen reacts rapidly with the surface carbonyl, causing the release of CO and the oxidation of the chromium. A carbon monoxide molecule then migrates until an unoxidized tricarbonyl molecule is encountered. Through the step-by-step addition of CO molecules to a chromium carbonyl, a physisorbed $Cr(CO)_6$ molecule is eventually formed. Since the physisorbed $Cr(CO)_6$ is not expected to react with oxygen, while the lower carbonyls are highly reactive, some physisorbed hexacarbonyl remains after the sample is exposed to oxygen. In the NMR spectra of Figure 4, resonances from intermediate carbonyls are again small.

The temperature-programmed decomposition of $Cr(CO)_6$ on γ -alumina (calcined at 773 K) by Hucul¹⁶ shows that the reaction of $Cr(CO)_6$ with alumina is quite different from the reaction of $Mo(CO)_6$ or $W(CO)_6$ with alumina. The evolution of carbon monoxide from $Cr(CO)_6$ /alumina in a helium flow mainly occurs between 373 and 473 K with no peak separations.¹⁶ The evolution of hydrogen begins at 380 K and indicates substantial oxidation of the chromium below 473 K.¹⁶ Thus there is no expectation that a surface tricarbonyl can be formed except as part of a mixture of surface species. IR bands due to $Cr(CO)_6$, $Cr(CO)_5$, and $Cr(CO)_4$ on alumina were assigned by Kazusaka and Howe.^{2,13}

The surface stoichiometry obtained by heating the $Cr(CO)_6$ and alumina mixture at 393 K depends on the loading. The low CO/Cr ratio for sample G may indicate that a larger fraction of the chromium is decarbonylated and oxidized by surface hydrogens when there is low loading. The reflectance spectra for the chromium carbonyl supported on alumina indicate the presence of surface metal carbonyls whose broad absorption bands at 420 and 600 nm disappear when CO is added. An increased absorbance around 280 nm shows that some of the carbonyls are reconverted into the hexacarbonyl. Bands from oxidized species have not been identified in the spectra.

The ^{13}C CP/MAS NMR signals found at 216 and 207 ppm for the $Cr(CO)_{4.2}/Al_2O_3$ sample (I) are near the 213 ppm resonance found for physisorbed $Cr(CO)_6$ on Na-X. The carbonyl responsible for the 225 ppm resonance is either very remote from the surface protons or it is translationally mobile, since the peak does not appear with CP. The resonance of a chromium carbonyl with less than six CO ligands is expected to be shifted downfield from the 213 ppm resonance of the hexacarbonyl.¹⁹ Assignment of structures to the resonances would be pure speculation at this time. Although solid-state NMR spectroscopy is clearly a major tool in the study of supported complexes, a variety of spectroscopic techniques is needed to determine many aspects of the surface species.

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Supplementary Material Available: Two figures containing diffuse reflectance spectra, one showing the effects of oxygen addition to the $Cr(CO)_3$ /Na-X sample (B) and the second showing the effects of CO addition to the $Cr(CO)_{2.01}/Al_2O_3$ sample (G) (2 pages). Ordering information is given on any current masthead page.

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