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Reactivity of Ruthenium Carbonyls on Metal Oxide Surfaces: Effects of the Surface Acid–Base Chemistry

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Abstract

The reactivity of tetraruthenium carbonyl clusters supported on metal oxides (SiO_2, TiO_2, γ-Al_2O_3, and MgO) under various atmospheres has been investigated by infrared and ultraviolet–visible spectroscopies and electron microscopy. $[H_4Ru_4(CO)_{12}]$ physisorbed on SiO_2 easily decomposes and aggregates to form metal particles. The tetraruthenium clusters supported on TiO_2 are oxidized by surface hydroxyl groups, giving mononuclear complexes; virtually the same chemistry occurs, but less readily, on γ-Al_2O_3. The tetraruthenium clusters supported on MgO, in contrast, are highly resistant to oxidation. The strong basicity of this support leads to an increased stability of small polynuclear complexes, hindering the formation of oxidized complexes and aggregated metallic structures. The unique character of the basic support appears to be related to the tendency of the support to form and stabilize cluster anions.

Introduction

The reactions of molecular metal carbonyls on the surfaces of metal oxides provide sensitive probes of the surface chemistry [1, 2]. The reactivity of a metal oxide with a metal carbonyl is to a large extent determined by its acid–base properties, which are influenced by the nature of the metal ions exposed at the surface and by the degree of surface hydroxylation and water content. The reactions of ruthenium carbonyls are a particularly sensitive probe of the surface reactivity, since ruthenium can form a range of stable mononuclear carbonyl complexes, polynuclear carbonyl complexes, and dispersed metal particles on the surface [1]. There have been numerous investigations of the reactions of $[Ru_3(CO)_{12}]$ with metal oxide surfaces (these reactions are complex and in still need of investigation [1]), but there have been only a few investigations of the surface reactivity of $[H_4Ru_4(CO)_{12}]$. This weak proton donor ($pK_a = 11.7$ in methanol [3]) is regarded as an attractive probe of the acid–base properties of the metal oxides, since it has been observed that simple physisorption occurs on the neutral SiO_2 [4], whereas deprotonation occurs on the basic metal oxides MgO [5] and γ-Al_2O_3 [6].

The objective of this research was to use $[H_4Ru_4(CO)_{12}]$ to probe the reactivities of a series of largely dehydroxylated metal oxides with a wide range of acid–base properties: SiO_2, TiO_2, γ-Al_2O_3 and MgO. Infrared spectroscopy was the principal technique used to characterize the surface species. Results of experiments to be reported elsewhere [7] characterize the catalytic properties for CO hydrogenation of the samples prepared from $[H_4Ru_4(CO)_{12}]$ and these metal oxide supports.

Experimental

Samples were prepared by bringing metal oxide supports in contact with dry hexane solutions of $[H_4Ru_4(CO)_{12}]$ (Strem) under dry nitrogen at room temperature. After stirring for 2 h, the solvent was evaporated from the slurry under vacuum. Each of the supports [SiO_2 (Cab-O-Sil, M-5; $\sim$200 m^2/g), γ-Al_2O_3 (Degussa C; $\sim$100 m^2/g), TiO_2 (Degussa P25; $\sim$50 m^2/g) and MgO (MCB; $\sim$50 m^2/g)] had been partially dehydroxylated by pretreatment in flowing oxygen at 450 °C overnight and then evacuated at 450 °C for 2 h. The Ru contents of the samples (in wt.% Ru), as measured by X-ray fluorescence, were as follows: 1.16% on SiO_2; 1.03% on TiO_2; 1.20% on Al_2O_3; and 1.45% on MgO.

Infrared spectra of the solid samples were measured with a Nicolet 7199 instrument. Powder samples were pressed into wafers between paper disks and mounted in an infrared cell, all the steps being carried out under nitrogen in a glove box. The cells and gas handling apparatus are described elsewhere [8].

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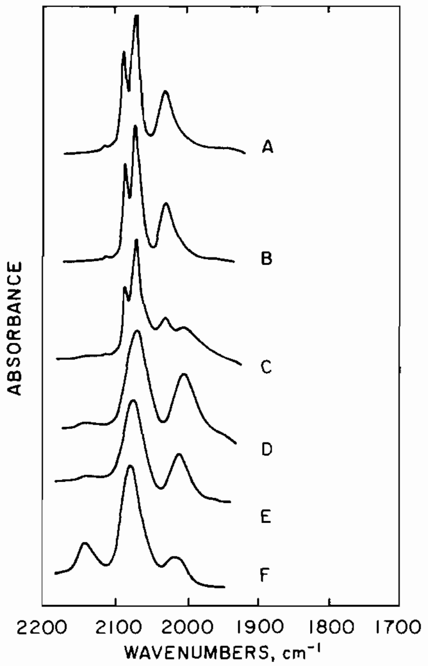

Fig. 1. IR spectra of sample prepared from $[H_4Ru_4(CO)_{12}]$ and SiO_2 after treatment in air at various temperatures. A, initial sample; B, 51 °C, 30 min; C, 75 °C, 20 min; D, 98 °C, 20 min; E, 122 °C, 20 min; F, 150 °C, 2 h, followed by exposure to CO at 95 °C for 1 h (spectra were corrected by subtraction of absorption by the SiO_2 support).

Electronic absorption spectra in the ultraviolet–visible region were recorded with a Cary 219 spectrometer. Sample powders were loaded into a quartz cell under nitrogen. The data were corrected for absorption by the supports. Since TiO_2 is opaque to the radiation in the 200–400 nm region, no results were obtained for the sample made from this support.

Small particles of ruthenium metal on the supports were observed with a Philips EM 400T transmission electron microscope. Samples were ground and dispersed on a Cu grid, which was mounted on a sample holder; the procedures were carried out under a nitrogen atmosphere; however, samples were exposed to air for a few seconds when the sample holder was attached to the electron microscope.

Results and Discussion

When $[H_4Ru_4(CO)_{12}]$ was brought in contact with SiO_2, it was simply physisorbed, as expected from the literature [4,9]. The evidence for this conclusion is the infrared spectrum of the sample (ν(CO): 2111vw, 2084s, 2069s, 2027m cm^{-1}), which is in good agreement with the spectrum of the cluster in hexane solution [7] and with the results reported by Hunt *et al.* [4] and Doi *et al.* [9] for the physisorbed cluster.

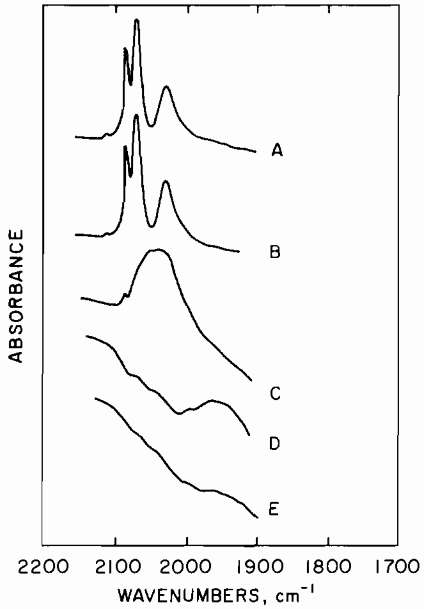

Fig. 2. IR spectra of sample prepared from $[H_4Ru_4(CO)_{12}]$ and SiO_2 after treatment in hydrogen at various temperatures. A, initial sample; B, 53 °C, 30 min; C, 75 °C, 30 min; D, 100 °C, 30 min; E, 350 °C, 30 min, followed by exposure to CO at 98 °C for 1 h (spectra were corrected by subtraction of absorption by the SiO_2 support).

The reactivity of the physisorbed cluster was investigated by infrared spectroscopy as air was allowed to flow over the sample at elevated temperatures (Fig. 1). Two strong bands and a weak band appeared at 2066 and 2000 and 2136 cm^{-1}, respectively, as the temperature increased from room temperature to 98 °C. Three infrared bands in the carbonyl region were observed to be shifted to higher wavenumbers (2140m, 2076s, 2010m,br cm^{-1}) after treatment of the sample in air at 150 °C, followed by exposure to CO at 100 °C. Similar results have been reported by Zanderighi *et al.* [10] with samples prepared from $[Ru_3(CO)_{12}]$ supported on SiO_2, in which three bands at 2140–2145w, 2070–2075s and 2005–2010m cm^{-1} were observed after treatment in oxygen, followed by exposure to CO; these bands were assigned to the oxidized mononuclear complexes $[Ru(II)(CO)_{2\text{ or }3}]$.

Treatment of the SiO_2-supported sample in hydrogen resulted in facile decomposition of the physisorbed $[H_4Ru_4(CO)_{12}]$. The infrared spectrum obtained after treatment in hydrogen at 75 °C (Fig. 2) was much different from the spectrum of the fresh sample or that of the oxidized sample. The low intensities of the bands in this spectrum as compared with those of the fresh sample suggest that partial decarbonylation occurred and that, simultaneously, formation of ruthenium metal particles took place, as evidenced by a broad, weak band near 2020 cm^{-1}, indicative of CO linearly absorbed on

TABLE I. Results of Electron Microscopy: Sizes of Metal Particles Observed on Samples Prepared from $[H_4Ru_4(CO)_{12}]$

Support	Particle size (Å)	
	Treatment in He[a]	Treatment in H_2[b]
SiO_2	20–30	20–35
TiO_2		12–16
MgO	nd[c]	8–12

[a]Measured for the samples treated with helium at 150 °C for 1 h. [b]Measured for the samples treated with hydrogen at 350 °C for 2 h. [c]Not detected.

the metal. Theolier and coworkers [11] have reported similar results for a sample prepared from $[Ru_3(CO)_{12}]$ supported on SiO_2, in which they observed a broad infrared band at 2037 cm^{-1} after thermal decomposition at temperatures $\geqslant$120 °C. When the sample made from $[H_4Ru_4(CO)_{12}]$ was heated to 100 °C in hydrogen, all the infrared bands in the carbonyl region disappeared, indicating that decomposition was complete and suggesting that ruthenium metal aggregates had formed on the surface.

The thermal decomposition of the SiO_2-supported sample in helium at 150 °C also resulted in the formation of ruthenium metal particles about 20–30 Å in diameter, as observed by electron microscopy (Table I). The intensities of the infrared bands characterizing this sample in the carbonyl region were quite low as compared with those of the fresh sample, suggesting that the cluster decomposition was almost complete. The ultraviolet–visible spectrum of this sample is consistent with the formation of metal particles, as indicated by the broad, continuous absorption (Fig. 3A) [12].

In summary, these results indicate that $[H_4Ru_4(CO)_{12}]$ physisorbed on SiO_2 easily underwent decomposition and aggregation to form metal particles. Similarly, in the case of $[Ru_3(CO)_{12}]$ supported on SiO_2, ruthenium metal particles with an average size of 14 Å were formed after thermal decomposition at temperatures $\geqslant$120 °C [11]. Other group VIII metal carbonyl clusters on SiO_2 have been found to undergo facile conversion into metal particles [1]. Occasionally, cluster aggregation is hindered, e.g. by formation of a surface-bound metal carbonyl such as $HOs_3(CO)_{10}$-{O-Si} (formed from $[Os_3(CO)_{12}]$ and surface hydroxyl groups [13]) (here the curly brackets { } represent groups terminating the bulk SiO_2). But even in the latter case, metal aggregates are formed at elevated temperatures (~250 °C) [14]. The quite general result is that group VIII metal carbonyls (and/or fragments formed from them) are mobile on the nearly neutral surface of partially dehydroxylated SiO_2 and readily form metallic aggregates, which are often quite small (approximately 20 Å); metal carbonyls are therefore regarded as a preferred class of precursor for preparation of samples consisting of small metal aggregates on neutral supports in the absence of contamination by adsorbed anions such as chloride, which are present when salt precursors are used in conventional catalyst preparation.

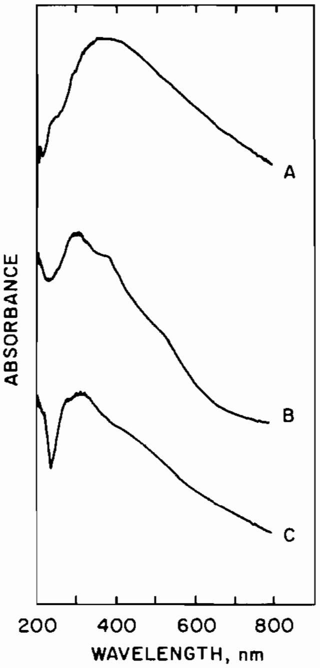

Fig. 3. UV–Vis spectra of supported ruthenium samples after treatment in helium at 150 °C. A, sample prepared from $[H_4Ru_4(CO)_{12}]$ and SiO_2; B, sample prepared from $[H_4Ru_4(CO)_{12}]$ and γ-Al_2O_3; C, sample prepared from $[H_4Ru_4(CO)_{12}]$ and MgO.

The behavior of $[H_4Ru_4(CO)_{12}]$ on γ-Al_2O_3 is markedly different from that of the cluster on SiO_2, consistent with the different acid–base properties of the two metal oxides. Both SiO_2 and γ-Al_2O_3 have surface hydroxyl groups that are weak proton donors; γ-Al_2O_3 also has basic surface groups, which are oxygen anions and also –OH groups. When the γ-Al_2O_3 surface is dehydroxylated by heating, additional basic sites (oxygen anions) are formed along with Lewis acid sites (Al^{3+} ions). The basic character of partially dehydroxylated γ-Al_2O_3 dictates its reactivity with $[H_4Ru_4(CO)_{12}]$, which is initially deprotonated to give $[H_3Ru_4(CO)_{12}]^-$ on the surface, as reported in the literature [5–7] and confirmed in this work; the infrared spectrum of $[H_3Ru_4(CO)_{12}]^-$ in acetone has bands at 2071vw, 2040s, 2034s, 2019s, 2004s, 1978m, 1950w, and 1932w cm^{-1} [15].

The reactivity of these surface-bound anions in air has been followed with infrared spectroscopy

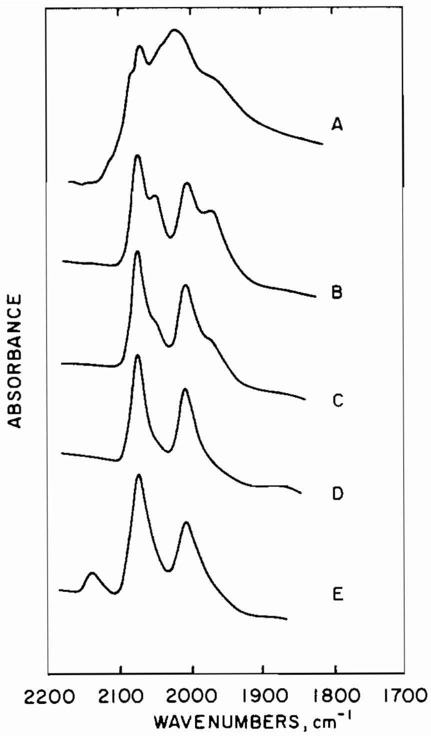

Fig. 4. IR spectra of sample prepared from [$H_4Ru_4(CO)_{12}$] and γ-Al_2O_3 after treatment in air at various temperatures. A, initial sample; B, 98 °C, 30 min; C, 121 °C, 30 min; D, 149 °C, 30 min; E, D, followed by exposure to CO at 96 °C for 50 min.

(Fig. 4). After treatment of the sample in air at 100 °C, four distinct bands were observed in the carbonyl region (ν(CO): 2065s, 2042m, 1992s, and 1958m cm^{-1}). A similar spectrum was also obtained in a separate experiment in which the sample incorporating adsorbed [$H_3Ru_4(CO)_{12}$]$^-$ was heated in helium to 150 °C. Evidently, the ruthenium carbonyl clusters underwent oxidation, the oxidizing agent in the latter experiment being surface hydroxyl groups [16]. The same sample showed evidence of the retention of Ru–Ru bonding, as suggested by the ultraviolet–visible spectrum (Fig. 3B): the absorption maxima observed in the range 300 to 400 nm have been assigned to transitions involving orbitals associated with Ru–Ru bonds [4, 17].

A pair of bands in the infrared spectrum (at 2042 and 1958 cm^{-1}) gradually disappeared with increasing temperature in air. These bands have been assigned by Zecchina *et al.* [18] as polynuclear complexes [$Ru(0)(CO)_2$]$_n$ ($n \geqslant 2$). Upon treatment of the sample in air, these low-valent ruthenium complexes were gradually oxidized to give higher-valent species such as [$Ru(II)(CO)_2$] or [$Ru(III)(CO)_2$] [18]. After treatment of the sample in air at 150 °C, followed by exposure to CO at 100 °C, a new band appeared at 2134 cm^{-1}; two other bands appeared (at 2071 and 2002 cm^{-1}), with slight shifts to higher wavenumbers in comparison with the bands observed after treatment in air at 100 °C. These results are virtually the same to those reported by Zecchina *et al.* [18] for samples prepared from [$Ru_3(CO)_{12}$] supported on Al_2O_3. Evidently, the final mononuclear complexes on Zecchina's samples and ours were the same.

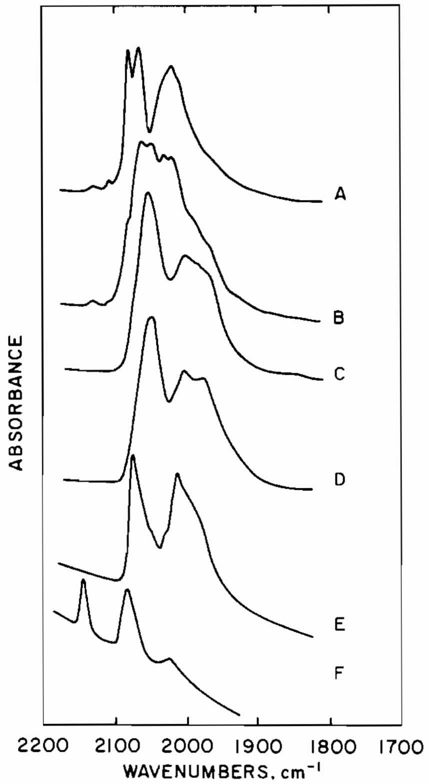

Fig. 5. IR spectra of sample prepared from [$H_4Ru_4(CO)_{12}$] and TiO_2 after treatment in hydrogen at various temperatures. A, initial sample; B, 52 °C, 30 min; C, 76 °C, 20 min; D, 100 °C, 20 min; E, 124 °C, 20 min; F, 350 °C, 20 min, followed by exposure to CO at 100 °C for 15 min.

When the anion [$H_3Ru_4(CO)_{12}$]$^-$ on γ-Al_2O_3 was treated in hydrogen, even at temperatures as high as 175 °C, it resulted in a spectrum having bands in the carbonyl region at 2048 and 1970 cm^{-1}. No bands indicative of oxidized complexes were observed. The spectrum is suggestive of polynuclear ruthenium carbonyls, the formation of which may be facilitated by the relative stability of the [$H_3Ru_4(CO)_{12}$]$^-$ precursor. The formation of ruthenium metal on γ-Al_2O_3 was not obvious from the infrared spectra obtained after treatment in hydrogen at 350 °C, followed by exposure to CO at 100 °C. The nature of these surface species remains to be elucidated.

In summary, it is the basic character of the γ-Al_2O_3 surface that accounts for the deprotonation of [$H_4Ru_4(CO)_{12}$] to give [$H_3Ru_4(CO)_{12}$]$^-$ as the initial surface organometallic species. The relative stability of this anion apparently aids in the formation of poorly defined polynuclear ruthenium car-

Fig. 6. Electron micrograph showing ruthenium metal particles formed by reduction (at 350 °C in hydrogen) of sample prepared from $[H_4Ru_4(CO)_{12}]$ and TiO_2.

bonyls on the surface, without facile formation of metallic aggregates.

The reactivity of the supported tetraruthenium clusters on TiO_2 is similar to that of the clusters on γ-Al_2O_3 (the initially formed surface species were physisorbed $[H_4Ru_4(CO)_{12}]$ in a mixture with chemisorbed $[H_3Ru_4(CO)_{12}]^-$ [7]). The former was more easily oxidized than the latter; the polynuclear complexes were no longer observed after treatment of the TiO_2-supported samples in air at 75 °C (Fig. 5).

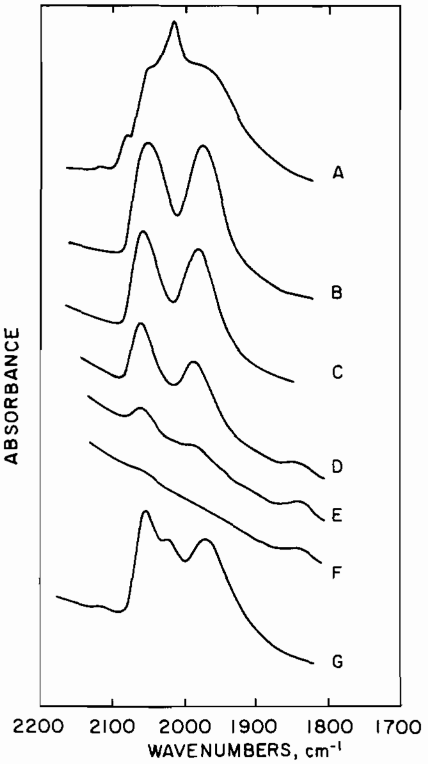

Fig. 7. IR spectra of sample prepared from $[H_4Ru_4(CO)_{12}]$ and MgO after treatment in air at various temperatures. A, initial sample; B, 58 °C, 30 min; C, 77 °C, 30 min; D, 100 °C, 30 min; E, 123 °C, 35 min; F, 149 °C, 30 min; G, F, followed by exposure to CO at 101 °C for 30 min.

After treatment in hydrogen at 125 °C, the TiO_2-supported clusters were converted into mononuclear complexes inferred to be $[Ru(II)(CO)_2]$; infrared bands in the carbonyl region were observed at 2074 and 2013 cm^{-1}, having nearly equal intensities (Fig. 5E). Evans and McNulty [19] also reported the same assignment for these bands observed after reaction of $[Ru_3(CO)_{12}]$ and TiO_2 in the presence of refluxing hexane.

The infrared spectrum obtained after treatment of the sample in hydrogen at 350 °C, followed by exposure to CO at 100 °C, suggests the formation of ruthenium metal; a weak and broad band was observed at about 2020 cm^{-1}; this spectrum also indicates the presence of mononuclear complexes $[Ru(III)(CO)_2]$ [18], which had infrared bands at 2140 and 2080 cm^{-1}. Electron microscopy confirmed the presence of metal particles, 12–16 Å in diameter, after treatment of the sample in hydrogen at 350 °C (Fig. 6).

In summary, the results obtained for the TiO_2-supported sample suggest that the ruthenium clusters supported on TiO_2 were oxidized to give mononuclear complexes more easily than those supported on γ-Al_2O_3. However, the presence of hydrogen apparently suppressed the oxidation of the ruthenium species (or prevented the rupture of Ru–Ru bonds in the cluster framework). Evidently some ruthenium clusters aggregated, ultimately forming metal particles; the tendency of the sample to form ruthenium metal upon treatment in hydrogen seems to correlate with the amount of $[H_4Ru_4(CO)_{12}]$ physisorbed on the oxide surface.

The initial organometallic species formed from $[H_4Ru_4(CO)_{12}]$ on MgO, as indicated by infrared spectroscopy, were the anions $[H_3Ru_4(CO)_{12}]^-$ and $[H_2Ru_4(CO)_{12}]^{2-}$, formed by deprotonation of the neutral cluster on this strongly basic support [7]. When the sample incorporating these chemisorbed anions was brought in contact with air at 60 °C, infrared bands in the carbonyl region were observed at 2048 and 1973 cm^{-1} (Fig. 7B); as the temperature increased, these bands shifted slightly to higher wavenumbers. Closely similar spectra were observed when the original sample was treated in helium at 100 °C, demonstrating that the oxidation could also be carried out by surface hydroxyl groups. These spectra suggest that polynuclear ruthenium complexes were present, in contrast to the mononuclear complexes formed on TiO_2 and γ-Al_2O_3 under similar conditions. The ultraviolet–visible spectrum of this sample treated in helium at 150 °C, with an absorption maximum at about 320 nm (Fig. 3C), also suggests the retention of Ru–Ru bonding [4, 17].

Upon treatment of the MgO-supported ruthenium cluster in hydrogen, the infrared spectra became

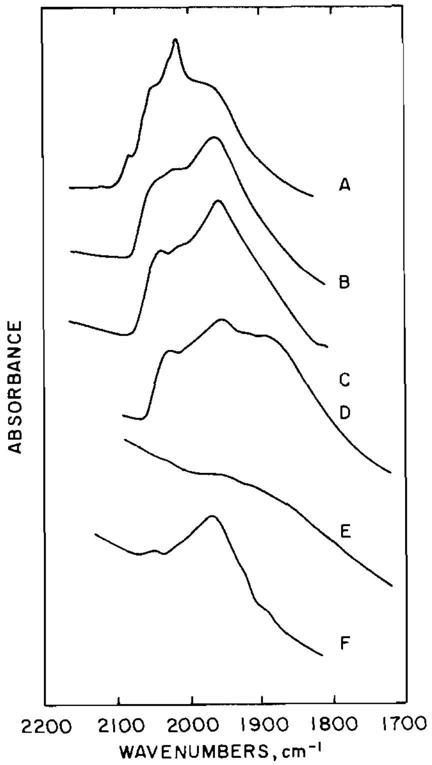

Fig. 8. IR spectra of sample prepared from $[H_4Ru_4(CO)_{12}]$ and MgO after treatment in hydrogen at various temperatures. A, initial sample; B, 75 °C, 30 min; C, 99 °C, 30 min; D, 147 °C, 30 min; E, 199 °C, 30 min; F, 350 °C, 30 min, followed by exposure to CO at 100 °C for 30 min.

broader and shifted to lower wavenumbers (Fig. 8). This change suggests that the decarbonylation of the clusters proceeded gradually with the formation of CO bridge-bonded to ruthenium ensembles or aggregates on the MgO surface. The infrared spectrum obtained after treatment in hydrogen at 350 °C, followed by exposure to CO at 100 °C, suggests that high-nuclearity ruthenium complexes (with unknown structures) were present on the MgO surface; the spectrum shows bands at 2043w,br, 1966m,br, 1928w,sh, and 1890w,br cm^{-1}. Electron microscopy gave evidence of very small metal entities (about 8–12 Å in diameter) after treatment in hydrogen at 350 °C.

The major difference between MgO and the other supports is the strong tendency of this strongly basic support to favor the retention of Ru–Ru bonding originally present in the cluster framework, irrespective of the atmosphere used in the treatment. The anionic clusters formed on MgO evidently are highly resistant to oxidation.

In summary, an increase in basicity of the support leads to an increased tendency of the support to stabilize small polynuclear ruthenium carbonyls and hinders the formation of oxidized (mononuclear) complexes and reduced (aggregated) metallic structures. The unique stabilizing character of the basic supports appears to be related to the tendency of the support to form and stabilize cluster anions such as $[H_3Ru_4(CO)_{12}]^-$. Other stable anions such as $[Ru_6C(CO)_{16}]^{2-}$ have been observed to form on the MgO surface [5, 7], and it may be the stability of these possible surface intermediates that accounts for the preferential formation of very small metal entities on the basic supports.

Acknowledgements

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