from the atmosphere. XPS results confirm the findings reported in Figure 3, that there is no C enrichment in the catalyst due to the reaction.

Figure 8 presents the XPS peaks in the Mo 3d region for (1) $CoMoO_4$ reacted 740 °C, 3h; (2) reacted 735 °C, 24 h; (3) Na_2MoO_4 reacted 710 °C, 12 h; (4) $MnMoO_4$ reacted 765 °C, 12 h. The peaks for Na_2MoO_4 and $MnMoO_4$ are well defined and show a doublet Mo $3d_{5/2}$. These narrow well-defined peaks are indicative of one chemical state for the Mo. The $CoMoO_4$ spectra in Figure 8 show broader peaks which could be ascribed to a superposition of two different chemical species, e.g., $CoMoO_4$ and MoO_3. The energy values used to reference Figures 7 and 8 are found in refs 20, 21 and 43–45. Partly, the different binding energies and structures shown by the $CoMoO_4$ spectra are due to the fact that the O 1s signal in $CoMoO_4$ has a different binding energy (530.9 eV) than the O 1s state in MoO_3 (531.3 eV).[20,21] It is seen from Table II that Mo in $CoMoO_4$ shows a marked surface enrichment during the reaction. In effect, this value increases from 0.7% in a fresh catalyst to 4.5 and 4.8% in $CoMoO_4$ reacted under the conditions of Table II. This effect was not present in the case of Na_2MoO_4 and $MgMoO_4$ and less pronounced in the case of $MnMoO_4$ (see Table II).

X-ray diffraction pattern for Na_2MoO_4 of the nonreacted material shows peaks characteristic of Na_2MoO_4 anhydrous material.[46] Also up to 10% oxide–hydrate was found in the unreacted sample and 1–3% of the same oxide–hydrate with 2% additional phases were detected in the reacted material under the conditions of experiments presented in Table II. Therefore, the

oxidative coupling does not introduce additional phases in Na_2-MoO_4. This is a further proof that the catalyst is not affected during long-term catalysis.

Conclusion

This report helps in understanding the nature of involvement of molybdate catalysts in the oxidative coupling of methane. The effect of several operating variables was studied to derive an optimum set of conditions suitable to achieve reasonably high yields of C_2H_4 and C_2H_6. C_2H_4 generation is favored at higher temperatures, indicating that C_2H_4 is produced additionally by a secondary reaction of C_2H_6. CO and CO_2 are the main oxidation products. The dimensions of the reactor were found to influence significantly the product distribution. The CO and H_2 produced could be used for "synthesis gas" and is therefore useful. The separation of CO and H_2 from other products is not a serious problem, as technologies are available for its economic recovery.[11,12]

Further studies involving molybdates are warranted in order to understand the mechanism taking place on the catalyst surface and to precisely characterize the active sites. In this way higher selectivities and C_2 yields could be achieved than those observed in this study. Such studies are currently in progress in our laboratory.

(46) *Powder Diffraction File*; International Center for Diffraction Data: Swarthmore, PA, 1978.

CO-Induced Changes in Structure of Supported Rhenium

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The interaction of CO with highly reduced Re/Al_2O_3 was investigated at 100–673 K by means of infrared spectroscopy. The adsorption of CO at 100 K produced absorption bands characteristic of linearly and bridge bonded CO. At 200–300 K well-observable spectral changes were experienced, their extent depending on the temperature and adsorption time. The absorption bands formed suggest the occurrence of CO-induced structural changes in the Re crystallites and the formation of Re carbonyls with higher CO/Re ratio, most probably $Re_2(CO)_{10}$. Further spectral changes occurred at 373–473 K, indicating the transformation of the more complex Re carbonyl into Re tricarbonyl. This transformation was promoted by H_2O. The formation of Re tricarbonyl from Re_x–CO species was found to be very limited.

1. Introduction

Study of the properties of supported rhenium is justified for at least two reasons: rhenium-containing supported catalysts are currently used in the reforming of petroleum feedstocks,[1] and Re seems to exhibit oxygen storage properties in automotive three-way catalysts.[2] The primary aim of this work is to explore whether the adsorption of CO on supported Re induces any morphological changes detectable by means of infrared (IR) spectroscopy.

Whereas the characterization of supported Re catalyst has been the subject of several detailed studies,[3–11] little information is to

be found in the literature with regard to the IR spectrum of CO adsorbed on supported Re. Guerra and Schulman[12] in their classical paper reported the IR spectrum of CO adsorbed on 9% Re/SiO_2 (reduction temperature, R_T, of 648 K). They obtained a very broad absorption, consisting of several bands at 1950,

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2050–2030, and 2010–1992 cm^{-1}. The first of these was assigned to Re$_2$–CO and the other two to Re(CO)$_2$ and Re–CO species. Yates and Sinfelt[3] studied the catalytic properties of a 10% Re/SiO$_2$ sample (R_T = 773 K) and mentioned that the IR spectrum did not contain a band due to a bridged structure in the vicinity of 1800–1900 cm^{-1}. Russian authors[13] investigated 10% Re/Al$_2$O$_3$ (R_T = 673 K) and observed a band at 1890 cm^{-1}, attributed to Re$_2$–CO, and others at 1940 and 2050 cm^{-1}, ascribed to Re carbonyls. In contrast, neither Olsthoorn and Boelhouwer[4] nor Sachtler et al.[8] detected CO adsorption on oxidized or room temperature reduced Re/Al$_2$O$_3$. Sachtler et al. noted a weak CO band for 2% Re/Al$_2$O$_3$, which rapidly vanished and could not be restored on further exposure. They explained this phenomenon by the dissociation of CO and blocking of the surface by carbide formation. Bolivar et al.[14] and Peri[15] identified two absorption bands at 2040–1940 (R_T = 773 K) and 2050–1950 cm^{-1} (R_T = 773 K), respectively. Iizuka[16] recorded the IR spectrum of 7% Re/ZrO$_2$ (R_T = 673 K) in a mixture of CO and H$_2$ and found two sharp bands at 2040 and 2190 cm^{-1} and a broad one at 1920 cm^{-1}. Komiyama et al.[17] identified four absorption peaks in the IR spectrum under high-pressure CO hydrogenation conditions on Re/TiO$_2$ and Re/ZrO$_2$, two in the linear (2030 and 1995 cm^{-1}) and two in the bridged (1920 and 1885 cm^{-1}) CO stretching region.

It has recently been demonstrated by means of EXAFS[18] and IR spectroscopy[19–21] that CO not only is adsorbed strongly on supported Rh crystallites at 300 K but also causes morphological changes, i.e., the disruption of Rh clusters to isolated Rh atoms at lower temperatures, <423 K, and the agglomeration of the latter above 423 K. IR spectroscopy proved to be a very convenient and sensitive method of following these processes,[19–21] and several details of CO-induced structural changes have since been reported.[22–26] A recent independent confirmation of the CO-induced changes in the valence state of rhodium was provided by an XPS study of the CO + Rh/TiO$_2$ system.[26] CO-induced structural changes were observed by means of IR spectroscopy for supported Ru[27,28] and confirmed by EXAFS measurements.[29] Similar features were recently established for Ir/Al$_2$O$_3$.[30]

As such structural changes in metals are of great importance in the understanding of the catalytic properties of metals, we have extended our investigations to supported Re catalysts.

2. Experimental Section

Materials. Supported rhenium catalyst was prepared by impregnating the support in an aqueous solution of (NH$_4$)$_2$Re$_2$O$_8$ or H$_2$Re$_2$O$_8$ (Merck). After impregnation, the suspensions were

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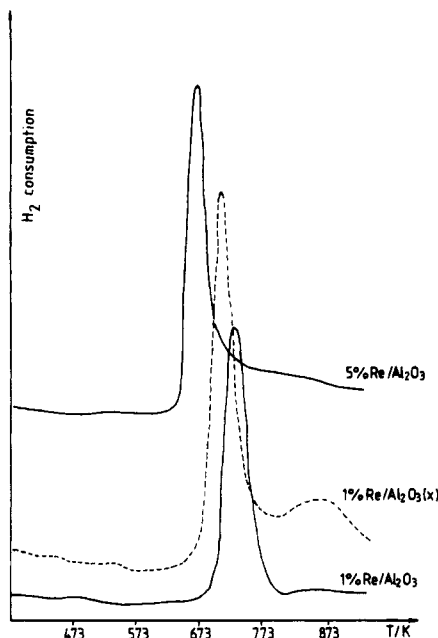(30) Solymosi, F.; Novák, É.; Molnár, A. *J. Phys. Chem.* **1990**, *94*, 7250.

Figure 1. Temperature-programmed reduction of Re/Al$_2$O$_3$·(x) after treatment at 773 K in N$_2$ for 16 h.

dried in air at 383 K. The dried and pulverized samples were pressed into thin self-supporting wafers (30 × 10 mm, ~60 mg/cm^2). Further treatment was applied in situ: it consisted of oxidation at 573 K (100 Torr of O$_2$ for 30 min), evacuation at 573 K for 30 min, reduction at selected temperature, between 673 and 1273 K (100 Torr of H$_2$ for 60 min), and evacuation at the temperature of reduction for 30 min. Note that the heating of the sample from 573 K to the temperature of reduction was carried out in the presence of hydrogen.

The alumina support was the product of Degussa (100 m^2/g). Gases used were of commercial purity. CO and H$_2$ were purified by bubbling through a Mn(OH)$_2$ suspension. Water vapor was frozen out by a trap cooled with a dry ice–acetone mixture. The other impurities were adsorbed on a 5-Å molecular sieve at the temperature of liquid air.

Methods. Temperature-programmed reduction was carried out in a microreactor incorporated between the sample inlet and the analytical column of the gas chromatograph. The dead volume was filled with quartz beads. The reactor was heated by an external oven at a linear rate of 40 K min^{-1} to a final temperature of 1000 K. The catalysts were flushed with nitrogen containing 10% H$_2$, and the hydrogen consumption was measured.

Most of the infrared spectra were recorded with a Specord M80 double-beam spectrometer that contained a data system. The IR cell used made it possible to register the spectra at the temperature of CO adsorption at both low and high temperatures. The cell was connected to a closed circulation system, where gases were circulated during pretreatment and adsorption studies by a small magnetic pump.

3. Results

3.1. Temperature-Programmed Reduction (TRP). Figure 1 shows TRP curves of dried (130 K) and oxidized (573 K) rhenium deposited on alumina support. For 1% Re/Al$_2$O$_3$ the reduction started at 663 K, and the maximum occurred at 733 K, but the hydrogen consumption did not cease even above 793 K. These characteristic values were shifted somewhat to lower temperature for 5% Re/Al$_2$O$_3$. When the sample was treated for 16 h at 773 K in a N$_2$ stream, which according to Yao and Shelef[7] leads to an enhancement of the dispersion of rhenium, a new high-temperature peak appeared with T_p = 858 K. The corresponding temperature values differed only slightly when the catalyst was prepared from perrhenic acid, H$_2$Re$_2$O$_8$.

3.2. Infrared Studies. Adsorption of CO at 100–300 K. No IR bands were identified for a low-temperature-reduced sample,
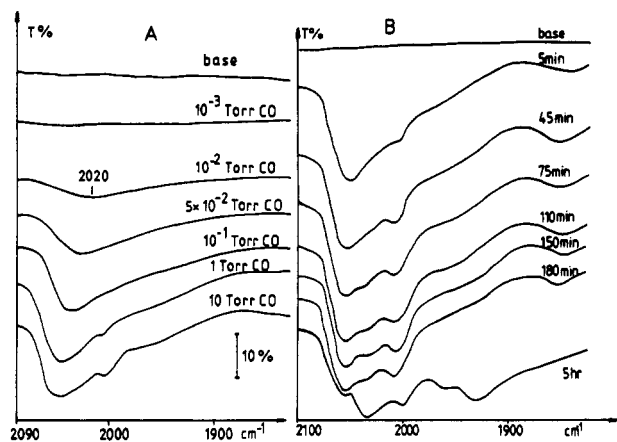
Figure 2. Infrared spectra of adsorbed CO on 1% Re/Al$_2$O$_3$ ($T_R = 1073$ K) at 300 K as a function of CO pressure (A) and adsorption time (B). After CO introduction, the time of equilibrium before the registration of spectra was 5 min.
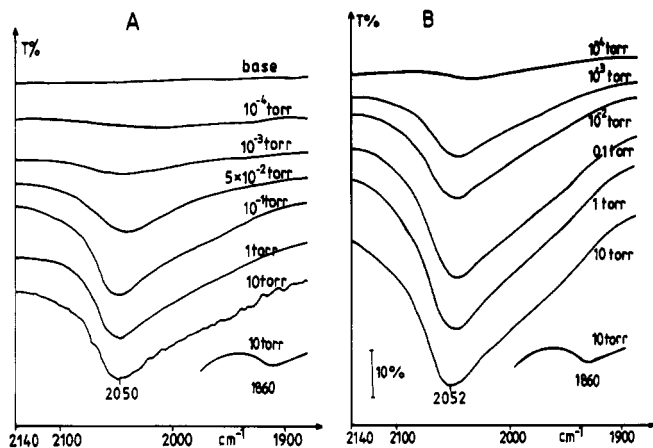

Figure 3. Infrared spectra of adsorbed CO on Re/Al$_2$O$_3$ ($T_R = 1073$ K) at 100 K as a function of CO pressure. (A) 1% Re; (B) 5% Re.

Figure 4. Changes in the infrared spectra of adsorbed CO on 1% Re/Al$_2$O$_3$ ($T_R = 1073$ K) during warming up in the presence of 10 Torr of CO. Adsorption temperature was 100 K. $T_R = 1073$ K.

Figure 5. Changes in the infrared spectra of adsorbed CO on 1% Re/Al$_2$O$_3$ ($T_R = 1273$ K) at ~170 (A) and 203 K (B) in the presence of 10 Torr of CO.

even after 24 h of adsorption. A broad absorption band peaking at 2040 cm^{-1} was detected first for the sample reduced at 873 K; this is clearly composed of several bands. The same spectral feature developed with almost identical intensity and position for samples reduced at higher temperatures. A weaker absorption band can also be seen at 1850 cm^{-1}.

The variation in the absorption bands at 300 K as a function of CO pressure is shown in Figure 2A. Even at the lowest pressure of CO a broad absorption band peaking at 2020 cm^{-1} appeared, which shifted to 2050 cm^{-1} at higher pressure. After 2–3 h of adsorption time, however, several bands can be clearly distinguished at 2055, 2030, 2008, and 1962 cm^{-1}. Note that these spectral changes were not accompanied by any alteration in the OH frequency range. With further extension of the adsorption time the 2030-cm^{-1} band intensified and a new weak band also developed at 1925–1920 cm^{-1}, which slowly grew in time (Figure 2B).

The measurements were repeated at 100 K. Apart from the bands of physisorbed CO, no absorption bands appeared in the range 1800–2100 cm^{-1} for samples reduced below 973 K. The band which developed for other samples ($R_T = 1073$ and 1273 K) was much less broad than that recorded at 300 K (Figure 3). At the lowest CO pressure used (1 × 10^{-3} Torr), a weak band was observed at 2030 cm^{-1} for 1% Re/Al$_2$O$_3$, which grew in intensity and gradually shifted to higher frequencies as the CO coverage was increased. At saturation, the band was situated at 2050 cm^{-1}. When a larger amount of Re (5%) was used, the same spectral features were observed.

When the sample was heated to higher temperature, first the low-frequency CO band at 2005 cm^{-1} appeared at 120–150 K, and then the intense absorption band at 2050 cm^{-1} broadened on the low-frequency side at 213 K. This change became more
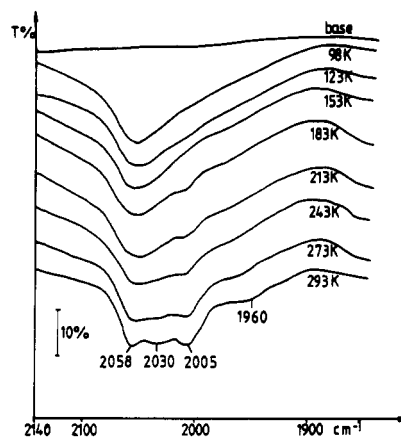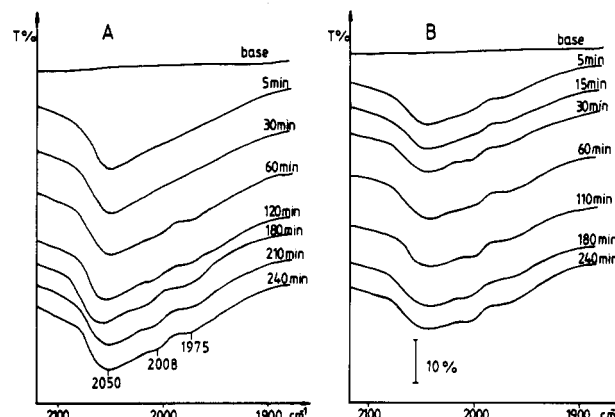
pronounced at 273 and 300 K, where four bands could be distinguished, at 2058, 2030, 2005, and 1960 cm^{-1} (Figure 4). These features, the time dependence, and the positions and the intensities of the bands were practically the same for samples reduced at 1073 and 1273 K. No spectral changes were detected in the OH frequency range for either sample.

In subsequent measurements, spectral changes were followed at 170 and 203 K with time (Figure 5). At 170 K, we found only one absorption band at 2050 cm^{-1} which was slightly broadened on the low-frequency side. After several hours, the development of new bands at 1975 and 2008 cm^{-1} was registered. At 203 K, the latter bands were detected even at the beginning of the CO adsorption.

On evacuation of the sample at 300 K, the bands at 2058 and 2005 cm^{-1} gradually attenuated and absorption bands at 2030–2035 and 1920–1925 cm^{-1} appeared or, if they were already present, became more intense (Figure 6). However, a complete elimination of the bands at 2058 and 2005 cm^{-1} at 300 K was not achieved even after 3–5 h. These changes were more pronounced at 323 K. The 2058- and 2005-cm^{-1} bands both disappeared at 373–473 K, accompanied by further intensification of the bands at 2035 and 1925 cm^{-1}. They started to attenuate at 573 K and were eliminated completely only after extended evacuation at 773 K.

The dotted line in Figure 6 demonstrates that the readsorption of CO after evacuation at 373 K slowly restored the original spectrum and even led to an attenuation of the band at 1925 cm^{-1}. This was not the case after evacuation above 473 K. When absorption bands at 2035 and 1925 cm^{-1} were eliminated at 773 K, the readsorption of CO (10 Torr) at room temperature did not produce any new absorption bands (Figure 6). The same procedure was repeated with the sample prepared from H$_2$Re$_2$O$_8$,
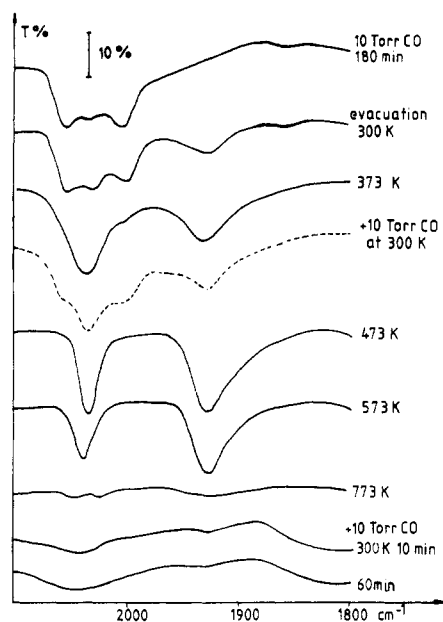
Figure 6. Effects of evacuation of 1% Re/Al$_2$O$_3$ (T_R = 1073 K) at different temperatures following adsorption of CO at 300 K for 3 h. Evacuation time was 30 min.
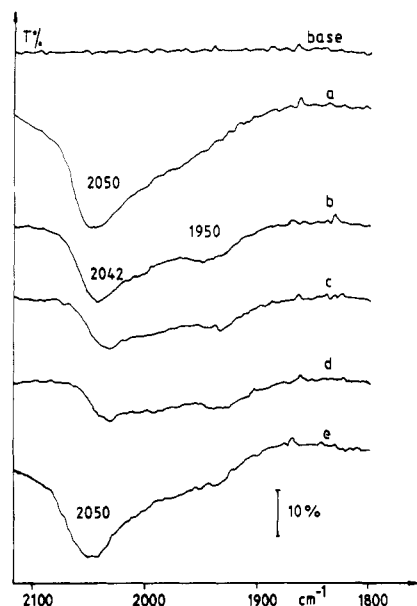

Figure 7. Effects of evacuation of 1% Re/Al$_2$O$_3$ (T_R = 1073 K) at 473 K following CO adsorption at 100 K for 5 min. All of the spectra were taken at 100 K. (a) Adsorption of CO (10 Torr) at 100 K and after treatments at 473 K for 5 (b), 30 (c), and 90 min (d). (e) Readsorption of CO at 100 K.

and exactly the same picture was obtained.

To establish whether the species responsible for the pair of bands at 2035 and 1925 cm^{-1} can be formed from the linearly bonded CO, Re$_x$–CO, the following experiment was performed. Ten Torr of CO was adsorbed on a 1% Re/Al$_2$O$_3$ sample (T_R = 1073 K) at 100 K, when only an intense absorption band at 2050 cm^{-1} was produced. The sample was degassed at 100 K and then raised to a zone preheated to 473 K. After certain periods of time, the sample was lowered to the cold zone and spectral changes were registered. As the spectra presented in Figure 7 show, the intense absorption band produced at 100 K moved to 2042 cm^{-1} after the adsorbed layer was heated to 473 K. Another weak band developed at 1950 cm^{-1}. After longer treatment at 473 K, the 2042-cm^{-1} band decayed and shifted somewhat to lower frequencies, together with the other band. Readsorption of CO at 100 K restored the spectrum obtained before evacuation at 473 K.
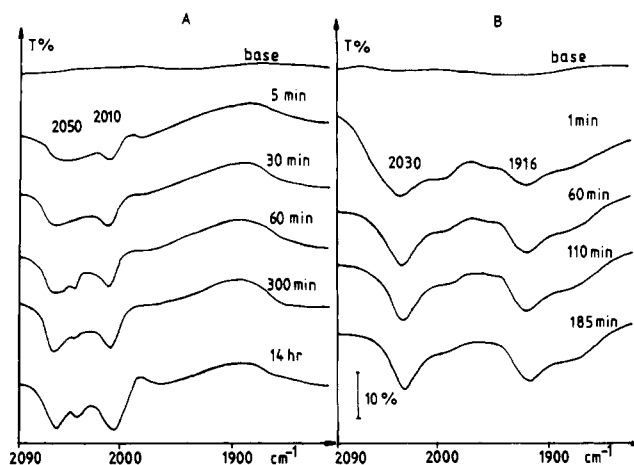

Figure 8. Spectral changes observed following adsorption of CO (10 Torr) + O$_2$ (5 Torr) (A) and CO (10 Torr) + H$_2$O (2 Torr) (B) gas mixture on 1% Re/Al$_2$O$_3$ (T_R = 1073 K) at 300 K.
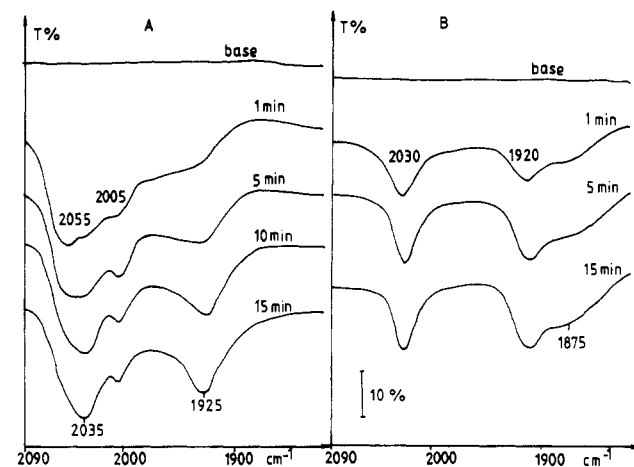

Figure 9. Spectral changes observed following adsorption of CO (10 Torr) (A) and CO (10 Torr) + H$_2$O (2 Torr) (B) gas mixture on 1% Re/Al$_2$O$_3$ (T_R = 1073 K) at 473 K.

Some measurements were carried out concerning the effects of H$_2$, O$_2$, and H$_2$O on the spectral changes observed following CO adsorption. In the presence of H$_2$ (10–100 Torr), we found negligible differences at 300 K. When the sample kept in CO at 300 K for 3 h was heated to 473 K in the presence of 10–100 Torr of H$_2$, the pair of bands at 2030 and 1925 cm^{-1} developed in the same way as during evacuation at 473 K. In contrast, oxygen preadsorbed at 300 K completely prevented the development of CO bands at 300 K. When an O$_2$ + CO gas mixture was coadsorbed, the same absorption bands appeared as in the absence of O$_2$ but with lower intensities. However, there was no indication of the band at 1920 cm^{-1} even after 14 h (Figure 8A). On the other hand, in the presence of 1–2 Torr of H$_2$O the absorption bands at 2030 and 1916 cm^{-1} appeared at the very beginning of CO adsorption at 300 K (Figure 8B).

When the spectral changes were followed in the presence of CO at 373–473 K, the absorption bands at 2055 and 2005 cm^{-1} developed first. The 2035- and 1925-cm^{-1} bands then appeared and became the dominant spectral features (Figure 9A). The promoting effect of H$_2$O was exhibited at 473 K, when only the latter bands were identified even after an adsorption time of 1 min (Figure 9B). At these temperatures, a slight alteration was observed in the OH frequency region (Figure 10A). The absorption band at 3670–3700 cm^{-1} was attenuated to a greater extent than at lower temperatures, as exhibited by the more intense negative feature at 3670 cm^{-1} in the difference spectra (Figure 10B).

The stability of the two intense bands at 2035 and 1925 cm^{-1} was examined in the presence of H$_2$ and O$_2$. Both bands exhibited a marked resistivity toward both H$_2$ and O$_2$, even at 473 K, where
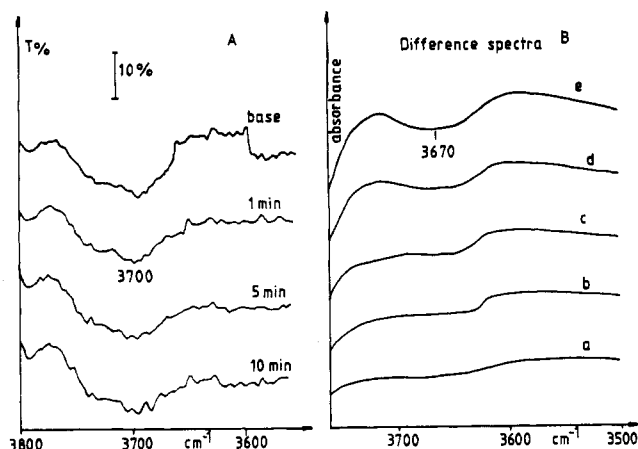
Figure 10. Spectral changes observed in the OH frequency region of 1% Re/Al$_2$O$_3$ (T_R = 1073 K) following CO (10 Torr) adsorption. (A) Direct spectra taken after CO adsorption at 473 K; (B) difference spectra obtained after CO adsorption at 300-473 K. Temperature of CO adsorption: (a) 300 K, 10 min; (b) 373 K, 30 min; (c) 373 K, 60 min; (d) 473 K, 15 min; (e) 473 K, 60 min. In this case the spectra were taken at 300 K, and the base line before CO adsorption was subtracted from each spectrum obtained after CO treatment.

practically no change was experienced in their positions and intensities. The band intensity decreased at 573 K at the same rate as measured under continuous evacuation.

4. Discussion

4.1. Reducibility of Supported Rhenium. In the study of the adsorption of CO on supported Re the reduction of the sample is a crucial factor. It appears almost certain that the absence of the CO bands or their weakness is associated with the limited reduction of supported Re. Another important factor is the pretreatment of the Re/support before reduction.
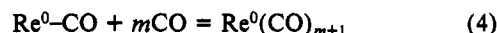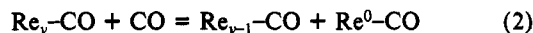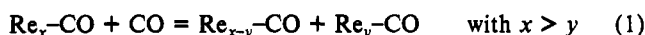
Before discussing our results, we shall summarize briefly the main findings of previous studies. Johnson and LeRoy[5] reported that rhenium on alumina is reduced by hydrogen exclusively to the Re^{4+} state. In contrast, Webb[6] found that alumina-supported rhenium is completely reducible at 673 K. A brief TPR study by Wang and Hall[9] revealed that most of the rhenia on an alumina support could be reduced to Re^0 at 548 K, but a very small amount appeared to resist reduction up to 773 K. A more detailed study of the reducibility of rhenia and of the structure of reduced Re/Al$_2$O$_3$ was carried out by Yao and Shelef.[7] They demonstrated the existence of a dispersed, two-dimensional phase and three-dimensional crystallites in the reduced system. The dispersed phase of Re interacts strongly with γ-Al$_2$O$_3$, and as a result it can be reduced by hydrogen only above 773 K. Re/γ-Al$_2$O$_3$ containing 1.21% Re and dried at 573 K underwent almost 60% reduction at 573-673 K. The extent of dispersion could be enhanced by thermal treatment in nitrogen at 773 K. An important observation is that highly dispersed Re does not dissociate H$_2$ readily at room temperature. It begins to do so at 473 K.[7]

Our TPR studies support the conclusion of Yao and Shelef.[7] Without any high-temperature treatment, 70-80% of the hydrogen consumption for the reduction of the dried 1% Re/Al$_2$O$_3$ sample occurred between 663 and 793 K, but the reduction was complete only at around 900 K (Figure 1). The same features were observed for the sample containing 5% Re. In this case, the main stage of the reduction occurred in a somewhat lower temperature range, indicating that the stabilizing effect of the support played a smaller role than at low Re content. Heat treatment of the dried sample for 16 h at 773 K in nitrogen increased the extent of the reduction occurring only above 773 K and produced a well-defined peak at 858 K.

4.2. Infrared Studies. The results unequivocally show that adsorbed CO exhibits different IR spectra, depending on the adsorption temperature and the duration of adsorption. On highly reduced Re/Al$_2$O$_3$ (R_T = 1073 and 1273 K), we found two bands at 2030 and 1860 cm^{-1} at an adsorption temperature of 100 K.

At low coverage the first band appeared at 2030 cm^{-1} and moved to higher frequencies as the coverage of adsorbed CO increased, with a maximum of 2040 cm^{-1} at saturation. Taking into account the position of this single band, it can be safely assigned to CO linearly bonded to a reduced rhenium cluster, Re$_x$-CO. The coverage-dependent position, which is a generally observed phenomenon for metals,[31] is very probably associated with the dipole-dipole interaction of adsorbed CO molecules. The much weaker band at 1850-1870 cm^{-1} is assigned to bridged CO, Re$_2$-CO.

The spectral changes observed at higher temperatures, 250-300 K, i.e., the development of new bands at 2058, 2005, and 1956 cm^{-1}, suggest that new surface species have been formed. We may speculate that CO-induced changes occurred in the structure of the Re crystallite, similar to those established for supported Rh, Ru, and Ir.[17-30] This probably consists in the disruption of Re crystallites, Re$_x$, to smaller ones and finally to isolated Re^0 atoms:

$$Re_x\text{-}CO + CO = Re_{x-y}\text{-}CO + Re_y\text{-}CO \quad \text{with } x > y \quad (1)$$

$$Re_y\text{-}CO + CO = Re_{y-1}\text{-}CO + Re^0\text{-}CO \quad (2)$$

$$Re_{y-1}\text{-}CO + mCO = Re_{y-1}(CO)_{m+1} \quad (3)$$

$$Re^0\text{-}CO + mCO = Re^0(CO)_{m+1} \quad (4)$$

In the case of Rh, Ru, and Ir it was established that the final product of the disruption process is the isolated metals.

If similar processes take place during the CO-induced structural changes as for supported Rh, Ru, and Ir or during the interaction of metal carbonyls with the alumina support at high temperature,[32] then the oxidation of isolated Re^0 may occur by means of the OH groups of the support or by the adsorbed O formed in the dissociation of CO on the Re$_x$ cluster. While the latter process may proceed on Re/Al$_2$O$_3$ at and above 373 K,[33] it is highly unlikely to occur at 200-300 K. However, the spectrum in the OH frequency range did not show any attenuation of the bands of OH groups as the new CO bands developed with increasing CO pressure at 300 K or when the adsorption temperature was increased from 200 to 300 K.

The complexity of the spectrum, obtained after an extended adsorption time at 300 K, and its behavior during several treatments suggest that the nature of the interaction of CO with supported Re is different in many respects from those for Pt metals. For determination of the composition of the surface complex responsible for the spectral features registered at 300 K, a precise assignment of the absorption bands observed is required. In this context, a consideration of the IR spectra of various Re carbonyls is of great help.

The Re carbonyls have a very rich chemistry[34-48] and several

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**TABLE I: CO Vibrational Frequencies in Re Carbonyls**

compound	freq, cm^{-1}	ref
c-Re(CO)$_2$ (DFE)	1920, 1860, 1800	34
t-Re(CO)$_3$ (DTE)	1985, 1905, 1850	34
Re(CO)$_3$(H$_2$O)$_2$Br	2020, 1940	35
Re(CO)$_3$(CH$_3$CN$_3$)Br$_4$	2053, 1952	36
Re(CO)$_3$(OH)$_4$	2030, 1925	47
Re(CO)$_3$(OAl<)(>AlOAl<)$_2$	2028, 1901	37
Re(CO)$_3$(OSi<)(>SiOSi<)$_2$	2026, 1921	37
Re(CO)$_3$(OAl<)(HOAl<)$_2$	2026, 1913, 1896	38
c-Re(CO)$_4$(Py)Cl	2111, 2009, 1934	39
c-(H$_2$Re(CO)$_4$)$^-$	2020, 1995, 1930, 1895	40
HRe(CO)$_5$	2015, 2006	41
Re(CO)$_5$Cl	2151, 2044, 2013, 1979	42
Re$_2$(CO)$_{10}$	2073, 2014, 1976	43
Re$_2$(CO)$_{10}$/Al$_2$O$_3$	2127, 2073, 2015, 2009, 1967	37
Re$_2$(CO)$_{10}$/SiO$_2$	2073, 2007, 1962	37
H$_2$Re$_2$(CO)$_8$	2093, 2020, 2000, 1979	44
H$_3$Re$_3$(CO)$_{12}$	2093, 2030, 2008, 1983	45
H$_3$Re$_3$(CO)$_{12}$/SiO$_2$	2095, 2035, 2012, 1983	47
HRe$_3$(CO)$_{14}$/SiO$_2$	2095, 2053, 2017, 1995, 1956, 1900	47
H$_4$Re$_4$(CO)$_{12}$	2042, 1990	46

illuminating papers have recently been published on the formation and reactivity of different Re carbonyls on oxidic supports.[49-56] The various ν_{CO} stretching vibrations observed and their assignments are listed in Table I. The absorption bands recorded at 2058, 2005, and 1960 cm^{-1} after an extended adsorption time at 300 K are practically the same as those observed for unsupported and supported Re$_2$(CO)$_{10}$ (Table I). This suggests that the interaction of the highly reduced supported Re with CO could yield a relatively complex carbonyl compound, very probably Re$_2$(CO)$_{10}$, with a higher CO/metal ratio than those of the carbonyls formed in the cases of Rh, Ru, and Ir. Another difference is that the Re–Re bond is preserved in this surface compound so the formation of isolated Re^0 atoms (eq 2) is very limited at and below 300 K. The valence state of the Re in this Re carbonyl is probably zero as we found no consumption of OH species in the CO-induced surface rearrangement.

Support for this assignment is provided by the fact that the bridged CO band at 1860 cm^{-1} characteristic of Re$_x$ clusters disappears when Re$_2$(CO)$_{10}$ is formed (Figure 2B, 5 h). In addition, the thermal behavior of this surface complex is consistent with this assignment. The fact that outgassing of the sample at or above 300 K eliminated the bands at 2058 and 2005 cm^{-1} and at the same time produced new intense bands at 2035 and 1925 cm^{-1} in vacuum (Figure 6) suggests the decarbonylation of Re carbonyl and/or the transformation of the surface species into another one containing less CO. The intensities of the bands at 2035 and 1925 cm^{-1} and their behavior at high temperature were practically the same. They exhibited an unusually high thermal stability: they disappeared together after extended degassing only at 773 K. This feature strongly supports the idea that these two

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bands relate to the same surface species, very probably Re(CO)$_3$ or [Re(CO)$_3$OH]$_4$, coordinated to surface oxo and hydroxo ligands. The formation of such surface complexes allows the rhenium to attain the full 18e configuration, which leads to the high thermal stability of this species. Support for this assignment is provided by the IR spectra of various Re tricarbonyl complexes (Table I). This result means that further Re–Re bond rupture occurs in this surface rearrangement (eq 2). As the development of the 2030- and 1925-cm^{-1} bands was accompanied by the attenuation of the OH band at 3660 cm^{-1} (Figure 10), we can conclude that isolated Re is oxidized to mono or higher valence metal ions by OH groups on the alumina during the formation of Re(CO)$_3$ at 373–473 K. At this temperature, the oxidation of Re^0 by adsorbed O formed in the dissociation of CO can also contribute to the formation of higher valence Re.

Re tricarbonyl has two structures:[50-52] The stable structure A, [Re(CO)$_3$OH]$_4$, is characterized by IR bands at 2030 and 1920 cm^{-1}. The formation of structure B is indicated by the appearance

A   B
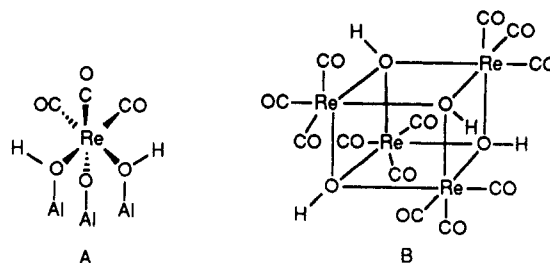
of a third band at 1885 cm^{-1}, which, together with bands at 2030 and 1920 cm^{-1}, was assigned to a tricarbonyl species possessing one axial and two equatorial CO ligands, depicted as [Re(CO)$_3${O–S}{L–S}$_2$] (S = Al or Mg of the support and L = OH or possibly μ-oxo).
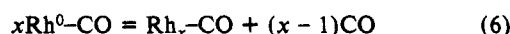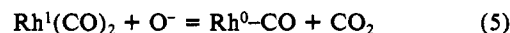
Inspection of the spectra presented in Figures 6, 8, and 9 indicates that in the present case the Re tricarbonyl has form A, as there was no sign of the presence of an absorption band at 1885 cm^{-1}. An exception was when H$_2$O and CO were coadsorbed at 473 K; in this case a weak absorption band developed at 1875 cm^{-1} (Figure 9B).

The transformation of Re(CO)$_{10}$, H$_3$Re$_3$(CO)$_{12}$, and other Re carbonyl species into Re tricarbonyl on oxidizing supports has been observed by a number of authors.[37,49-56] The XPS study by Guczi et al.[52,54] demonstrated that the Re in the cluster-derived Re(CO)$_3$ has different valence states: Re^{1+} (50%), Re^{4+} (40%), and Re^{6+} (5%). Komiyama et al.[56] identified only Re^{4+} in Re tricarbonyl on oxides.

Although it was initially thought that "there is no possibility for the formation of any tricarbonyl species if the catalyst is prepared from perrhenate",[52] very recent data indicated the occurrence of this process even in the interaction of CO with supported Re at high temperature.[55,56]

An interesting feature of the transformation of CO-rich carbonyl into Re tricarbonyl is its reversibility. Readmission of CO onto the sample at 300 K, after vacuum treatment at 300–473 K, partially restored the spectrum observed before evacuation (Figure 6). This involved not only the reappearance of the bands at 2055 and 2005 cm^{-1} but also the attenuation of the strong band at 1925 cm^{-1}, which nicely demonstrates the partial reversibility of the decarbonylation process.

4.3. CO Adsorption at 400–673 K. We made several attempts to detect the CO-induced reductive agglomeration of Re^1 or Re^{n+} at higher temperature. For supported Rh, this feature was exhibited by the transformation of the two bands of Rh^1(CO)$_2$ into a single band due to Rh$_x$–CO at 448–523 K,[19] which corresponded to the reaction

$$Rh^1(CO)_2 + O^- = Rh^0\text{–}CO + CO_2 \qquad (5)$$

$$xRh^0\text{–}CO = Rh_x\text{–}CO + (x - 1)CO \qquad (6)$$

Although we detected CO$_2$ evolution when the sample was held at 373–673 K in the presence of CO, we observed no spectral

changes indicative of the formation of Re$_x$–CO species. This confirms a high stability of the tricarbonyl as compared with that of the Rh, Ru, and Ir species on the one hand and the basically different behavior of the Re–CO system on the other hand.

However, the desorption and decomposition of Re(CO)$_3$ on alumina support in vacuum at 673–773 K caused a drastic change in the reactivity of the supported Re, as the readmission of CO at 300 K produced neither tricarbonyl bands nor any other absorption bands (Figure 6). It seemed very likely that CO decomposed in the Re tricarbonyl and adsorbed carbon and oxygen lead to the inaccessibility of rhenium toward CO adsorption. To confirm this assumption, the Re sample was titrated with hydrogen and oxygen pulses. In the first case methane formation was detected at 473 K, while in the second case H$_2$O and CO$_2$ evolution was observed: both findings suggest the presence of adsorbed carbon and oxygen species.

4.4. Conclusions. (i) The adsorption of CO on Re/Al$_2$O$_3$ produced IR bands only when the reduction temperature was higher than 773 K. (ii) The resulting infrared spectra depended sensitively on the adsorption temperature. (iii) At 100 K, an intense band was identified at 2020–2050 cm^{-1} and a weaker one at 1850 cm^{-1}, attributed to linearly and bridge bonded CO, respectively. (iv) At 300 K, new bands developed at 2058, 2005, and 1960 cm^{-1}, suggesting that the adsorption of CO led to the disruption of Re$_x$ crystallites, producing Re carbonyl species, e.g., Re$_2$(CO)$_{10}$ species. (v) After a longer adsorption time at 300 K or at 373–473 K, a new pair of bands was produced at 1920 and 2030 cm^{-1}, assigned to Re tricarbonyl, Re(CO)$_3$.

Infrared Studies of Water Adsorption on Model Organic Surfaces

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The adsorption of water on methyl and carboxylic acid terminated monolayers of *n*-alkanethiols adsorbed on gold substrates was studied using reflection–absorption infrared spectroscopy. Despite the differences in substrate polarity, the adsorption of multilayer quantities of water at temperatures <120 K yields films of amorphous solid water on both materials while adsorption at higher temperatures (>130 K) leads to the formation of polycrystalline ice. The transformation of the adsorbed overlayers from the amorphous to the polycrystalline state was followed using temperature-programmed infrared spectroscopy. Our results suggest that there is a critical layer thickness (critical mass coverage) necessary for this transition to occur. We also show that "free" OH (OH *not* hydrogen bonded to neighboring water molecules) is present on both substrates and that it is both more plentiful and stable on the acid terminated surface.

Introduction

The importance of interfaces formed between water and organic materials cannot be overstated. Such interfaces are ubiquitous in biological systems and are common to a wide variety of organic-based materials (paints, plastics, adhesives, etc.) present in our everyday life. Despite this importance, little is known about the molecular properties of water adsorbed on organic materials, a deficiency reflecting the inherent difficulty of studying such condensed-phase materials interfaces.

Recently, several research groups have shown that highly oriented (and potentially ordered) organic surfaces can be synthesized by the spontaneous assembly of chain-end-substituted alkanethiols on gold substrates.[1–6] These materials are stable under both ultrahigh-vacuum (UHV) and ambient conditions and provide a good template on which to conduct further studies of molecular adsorption and wetting. Toward this end, we, and others, have studied the interactions between water (and other small molecules) and the surfaces of these materials using such techniques as contact angle measurements[1,7,8] and temperature-programmed desorption (TPD).[9,10] Because infrared spectroscopy is sensitive to the local structure of adsorbed molecules, it provides an additional tool with which to explore the bonding of adsorbed overlayers.

In this paper we describe water adsorption studies conducted on both methyl and carboxylic acid terminated monolayer surfaces (substrates representative of both nonpolar and polar materials, respectively) using reflection–absorption infrared spectroscopy. For adsorption at temperatures below ~120 K, we find that the phase formed by water is metastable; on either substrate, a film of amorphous solid water, (H$_2$O)$_a$, is formed. At elevated substrate

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