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Interaction of Nitric Oxide with Supported Chromium, Molybdenum, and Tungsten Catalysts

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The interaction of NO with alumina-supported catalysts prepared from $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ has been investigated by means of infrared and EPR spectroscopy. Adsorption of NO on $Cr(CO)_6$–Al_2O_3 produces Cr^{2+} and Cr^{3+} nitrosyl species identical to those found on reduced CrO_3–Al_2O_3. A paramagnetic Mo^+NO^+ species has been detected on $Mo(CO)_6$–Al_2O_3, but the majority species on this catalyst is a Mo^{4+} dinitrosyl complex identical to that found on MoO_3–Al_2O_3. A corresponding W^{4+} dinitrosyl complex is formed on $W(CO)_6$–Al_2O_3.

INTRODUCTION

Alumina-supported transition metal oxide catalysts are notoriously difficult to reduce. Of the group VIB metals only chromium on alumina can be readily reduced to the 3+ or 2+ valence states from the 6+ oxide (*1*). The extensive studies of Hall and Lo Jacano have shown that molybdenum on alumina can be reduced readily only to the 4+ state, and to 3+ with difficulty (*2*). Tungsten on alumina catalysts have not been widely investigated, but a recent XPS study has shown that WO_3 on alumina cannot be reduced at all in hydrogen at 550°C (*3*).

A route to low-valence states of chromium, molybdenum, and tungsten on an alumina support which is gaining popularity is via zerovalent organometallic complexes. Yermakov (*4*) has recently reviewed the preparation of supported group VIB catalysts from the corresponding allyl complexes, and a number of studies have been reported of catalysts prepared from the hexacarbonyls of chromium, molybdenum, and tungsten adsorbed on alumina or silica (*5–10*). In all of these catalysts the existence of low-valence metal ions as intermediates in the oxidation of the adsorbed zero-valent precursors may be inferred, but has not been shown directly.

Nitric oxide is a useful spectroscopic probe for investigating surface sites on transition metal oxide catalysts (*11*). In this paper we describe infrared and EPR studies of the interaction of NO with catalysts prepared from adsorbed group VIB hexacarbonyls. The objective was to obtain direct spectroscopic evidence for the presence of low-valence metal ions in these catalysts.

EXPERIMENTAL

Samples for infrared experiments were prepared *in situ* in a high-vacuum infrared cell of conventional design which allowed the sample to be moved from a furnace region into the infrared beam. Pressed wafers of γ-alumina (Ketjen CK300, 192 m^2 g^{-1}) were outgassed in a vacuum of 10^{-5} Torr at 450°C for 1 h, cooled to room temperature, and exposed to hexacarbonyl vapor at its equilibrium vapor pressure. Spectra were then recorded on a Beckman IR-12 spectrophotometer as a function of subsequent activation by heating *in vacuo*, and after exposure to NO. Research-grade NO was purified by repeated trap to trap distillation and freeze–pump cycles. Iso-

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topically enriched ^{15}NO was supplied by Stohler Isotope Chemicals.

Samples for EPR experiments were prepared in a similar fashion in a high-vacuum EPR cell fitted with a side arm. EPR spectra were recorded at room temperature or 77 K with a Varian E115 spectrometer, fitted with a dual cavity. Spectra were calibrated by comparison with a DPPH standard ($g = 2.0036$), and spin concentrations obtained by numerical double integration and comparison with the standard (which had been calibrated against a single crystal of $CuSO_4 \cdot 5H_2O$). Spin concentrations quoted are subject to an absolute uncertainty of ±30%.

Used catalyst samples were analyzed for Cr, Mo, or W by atomic absorption (Galbraith Laboratories). Gas analyses were performed with an A.E.I. MS10 mass spectrometer.

RESULTS AND DISCUSSION

Infrared Spectra of NO on Chromium

Infrared spectra of NO adsorbed on $Cr(CO)_6$–Al_2O_3 catalysts activated at various temperatures generally showed up to six different bands in the region associated with NO stretching vibrations (1600–2000 cm^{-1}). Figure 1 shows some typical spectra. Figure 1a was recorded after adsorption of NO on a catalyst prepared by adsorbing $Cr(CO)_6$ onto the pretreated alumina followed by activation *in vacuo* at room temperature for 1 hr. In this case the catalyst still contained some physically adsorbed $Cr(CO)_6$, which gives carbonyl bands at 2120 and 2000 cm^{-1}, and was not affected by exposure to NO at room temperature. The lower-frequency carbonyl bands at 1880 and 1760 cm^{-1} assigned by us previously to dissociatively chemisorbed subcarbonyl species (7) were replaced by four new bands at 1940, 1890, 1825, and 1760 cm^{-1} on exposure to NO. Warming the sample to 100°C in NO gave the spectrum shown in Fig. 1b, in which the physically adsorbed $Cr(CO)_6$ was completely removed. Subsequent outgassing at 100°C removed two of the four new bands (Fig. 1c) and the remaining nitrosyl bands could be removed by outgassing at 200°C.

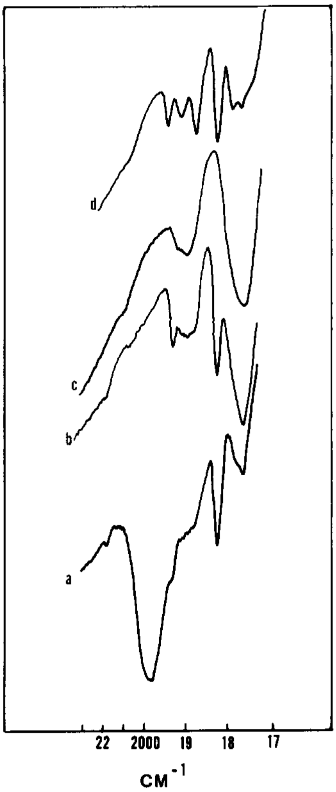

FIG. 1. Infrared spectra of NO on $Cr(CO)_6$–Al_2O_3 catalysts. (a) Catalyst activated at 25°C, exposed to NO 20 Torr; (b) warmed in NO at 100°C; (c) degassed 100°C; (d) catalyst activated at 300°C, exposed to NO 20 Torr.

The intensities of the nitrosyl bands varied considerably from one sample to the next, and also with the activation temperature of the catalyst. The sharp 1945- and 1825-cm^{-1} bands were sometimes not observed at all, but always maintained the same relative intensity when they did occur. Figure 1d shows a spectrum obtained after adsorbing NO on a catalyst prepared by decomposing adsorbed $Cr(CO)_6$ *in vacuo* up to 300°C. This shows some similarities to the spectra obtained from catalysts activated at lower temperatures; major differences are the reduced relative intensity of the 1760-cm^{-1} band, replacement of the broad 1890-cm^{-1} band by a pair of bands at 1910 and 1875 cm^{-1}, and appearance of a new band at 1785 cm^{-1}.

The spectra of NO adsorbed on $Cr(CO)_6$–Al_2O_3 show a striking resemblance to those reported by Peri (*12*) for NO on a conventional reduced CrO_3–Al_2O_3 catalyst. Several of the bands also resemble those reported much earlier by Terenin and Roev (*13*) for NO on $Cr(CO)_6$–Al_2O_3 (but attributed by them to adsorption on metallic chromium). Table 1 summarizes the infrared frequencies of NO adsorbed on various alumina-supported chromium catalysts. The complexity of the spectra obtained from both the hexacarbonyl and oxide catalysts prevents the complete characterization of the many different nitrosyl species formed. Nevertheless, some general conclusions can be drawn.

The spectra obtained from hexacarbonyl catalysts activated at low temperatures most resemble those described by Peri for well-reduced CrO_3–Al_2O_3 catalysts. For example, the bands at 1890 and 1760 cm^{-1}, which are evidently due to strongly held NO, dominate the spectra for low activation temperatures, and can reasonably be assigned (following Peri) to NO on Cr^{2+} sites. Peri has suggested that a 1755-cm^{-1} band is due to a dimeric $(NO)_2$ species formed on pairs of Cr^{2+} sites. While such pair sites may exist on CrO_3–Al_2O_3 catalysts which contain relatively high loadings of Cr, their presence on the hexacarbonyl catalysts which contain on average about 0.05 wt% Cr seems unlikely. We prefer to assign both the 1890- and 1760-cm^{-1} bands to single NO ligands on different single Cr^{2+} sites (perhaps Cr^{2+} occupying octahedral and tetrahedral sites on the alumina support), since the relative intensities of the bands were not constant.

TABLE 1

Infrared Frequencies for NO Adsorbed on Cr–Al_2O_3 Catalysts

cm^{-1}			Adsorption site[c]
This work ($Cr(CO)_6$)	Terenin[a] ($Cr(CO)_6$)	Peri[b] (CrO_3)	
1910	1905	1905	Cr^{3+}
1940	(2010)	1940	Cr^{3+}
1825	1830	1820	
1890	—	1880	Cr^{2+}
1875	—	1875	Cr^{3+}
1785	—	1775	Cr^{3+}
1760	1735	1755	Cr^{2+}

[a] Reference (*13*).
[b] Reference (*12*).
[c] According to (*12*).

The pair of bands at 1940 and 1825 cm^{-1} associated with weakly held NO were assigned by Peri to a dinitrosyl complex formed on Cr^{3+} sites having two vacant coordination sites, and the 1910- and 1875-cm^{-1} bands to single NO ligands on different Cr^{3+} sites. Our observations are consistent with these assignments; the Cr^{3+} nitrosyl species dominate the spectra obtained from catalysts activated at high temperatures (which resemble slightly reduced CrO_3–Al_2O_3 catalysts).

The appearance of Cr^{2+} and Cr^{3+} nitrosyl species after adsorption of NO on $Cr(CO)_6$–Al_2O_3 catalysts activated above 100°C is not unexpected, since it is known that high-temperature activation causes oxidation of the chromium by surface hydroxyl groups of the alumina support, as measured by the desorption of H_2 (*10*). However, the appearance of Cr^{2+} nitrosyl species after exposure to NO of $Cr(CO)_6$–Al_2O_3 catalysts activated even at room temperature strongly suggests that NO can oxidize the zerovalent chromium. Indeed, the nitrosyl bands obtained from room-temperature-activated samples were found to grow in intensity on standing for several hours at room temperature, which did not occur with catalysts activated at higher temperatures. Carbonyl ligands on the chemisorbed subcarbonyl species present on catalysts activated at low temperature (*7*) are displaced by NO, which also oxidizes the chromium. No mixed carbonyl–nitrosyl complexes were observed as intermediates in this reaction, although such species might be detected if experiments were carried out below room temperature. Activation above 100°C causes complete decarbonylation (*7*), so that addition of NO to catalysts activated at higher temperatures gives Cr^{2+} or Cr^{3+} nitrosyl species directly.

EPR Spectra of NO on Chromium

Several reports have appeared in the literature of paramagnetic nitrosyl complexes formed by adsorbing NO onto chromium catalysts containing exposed Cr^{2+} sites (*14–17*). Formulation of the complexes as Cr^+NO^+, giving a d^5 (low-spin) configuration on the chromium, appears consistent with the observed spectral parameters, which are closely similar to those of authentic d^5 nitrosyl complexes (*18*).

Figure 2A shows an EPR signal recorded at room temperature after adsorbing NO on a $Cr(CO)_6$–Al_2O_3 catalyst activated at 80°C. This signal was not observed in blank experiments with alumina alone, or with $Cr(CO)_6$–Al_2O_3catalysts activated above 150°C. (The spectrum at 77 K showed both the signal in Fig. 2A and a signal due to NO physically adsorbed on the alumina support (19).) From the similarity to the published spectra, we assign the signal to a Cr^+NO^+ species (Table 2). A maximum concentration of this species (about 4 × 10^{18} spins g^{-1}) was obtained by activating the $Cr(CO)_6$–Al_2O_3 catalyst between room temperature and 100°C and then exposing to NO at 80°C before recording the spectrum at room temperature. This upper limit corresponds to reaction of about $\frac{2}{3}$ of the chromium in the catalyst with NO to form the paramagnetic species.

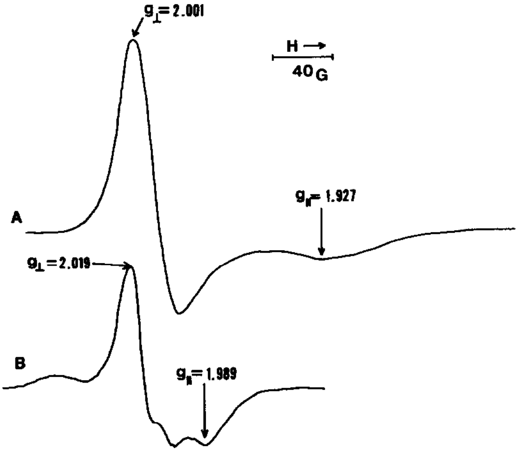

FIG. 2. EPR spectra of d^5 nitrosyl complexes (X-band, 25°C). (A) $Cr(CO)_6$–Al_2O_3 activated 80°C and exposed to NO 20 Torr; (B) $Mo(CO)_6$–Al_2O_3 activated 100°C and exposed to NO 20 Torr.

TABLE 2

EPR Parameters of d^5 Nitrosyl Complexes

	$g_\perp$	go	Ref.
$(CrNO)^{2+}$			
$Cr(H_2O)_5NO$	1.916	1.991	(*18*)
Cr Y zeolite	1.917	2.000	(*15*)
Cr A zeolite	1.903	1.997	(*16*)
CrO_3–$ASiO_2$	1.917	1.997	(*17*)
CrO_3–Al_2O_3	1.92	1.982	(*14*)
$Cr(CO)_6$–Al_2O_3	1.927	2.001	This work[a]
$(MoNO)^{2+}$			
$Mo(CO)_6$–Al_2O_3	1.989	2.019	This work[a]

[a] *g* values accurate to ±0.001.

The high relative concentration of the paramagnetic nitrosyl complex suggests that the nitrosyl stretching vibration of this complex should be observable in the infrared spectrum. The 1880-cm^{-1} band observed in the spectra of NO adsorbed on samples activated at low temperatures appears to correlate with the EPR signal; both are removed by outgassing above 100°C. This frequency is considerably higher than that of the d^5 complex $[Cr(H_2O)_5NO]^{2+}$ in solution (1747 cm^{-1} (*18*)), however, so that assignment of the 1880-cm^{-1} band to the paramagnetic species is by no means certain.

The EPR experiments thus confirm the infrared result that NO adsorption on $Cr(CO)_6$–Al_2O_3 catalysts gives species identical to those formed on conventional chromia–alumina catalysts, either through displacement of CO ligands and oxidation of the chromium, or by direct adsorption onto oxidized chromium sites.

EPR Spectra of NO on Molybdenum

Figure 2B shows an EPR signal obtained by adsorbing NO at room temperature onto an $Mo(CO)_6$–Al_2O_3 catalyst activated at 100°C. This signal is quite similar to those observed with various chromium catalysts, suggesting that it may be due to an analogous low-spin d^5 Mo^+NO^+ complex. The signal does not show ^{14}N hyperfine splitting, but any such splitting would be extremely small and not resolved in the powder spectrum, since the unpaired electron occupies a Mo_{4d} orbital (the isotropic ^{14}N splitting for $[Cr(H_2O)_5NO]^{2+}$ in solution is about 6 G (*18*)). A maximum concentration of the paramagnetic nitrosyl species of about 1×10^{18} spins g^{-1} was obtained by adsorbing NO on catalysts activated at 100°C. Although this figure is comparable to that obtained with $Cr(CO)_6$–Al_2O_3 catalysts, in the case of $Mo(CO)_6$–Al_2O_3 it represents a very much smaller fraction of the total molybdenum content. A major difference between the two systems is the 20-fold higher concentration of transition metal that can be retained on the support after desorption of physically adsorbed $Mo(CO)_6$ compared with $Cr(CO)_6$ (*7*). The concentration of paramagnetic nitrosyl species on $Mo(CO)_6$–Al_2O_3 corresponds to less than 2% of the total molybdenum present.

$Mo(CO)_6$–Al_2O_3 catalysts activated above 200°C give an EPR signal characteristic of Mo^{5+} ($g_\perp = 1.954$, $g_\parallel = 1.897$ (*5*)). Heating above 200°C causes complete decarbonylation of the catalyst and evolution of H_2, indicating oxidation of molybdenum (*8*). No changes occurred in the EPR spectra of such catalysts on exposure to NO at room temperature. The paramagnetic nitrosyl complex was not formed, and there was evidently no interaction between NO and the Mo^{5+} sites. We have also attempted to form the nitrosyl complex by adsorbing NO on a conventional MoO_3–Al_2O_3 catalyst extensively reduced in H_2 at 500°C, but no new signals were observed.

We conclude that the paramagnetic Mo^+NO^+ complex can be formed only from the zerovalent subcarbonyl species present on $Mo(CO)_6$–Al_2O_3 catalysts activated at low temperatures. Mo^{2+} sites which might react directly with NO to form the paramagnetic complex cannot be formed by reduction of MoO_3–Al_2O_3 under normal conditions (*2*). Oxidation of the subcarbonyl species by surface hydroxyl groups of the support, which might also create Mo^{2+} adsorption sites, occurs only above 200°C, and the complex cannot be formed on catalysts activated in this temperature range. The Mo^+NO^+ is evidently formed as an intermediate in the oxidation of the zerovalent subcarbonyl species by NO; as described below most of the molybdenum is oxidized to the 4+ state by NO, and the concentration of paramagnetic complex is limited by its instability with respect to further oxidation.

Infrared Spectra of NO on Molybdenum

In contrast to the chromium catalysts, molybdenum catalysts prepared from $Mo(CO)_6$ on alumina gave very simple infrared spectra on exposure to NO. Only two nitrosyl bands were observed from catalysts activated between room temperature and 500°C, which were identical to the nitrosyl bands reported by Hall and Millman (*20*) and by Peri (*21*) for NO adsorbed on a conventional MoO_3–Al_2O_3 catalyst. Figure 3 shows typical spectra.

An $Mo(CO)_6$–Al_2O_3 catalyst activated at 100°C has a complex spectrum in the region 2000–1550 cm^{-1} due to terminal and bridging carbonyl ligands of various subcarbonyl species formed by decomposition of adsorbed $Mo(CO)_6$ (*7*). Exposure of such a sample to NO gave the spectrum shown in Fig. 3a. The two intense bands at 1815 and 1705 cm^{-1} are due to nitrosyl stretching vibrations (both shifted about 25 cm^{-1} to lower frequency when ^{15}NO was used), whereas the higher-frequency bands at 2160, 2050, and 1960 cm^{-1} are associated with carbonyl ligands, since they showed no frequency shift with ^{15}NO. Also evident

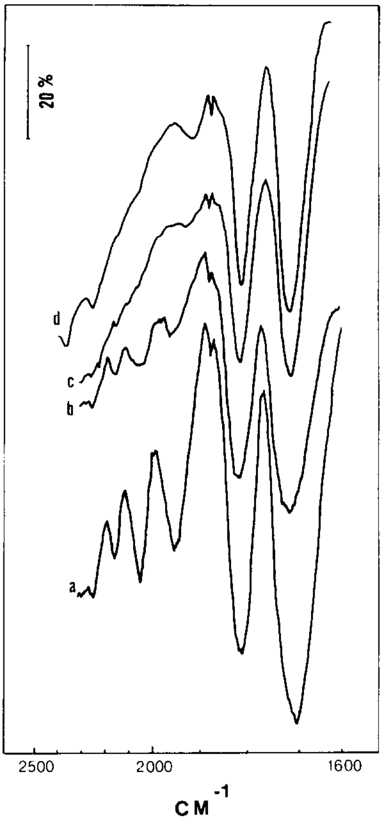

FIG. 3. Infrared spectra recorded after adsorbing NO on $Mo(CO)_6$–Al_2O_3 catalysts activated at: (a) 100°C; (b) 200°C; (c) 300°C; (d) 400°C.

in Fig. 3a is a weak band at about 2240 cm^{-1} which may be due to adsorbed N_2O (this band was not observed with ^{15}NO, and was presumably hidden beneath the 2160-cm^{-1} carbonyl band). Subsequent outgassing at 100°C completely removed the carbonyl bands (and the 2240-cm^{-1} band), whereas the nitrosyl bands could be removed only by outgassing at 400°C for several hours. Addition of a second dose of NO following the high-temperature outgassing gave very weak nitrosyl bands or none at all.

Figure 3b shows a spectrum recorded after adsorbing NO on an $Mo(CO)_6$–Al_2O_3 catalyst activated at 200°C. This is very similar to Fig. 3a, except that the relative intensity of the carbonyl bands is reduced (variations in absolute intensities in Fig. 3 are not significant, since each spectrum was obtained with a different sample). Samples activated at 300 to 400°C were almost completely decarbonylated, and no carbonyl bands were observed after adsorption of NO (Figs. 3c and d. The nitrosyl bands observed with catalysts activated at high temperatures were identical in frequency and relative intensity to those observed with low-temperature-activated samples.

The nitrosyl bands observed with MoO_3–Al_2O_3 catalysts were assigned by Hall and Millman (*20*) to a dimeric dinitrosyl species, which they suggested may be formed on Mo^{3+} sites. Their experiments with ^{14}NO–^{15}NO mixtures, also carried out by Peri (*21*) and repeated by us for $Mo(CO)_6$-derived catalysts, prove conclusively that the two nitrosyl ligands are strongy coupled. In a related study of silica-supported chromia catalysts, Kugler *et al.* (*22*) suggested that the coupled nitrosyl ligands were in the form of a *cis*-N_2O_2 dimer. Such a dimer seems unlikely on alumina-supported molybdenum catalysts; the species observed here is stable to quite high temperatures (unlike the N_2O_2 on chromia–silica), and the two nitrosyl bands have approximately the same intensity. We prefer to assign the nitrosyl bands to the symmetric and asymmetric stretching vibrations of a molybdenum dinitrosyl species $Mo(NO)_2$ of the type reported by Johnson (*23*) for example (see Table 3).

The oxidation state of molybdenum in the $Mo(NO)_2$ complex cannot be determined from the nitrosyl stretching frequen-

TABLE 3

Infrared Frequencies of Molybdenum and Tungsten Dinitrosyl Complexes

	cm^{-1}		Ref.
MoO_3–Al_2O_3	1820	1710	(*20*)
MoO_3–Al_2O_3	1810	1710	(*21*)
$Mo(CO)_6$–Al_2O_3	1815	1705	This work[a]
$W(CO)_6$–Al_2O_3	1795	1685	This work[a]
$[Mo(NO)_2Cl_2]_n$	1805	1690	(*23*)
$[W(NO)_2Cl_2]_n$	1800	1680	(*23*)

[a] Frequencies accurate to ±5 cm^{-1}.

cies. It is unlikely to be 3+ however. Dinitrosyl complexes of silica- or alumina-supported Cr^{3+} (*24, 12*) are relatively unstable and readily decomposed by outgassing above room temperature. A $Mo^{3+}(NO)_2$ species would be expected to be similarly unstable. All known inorganic dinitrosyl complexes contain an even number of *d* electrons (*25*). The dinitrosyl species formed on MoO_3–Al_2O_3 catalysts are observed even with slightly reduced catalysts (less than 1 *e*/Mo), which contain no Mo^{3+}, and certainly no Mo^{2+} (*26*). Since there is no evidence from the EPR spectra for any interaction of NO with Mo^{5+} sites, we assign the nitrosyl bands observed with both MoO_3–Al_2O_3 and $Mo(CO)_6$–Al_2O_3 catalysts to a dinitrosyl complex of Mo^{4+}. This complex is formed on $Mo(CO)_6$–Al_2O_3 catalysts activated at all temperatures between room temperature and 400°C.

Since oxidation of adsorbed $Mo(CO)_6$ by hydroxyl groups of the alumina support occurs only on activation above 200°C (*8*), formation of the $Mo^{4+}(NO)_2$ complex on catalysts activated at 200°C or lower temperatures must occur through oxidation of the zerovalent subcarbonyl species by NO. This was confirmed by mass spectrometric analysis of the gas phase. Small doses (corresponding to NO : Mo ratios of about 2) of NO added to $Mo(CO)_6$–Al_2O_3 catalysts activated at 100 or 200°C were completely reduced to N_2O. Addition of similar doses of NO to a catalyst activated at 400°C left most NO unreacted, although some N_2O was still formed. These analyses were not quantitative, and the possibility of N_2 formation cannot be dismissed (because of interference from desorbed CO). Oxidation of the catalyst presumably occurs through reactions such as

$$2NO + 2e \rightarrow O^{2-} + N_2O$$

which have been reported previously for reduced iron (*27*) and tin (*28*) oxide catalysts. The dinitrosyl species is then formed by adsorption of NO on the Mo^{4+} sites. Decomposition of the dinitrosyl species by high-temperature outgassing causes further oxidation; this has been noted also for the MoO_3–Al_2O_3 catalysts (*20*).

There is no evidence from the infrared spectra for formation of mixed carbonyl nitrosyl species when NO is adsorbed on catalysts activated at low temperatures. The carbonyl bands observed after adsorption of NO are assigned to CO adsorbed on oxidized molybdenum sites. CO adsorbed on a conventional MoO_3–Al_2O_3 catalyst reduced with H_2 or CO gives bands at 2190 and 2150 cm^{-1} (*29*). The nature of the CO adsorption sites on the conventional catalyst has not been established, but the 2160-cm^{-1} band observed with $Mo(CO)_6$–Al_2O_3 probably corresponds to the 2150-cm^{-1} band reported in (*29*), and may be CO on a Mo^{4+} site. The remaining carbonyl bands at 2050 and 1960 cm^{-1} cannot be assigned at this point. We suppose that CO is in general displaced from the molybdenum subcarbonyl species during the oxidation by NO, with some readsorption occurring on oxidized sites. Although the mechanism of the CO displacement and oxidation of the molybdenum by NO is not known, the end result of NO adsorption on $Mo(CO)_6$–Al_2O_3 catalysts is clearly the same $Mo^{4+}(NO)_2$ species as formed on MoO_3–Al_2O_3.

Infrared Spectra of NO on Tungsten

Figure 4 shows infrared spectra obtained by adsorbing NO onto a $W(CO)_6$–Al_2O_3 catalyst activated at 200°C. The activated catalyst showed at least five major carbonyl bands between 1500 and 2000 cm^{-1} (Fig. 4a); the subcarbonyl species responsible for these bands were discussed in (*7*). Subsequent exposure to NO caused an immediate reduction in intensity of all carbonyl bands, and the appearance of two new bands at 1795 and 1685 cm^{-1}. Figure 4b was recorded after exposure to 20 Torr of NO for 15 min. The new bands grew in intensity and the residual carbonyl bands decreased over a period of several hours at room temperature. Both bands shifted about 25 cm^{-1} to lower frequency when ^{15}NO was

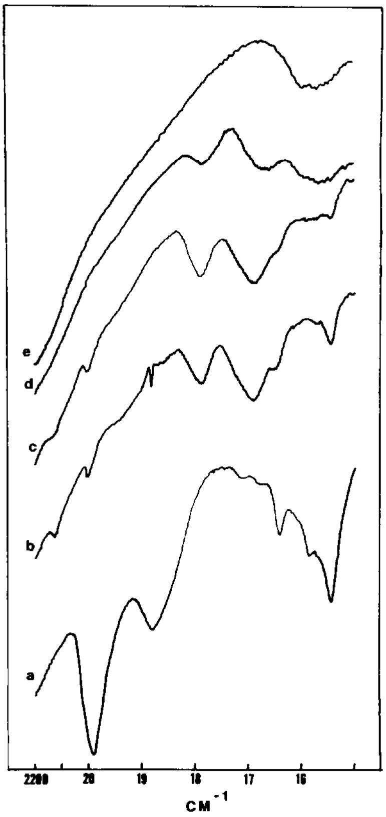

FIG. 4. Infrared spectra of NO on $W(CO)_6$–Al_2O_3. (a) Catalyst activated 200°C; (b) exposed to NO 20 Torr; (c) evacuated at 25°C; (d) outgassed 200°C 30 min; (e) outgassed 400°C 30 min.

used. The new bands were quite stable to evacuation at room temperature (Fig. 4c), but could be reduced in intensity by outgassing at 200°C (Fig. 4d) and completely removed at 400°C (Fig. 4e). No nitrosyl bands were formed on reexposure to NO. Spectra similar to those in Fig. 4 were obtained with $W(CO)_6$–Al_2O_3 catalysts activated at different temperatures in the range 50–400°C. The two nitrosyl bands maintained a constant intensity ratio in all experiments.

From the similarities between the spectra of NO on $Mo(CO)_6$–Al_2O_3 and $W(CO)_6$–Al_2O_3 catalysts we conclude that the pair of nitrosyl bands observed from the tungsten catalysts are probably due to a $W^{4+}(NO)_2$ species analogous to that formed on molybdenum. The absolute intensities of the nitrosyl bands on tungsten were significantly less than those on molybdenum; however it is known (*7*) that the maximum loading of tungsten on the support that can be achieved with $W(CO)_6$ (about 0.3 wt%) is substantially less than the figure for molybdenum (about 1 wt%). We have attempted unsuccessfully to form the $W^{4+}(NO)_2$ species on a conventional WO_3–Al_2O_3 catalyst. In view of the XPS result that WO_3–Al_2O_3 cannot be reduced in H_2 at 500°C (*3*), the absence of W^{4+} adsorption sites on the conventional catalyst is not surprising.

The chemistry of $W(CO)_6$ on alumina is very similar to that of $Mo(CO)_6$. In particular, complete decarbonylation and oxidation by the support occurs in the same temperature range (>200°C) (*10*). Formation of the $W^{4+}(NO)_2$ species on catalysts activated at 200°C or lower temperatures must therefore occur through an oxidative displacement of carbonyl ligands as suggested for molybdenum. In the case of tungsten, however, no paramagnetic W^+NO^+ species could be detected by EPR as an intermediate.

CONCLUSIONS

The following conclusions may be drawn regarding the presence of low-valence metal ions on catalysts prepared from the group VIB hexacarbonyls on alumina.

1. Supported chromium catalysts prepared by decomposition of $Cr(CO)_6$ above 200°C contain Cr^{2+} and Cr^{3+} ions. Adsorption of NO onto $Cr(CO)_6$–Al_2O_3 catalysts activated at low temperatures produces Cr^{2+} and Cr^{3+} nitrosyl species through oxidation of the chromium.

2. No spectroscopic evidence was obtained for the existence of Mo^{2+} ions on $Mo(CO)_6$–Al_2O_3 catalysts activated above 200°C. A Mo^{2+} nitrosyl complex was formed by reaction of NO with zerovalent molybdenum subcarbonyl species on catalysts activated at low temperatures.

3. No low-valence tungsten species were detected on $W(CO)_6$–Al_2O_3 catalysts.

The demonstrated tendency of NO to

oxidize low-valence ions means that the existence of Mo^{2+} and W^{2+} ions on activated $Mo(CO)_6$–Al_2O_3 and $W(CO)_6$–Al_2O_3 catalysts cannot be completely ruled out. A more gentle spectroscopic probe will be needed to investigate these systems further.

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