Chem. Mater. 1994, 6, 739–743

Articles

Formation of Molybdenum and Tungsten Cation Pairs on Silica from Cyclopentadienylmolybdenum Di- and Tricarbonyl Dimer, Cyclopentadienyltungsten Di- and Tricarbonyl Dimer, and 1,2-Bis(cyclopentadienyl)-1,1,2,2-tetracarbonylmolybdenumtungsten

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Received September 17, 1993. Revised Manuscript Received April 4, 1994[●]

Cyclopentadienylmolybdenum di- and tricarbonyl dimer, cyclopentadienyltungsten di- and tricarbonyl dimer, and 1,2-bis(cyclopentadienyl)-1,1,2,2-tetracarbonylmolybdenumtungsten was introduced to SiO_2, and the resulting chemically adsorbed structures were studied using Fourier transform infrared spectroscopy and temperature-programmed decomposition. The complexes react with surface hydroxyls of the silica as evidenced by the attenuation of the isolated silanol IR absorbance at 3742 cm^{-1} and the formation of cyclopentadiene. Changes in the carbonyl infrared bands during heating and the temperature programmed decomposition results suggest that this exchange reaction yields discrete cation–cation pairs. Removal of the carbonyl ligands leads to Mo or W cations with an average oxidation state of 4+.

Introduction

A great deal of effort has been devoted to the synthesis and characterization of silica-supported transition metals such as molybdenum and tungsten because of their widespread catalytic applicability.[1-7] Supporting metals on inert oxides affords a route to efficiently utilize expensive materials in a catalytic reaction. Techniques utilizing metal salts to deposit Mo on silica have been popular routes to study these systems but generally yield catalysts with large amounts of the supported oxide present in the form of crystallites.[7-9] Ekerdt and co-workers found that dehydrated Mo(VI) on silica, prepared from $Mo(\eta^3\text{-}C_3H_5)_4$, $Mo_2(\eta^3\text{-}C_3H_5)_4$, and cyclopentadienylmolybdenum dicarbonyl dimer $[Cp_2Mo_2(CO)_4]$, exists as an isolated cation.[7,10] While some controversy exists in the literature, a recent study has shown the dehydrated Mo(VI) supported structure is not related to the precursor structure.[7]

Reduced metal cation catalysts have been utilized in a variety of applications including olefin metathesis,[11-15] isomerization,[16] and polymerization.[17] There are a number of techniques that can yield oxide-supported Mo and W in a reduced oxidation state, and they usually involve starting with the fully oxidized metals. Thermal reduction in hydrogen[18-22] generally leads to cations in a range of oxidation states. Ultraviolet photoreduction of silica supported Mo(VI) has been reported to lead to oxidation states of 5+, 4+, 3+, 2+ and 0.[23-26] Ultraviolet photoreduction of silica supported W(VI) in CO likely leads to W(IV).[27]

Organometallic complexes with labile ligands offer yet another approach to the synthesis of supported, reduced Mo and W cations that are more homogeneous in both

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[●] Abstract published in *Advance ACS Abstracts*, May 1, 1994.

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composition and oxidation state. Yermakov[1,2] and Iwasawa[3,4,28] have demonstrated that silica-supported metal cations of discrete oxidation states can be synthesized from transition metal allylic precursors by controlling the conditions of oxidation and reduction. Additionally, Iwasawa reported Mo(II) and Mo(IV) cation pairs and cation dimers over silica, with Mo(II) dimers having a Mo–Mo bond.[3,4,29] Moller, et al. studied the interaction of $Cp_2Fe_2(CO)_4$ with different acid forms of zeolite Y using Fourier transform infrared (FTIR) spectroscopy, temperature-programmed decomposition–mass spectroscopy and extended X-ray absorption fine structure (EXAFS).[30] The acidic properties of the zeolite determined whether the complex fragmented into monomeric $CpFe(CO)_3^+$ and $CpFe^+$ or remained in a dimer form as $Cp_2Fe_2(CO)_4H^+$.

This paper reports the usage of $Cp_2Mo_2(CO)_4$, cyclopentadienyltungsten dicarbonyl dimer [$Cp_2W_2(CO)_4$], cyclopentadienylmolybdenum tricarbonyl dimer [$Cp_2Mo_2(CO)_6$], cyclopentadienyltungsten tricarbonyl dimer [$Cp_2W_2(CO)_6$], and 1,2-bis(cyclopentadienyl)-1,1,2,2-tetracarbonylmolybdenumtungsten [$Cp_2MoW(CO)_4$] precursors to generate supported, reduced-metal reagents in a single oxidation state and offers insight into the reaction of the organometallic complexes with the silica surface. These complexes were selected because the carbonyl ligands are infrared absorbing, thereby permitting the attachment process to be monitored and because the complexes feature bimetallic and heterobimetallic compositions.

Experimental Section

Sample Preparation and Temperature-Programmed Decomposition. Cab-O-Sil (HS-5, 325 m^2/g) SiO_2 was used after it had been contacted with a sufficient amount of water such that all the silica spheres were wet but no excess water was present. It was then dried at 200 °C and sifted through a 325-mesh sieve to yield a silica that was more easily handled. $Cp_2Mo_2(CO)_4$ and $Cp_2W_2(CO)_4$ were prepared from their hexacarbonyl analog following the method prescribed by Curtis et al.[31] $Cp_2MoW(CO)_4$ was synthesized by refluxing both $Cp_2Mo_2(CO)_6$ and $Cp_2W_2(CO)_6$ and then isolating the product by column chromatography.[31] $Cp_2Mo_2(CO)_6$ and $Cp_2W_2(CO)_6$ were purchased commercially (Aldrich, 98%).[32]

The silica was loaded into a 12-in. quartz U-tube (one side 6-mm i.d., the other side 10-mm i.d.) and evacuated for 30 min at 375 °C; it was then purged with Ar (Liquid Carbonic, 99.999%) under similar conditions. Crystalline precursor was dissolved in anhydrous benzene that had been distilled over Na/benzophenone and degassed in Ar. The benzene solution was introduced to the silica via syringe at room temperature and allowed to react with the isolated surface silanols. The mixture was allowed to bubble in flowing Ar at room temperature until all the benzene had evaporated.

The wet sample as also heated to vaporize the attachment byproducts and the resulting gas phase was sent to a Hewlett-Packard 5880 gas chromatograph (GC) equipped with a flame ionization detector. A 1 cm^3 sample was automatically injected onto a 30 ft × $^1/_8$ in. Supelco 23% SP-1700/Chromosorb P AW column. The GC was calibrated with cyclopentadiene produced by pyrolysis of dicyclopentadiene (Aldrich, 95%) at 170 °C.

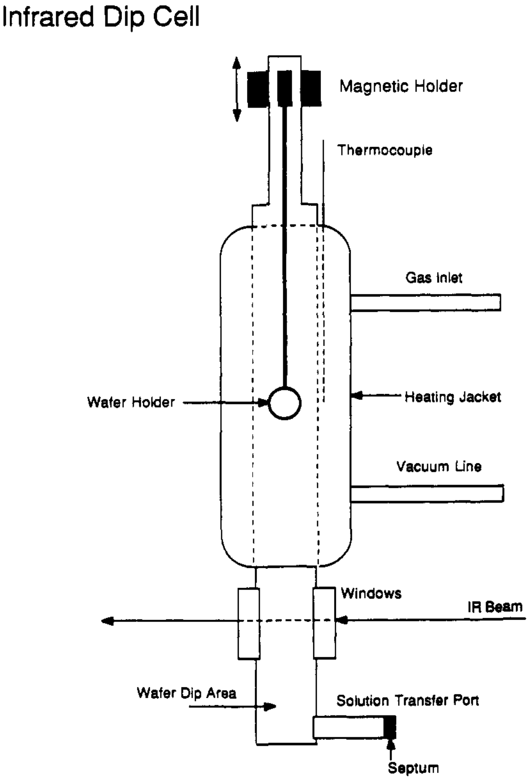

Figure 1. Schematic of the IR cell used in attachment experiments.

After drying the sample to remove solvent it was subjected to pure He while ramping the temperature 5 °C/min up to 400 °C to decompose the surface-tethered structure and remove the carbonyl ligands. The effluent from this temperature-programmed decomposition (TPDE) was sent to a Hewlett-Packard 5880 GC equipped with a single-filament thermal conductivity detector. A 1 cm^3 sample from an automatic sampling valve was injected every 2 min onto a 6-ft × $^1/_8$-in. Porapak T column. The detector was calibrated against a 990 ± 10 ppm CO/990 ± 10 ppm CO_2/He gas mixture (Wilson Oxygen).

IR Studies. A quartz IR cell was fabricated to permit the *in situ* study of the reaction of the organometallic complexes with silica. It is shown in Figure 1. Solutions of the organometallic compounds were introduced into the reservoir of this dip cell, whereby a self-supporting SiO_2 wafer could be lowered into the solution and react with the complexes. This procedure typically resulted in 1–2 wt % metal loading. The cell was then mounted into a Mattson RS1 FTIR spectrometer. The wafer could be manipulated, utilizing the magnetic wand, from the heated zone to the solution reservoir, and into the IR beam. The silica wafer was initially pretreated by evacuating at 375 °C for 30 min and then subjected to similar conditions in flowing He. The wafer was then allowed to cool, after which it was dipped into an approximately 0.1 M solution of the precursor in anhydrous, perdeuterated benzene for 2 min. After the organometallic compound had reacted with the silica wafer, the solution reservior was drained, and the cell was evacuated and prepared for the collection of spectra. Helium flowed through the cell during the removal of the carbonyl ligands.

Spectra were also collected of the pure complexes in solution. Solid $Cp_2Mo_2(CO)_n$, $Cp_2W_2(CO)_n$ (n = 4, 6), and $Cp_2MoW(CO)_4$ was dissolved in anhydrous, perdeuterated benzene and injected, via syringe, into a liquid IR cell equipped with CaF_2 windows. Solid-phase spectra of all complexes were taken in Nujol and fluorocarbon mulls for reference.

Oxidation State Determination. The oxidation state of the tethered Mo cations after complete ligand removal was determined by titrating the surface sites with a known amount of oxygen while assuming all cations were in the same oxidation state. After all ligands were removed, a 2% O_2 in He mixture (Wilson Oxygen) was delivered to the sample at a rate of approximately 8 μmol/min and the temperature was subsequently ramped at 9 °C/min up to 550 °C. The sample remained at this

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[32] The toxicity of these compounds has not been determined. All metal carbonyl compounds may be fatal if swallowed, inhaled, or absorbed through the skin and should be handled with caution in a hood with adequate protection.

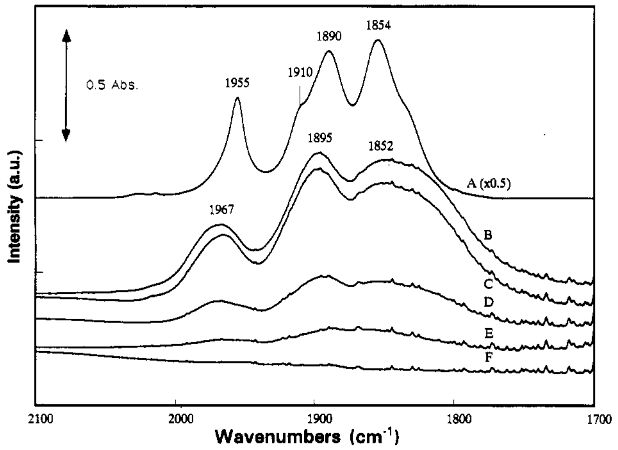

Figure 2. Infrared spectra of $Cp_2Mo_2(CO)_4$: (A) in benzene-d_6; (B) after reaction with silica, heated to 50 °C in vacuum; (C) after heating to 100 °C in vacuum; (D) after heating to 140 °C in vacuum; (E) after heating to 150 °C in vacuum; (F) after heating to 200 °C in vacuum.

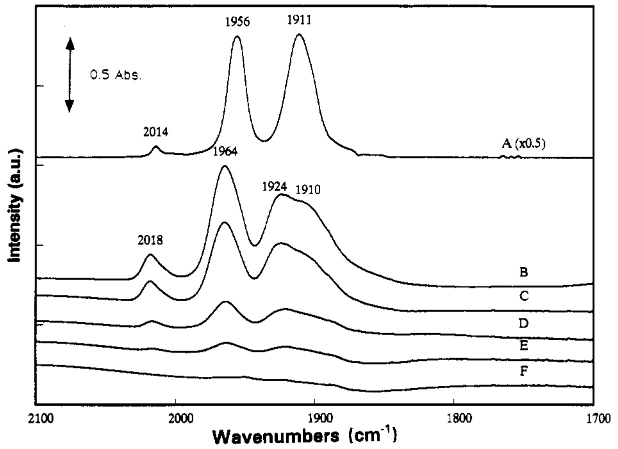

Figure 3. Infrared spectra of $Cp_2Mo_2(CO)_6$: (A) in benzene-d_6; (B) after reaction with silica, heated to 40 °C in vacuum; (C) after heating to 100 °C in vacuum, (D) after heating to 120 °C in vacuum, (E) after heating to 130 °C in vacuum, (F) after heating to 150 °C in vacuum.

temperature until no more oxygen was consumed. After allowing the sample to cool to ambient, the same procedure was performed on it to generate the oxygen breakthrough curve in the absence of oxidation. Oxygen concentration was measured using a Hewlett-Packard 5880 GC by automatically injecting a 1 cm^3 sample onto the Porapak T column every 4 min. A single-filament thermal conductivity detector was employed to measure O_2, CO_2, and H_2O. Residual carbonaceous residue, possibly from the solvent that remained on the silica after the ligand removal step, led to some CO_2 and H_2O during oxidation. The amount of oxygen needed to oxidize the cations was determined by accounting for all the oxygen consumed and the amount that reacted to CO_2 and H_2O. The procedure used to determine Mo loading has been described elsewhere.[7]

Results

Infrared results are presented for Mo dimer complexes; similar trends were observed for W dimer complexes and $Cp_2MoW(CO)_4$. Figures 2 and 3 (spectra A) present the carbonyl region for $Cp_2Mo_2(CO)_4$ and $Cp_2Mo_2(CO)_6$ dissolved in perdeuterated benzene, respectively. For the tetracarbonyl complexes in perdeuterated benzene, carbonyl absorbances are centered at 1955, 1890, and 1854, for the MoMo compound, at 1955, 1885, and 1830 cm^{-1} for the WW compound, and at 1950, 1905, and 1850 cm^{-1} for the MoW compound. All three tetracarbonyl complexes also displayed very weak absorbances at ca. 3105 and 1420 cm^{-1} corresponding to the C–H and C–C stretching modes of the cyclopentadienyl rings, respectively. The two hexacarbonyl complexes, $Cp_2Mo_2(CO)_6$ and $Cp_2W_2(CO)_6$, displayed slightly different absorbances in the carbonyl region but very similar absorbances attributable to the cyclopentadienyl rings. The Mo dimer [$Cp_2Mo_2(CO)_6$] possessed a weak carbonyl absorbance at 2014 cm^{-1} and two strong carbonyl absorbances at 1956 and 1911 cm^{-1}, while the W dimer [$Cp_2W_2(CO)_6$] possessed a weak carbonyl absorbance at 1996 cm^{-1} and absorbed strongly at 1953 and 1903 cm^{-1}. Spectrum 3A is very similar to the $Cp_2Mo_2(CO)_6$ complex in CCl_4, which absorbs strongly at 1961 and 1917 cm^{-1}.

Agreement between the major peaks (spectrum 2A) and published results[31] was very good for $Cp_2Mo_2(CO)_4$ in benzene, but there was noticeable contamination from the corresponding hexacarbonyl dimer, as evidenced by the small peak at 1910 cm^{-1}. At room temperature, solutions of the dicarbonyl dimers are rapidly attacked by oxygen, degrading into $Cp_2M_2(CO)_6$ and insoluble solids.[31] The pureness of both of the crystalline, homonuclear tetracarbonyl complexes was confirmed by IR spectroscopy of the Nujol mulls. However, it was difficult to maintain the integrity of the liquid cell, and oxygen readily attacked solutions of the complexes producing $Cp_2M_2(CO)_6$ from $Cp_2M_2(CO)_4$ and the CO evolved in the oxidation. Decomposition of a tetracarbonyl dimer into a hexacarbonyl dimer over silica was not apparent during experiments in the dip cell.

The spectra recorded following attachment of the complexes to silica and removal of the benzene solvent are presented in Figures 2B and 3B. Shifts in peak positions and peak broadening can be seen when comparing the solution spectra to the adsorbed spectra. Furthermore, the band at 2018 cm^{-1} appears more intense and the 1911-cm^{-1} band (Figure 3A) now appears to be two bands at 1910 and 1924 cm^{-1} (Figure 3B). Also shown in Figures 2 and 3 are the sequential spectra recorded after raising the silica wafer into the heated zone for 1 min at the designated temperatures and then lowering the wafer into the IR beam. Neither frequency changes nor intensity ratio changes are observed as a result of heating the sample. For both $Cp_2Mo_2(CO)_4$ and $Cp_2Mo_2(CO)_6$ the carbonyl ligands were completely removed at 200 °C. Infrared absorbance bands associated with the cyclopentadienyl ligands (aromatic), which are known from the solution- and solid-phase spectra, were not observed following attachment of the complexes to silica. Production of cyclopentadiene following reaction of $Cp_2Mo_2(CO)_6$ with silica was verified by GC analysis of the products and by the appearance of the characteristic peaks (aliphatic) of cyclopentadiene in FTIR.

Figure 4 presents the IR spectra of the hydroxyl region of silica. The sharp absorbance at 3742 cm^{-1} represents the isolated surface silanols.[33] Spectrum A represents a clean, dehydrated silica wafer. The absorbance intensity attenuated following attachment of the complex.

TPDE results for $Cp_2Mo_2(CO)_4$ and $Cp_2Mo_2(CO)_6$ are shown in Figure 5. The onset of CO evolution for the sample prepared from $Cp_2Mo_2(CO)_4$ begins at approximately 125 °C and reaches a maximum near 225 °C. Similar results were obtained for the sample prepared from $Cp_2Mo_2(CO)_6$. The IR results in Figures 2 and 3 also show loss of carbonyl ligands above 100 °C. During the TPDE

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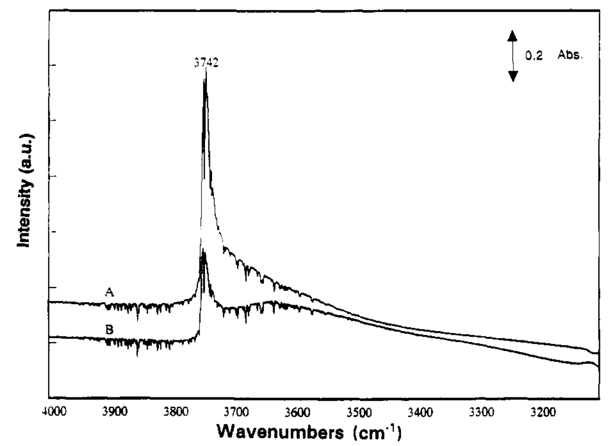

Figure 4. Infrared spectra of SiO_2 wafer: (A) after dehydrating at 400 °C in vacuum, (B) after reaction with $Cp_2Mo_2(CO)_4$ at 25 °C.

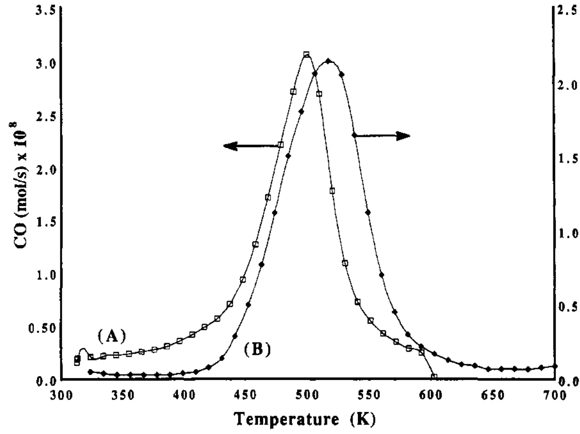

Figure 5. Temperature-programmed desorption of (A) $Cp_2Mo_2(CO)_4$ on SiO_2 (4.5 wt % Mo) and (B) $Cp_2Mo_2(CO)_6$ on SiO_2 (2.5 wt % Mo).

experiments, the samples turn from a light brick-red (tetracarbonyl) or light purple (hexacarbonyl) to gray. All TPDE studies show that CO ligands have effectively evolved when the temperature reaches 325 °C. Carbonyl ligands evolve slowly during the drying step that removes benzene solvent; therefore, the moles of CO evolved during TPDE cannot be used to establish the Mo/CO ratio for the adsorbed species. It is worthy to note here that the TPDE curve for samples prepared from $Cp_2W_2(CO)_4$ have a slight shoulder on the low-temperature side, but there was no evidence in the IR to suggest that the carbonyls are being liberated in a sequential manner.

The average oxidation state of the surface-attached Mo cations was determined by titrating the sample with a known amount of O_2 until all cations were in the fully-oxidized, 6+ oxidation state. (Oxidation-state measurements were not performed with the tungsten analogs because it was easier to establish Mo metal content.) Figure 6 contains a graph that illustrates the moles of oxygen consumed as a function of time for Mo/SiO_2 prepared from $Cp_2Mo_2(CO)_4$, and Figure 7 presents the corresponding amounts of CO_2 and H_2O formed during the oxidation of this sample. Curve 6A represents the moles of oxygen that passed through the reactor during the initial oxidation stage. Curve 6B portrays the amount of oxygen measured when the fully-oxidized sample is subjected to identical conditions of temperature and oxygen flow. The difference between the areas under the two curves is the total amount of oxygen taken up by the sample. As a way of checking the accuracy of this titration technique, Mo samples from $Mo(\eta^3\text{-}C_3H_5)_4$ were prepared and the oxidation state of the resulting surface-supported Mo cations was determined. It was found that the Mo cations had an oxidation state of 2.1+, which agrees well with the 2+ results based on electron spectroscopy for chemical analysis.[21] Table 1 summarizes the results of the oxygen titration experiments for samples of Mo/SiO_2 prepared from $Cp_2Mo_2(CO)_4$, $Cp_2Mo_2(CO)_6$, and $Mo(\eta^3\text{-}C_3H_5)_4$.

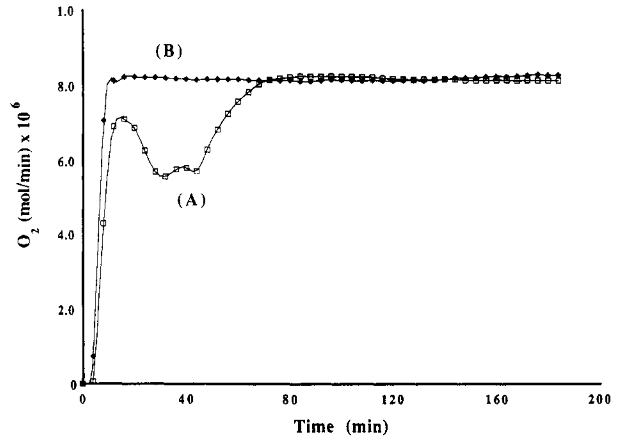

Figure 6. Oxidation curves obtained from the reaction of $Cp_2Mo_2(CO)_4$ with SiO_2 (2.6 wt % Mo): (A) moles of O_2 that passed through reactor during the initial oxidation stage; (B) moles of O_2 that passed through the fully oxidized sample.

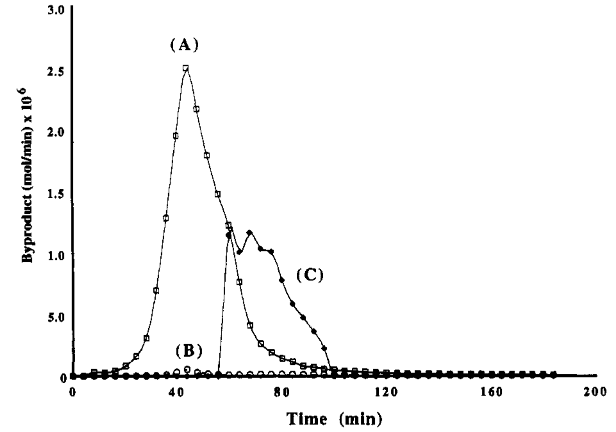

Figure 7. CO_2 and H_2O production resulting from oxidation of carbonaceous residue: (A) moles of CO_2 produced during initial oxidation stage; (B) moles of CO_2 produced by fully oxidized sample; (C) moles of H_2O produced during initial oxidation stage.

Discussion

The bridging carbonyl modes of $Cp_2Mo_2(CO)_4$ provide insight into the dimer nature of the complex after it has attached to the silica surface. Jemmis et al.[34] have determined that only a small energy difference separates a structure where all four of the carbonyls are linear and a semibridging structure, in which there is metal–carbon overlap. Therefore, $Cp_2Mo_2(CO)_4$, $Cp_2W_2(CO)_4$, and $Cp_2MoW(CO)_4$ exhibit a fluxional behavior in which carbonyls hop from one metal atom to the other. Frequencies exhibited by doubly bridging carbonyls typically lie between 1800 and 1850 cm^{-1},[35] and it is readily apparent that these complexes in solution possess this bridging character. The spectra (such as Figure 2A) represent an

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Table 1. Oxygen Titration Results

	wt % metal	O_2 consumption (mol/Mo)	CO_2 production (mol/Mo)	H_2O production (mol/Mo)	net O_2 consumed (mol/Mo)	oxidation state
$Cp_2Mo_2(CO)_4$						
1	2.6	1.51	0.84	[a]	0.67	3.3
2	3.3	2.61	1.37	1.54	0.47	4.1
3	5.3	2.18	1.42	0.64	0.48	4.1
						av 3.8
$Cp_2Mo_2(CO)_6$						
1	3.1	1.97	1.19	0.46	0.55	3.8
2	2.7	1.71	1.24	[a]	0.47	4.1
3	2.4	2.22	1.18	0.64	0.68	3.3
						av 3.7
$Mo(\eta^3\text{-}C_3H_5)_4$						
1	0.39	2.60	0.57	2.21	0.93	2.2
2	0.37	3.46	0.41	4.10	1.00	2.0
						av 2.1

[a] H_2O production was not measured.

average between semibridging and terminal carbonyl structures. When the $Cp_2M_2(CO)_6$ complexes containing only terminal carbonyls are examined (Figure 3A) only absorbances above 1850 cm^{-1} are observed.

After solutions of the various complexes are introduced to silica, reaction occurs between the cyclopentadienyl ligands and the hydroxyl groups in an exchange reaction that leads to cyclopentadiene, attachment of the metal via Si–O–M bonds, and retention of the dimer character of the precursor. The isolated silanol IR absorbance mode at 3742 cm^{-1} attenuated during attachment (Figure 4). Furthermore, the cyclopentadienyl C–H and C–C modes could not be detected in the IR following attachment, and cyclopentadiene was detected by GC and IR. Examination of the carbonyl region of these supported complexes reveals no appreciable change in the positions of the carbonyl absorbances; bands broadened and peaks shifted slightly and the 1911-cm^{-1} band for the hexacarbonyl appeared to split into two bands after attachment. Some slight changes are reasonable since the surface environment differs from the solvent and the cyclopentadienyl ligands have been replaced with oxygen ligands. The band splitting may have resulted from a change in symmetry for the carbonyl ligands on the hexacarbonyl complexes upon attachment. Spectra in Figure 2 show the bands expected for bridging carbonyls following adsorption. When the samples are thermally decomposed, as in the case of the Mo–Mo supported structure, the carbonyls are evolved simultaneously and not sequentially. This is apparent in the single-peak shape of the CO curve of Figure 5 and the IR spectra in Figures 2 and 3. The carbonyl absorbances simply attenuate and do not suggest any transitional carbonyl structures.

The results demonstrate that following attachment and prior to complete carbonyl ligand removal, the two metal cations of the $Cp_2M_2(CO)_4$ and $Cp_2M_2(CO)_6$ complexes retain their dimer character. (The metal cations become isolated after oxidation to the 6+ state.[10]) The oxygen titration experiments were performed after removal of the carbonyl ligands, and we do not know what oxidation state changes the cations may undergo as the carbonyl ligands are removed. Attempts to repopulate the carbonyls have been unsuccessful. In support of a dimer structure after ligand removal we offer the additional information that these MoMo, WW, and MoW systems have been employed to reductively couple acetaldehyde to 2-butenes in a process that requires the electron donating capacity of dimers in the 4+ state, and EXAFS results for a sample prepared from $Cp_2W_2(CO)_4$ that shows W–W bonding at 2.96 Å.[36]

Residual hydrocarbon contamination of the silica following cyclopentadienyl exchange with the silica led to considerable oxygen consumption for contaminant oxidation to CO_2 and H_2O, illustrated in Figure 7. We feel the titration technique illustrated in Figure 6 is valid since we find an oxidation state of 2.1+ for Mo deposited from the $Mo(\eta^3\text{-}C_3H_5)_4$ precursor, which is in close agreement with the 2+ oxidation state shown by electron spectroscopy for chemical analysis.[21] The range of values obtained resulted from the indirect method of calculation used that accounts for oxidation of the carbonaceous residue. It was assumed that after complete ligand removal and prior to oxidation, all cations were in the same oxidation state. Since the average values reported in Table 1 are near 4, a stable oxidation state that has been found for Mo/silica following photoreduction in CO,[26] it is reasonable to suggest the Mo cations resulting from $Cp_2Mo_2(CO)_n$ (n = 4, 6) were in the 4+ oxidation state.

The results put forth in this paper outline a synthetic route to arrive at silica-supported Mo and W cations in what is likely a single, 4+ oxidation state. They also lend insight into the reaction of $Cp_2Mo_2(CO)_n$ and $Cp_2W_2(CO)_n$ (n = 4, 6) with silica and suggest that the metal cations remain adjacent during deposition and ligand removal. These results agree with the prior studies by Iwasawa on other nonaqueous preparation routes for supported metals in that the hydrocarbon ligands are removed in exchange reactions with silanol ligands.[29] He showed that $Mo_2(\eta^3\text{-}C_3H_5)_4$ forms dimers with a Mo-Mo bond in the 2+ oxidation state after hydrogenolysis of residual ligands at 550 °C. Oxidation of $Mo^{2+}\text{–}Mo^{2+}$ produced Mo(IV) structures that did not feature a Mo–Mo bond. Moller et al. found somewhat different results when $Cp_2Fe_2(CO)_4$ was anchored into zeolite Y.[30] Notably the Cp ligands did not exchange with the zeolite protons and the ligands were not eliminated until heating to high temperatures during carbonyl removal. The differences between Mo and W dimers and Fe dimers could be due to the differences in the reactive properties of the complexes or to the differences between the zeolite surface and silica.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

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(36) Sullivan, D. L.; Ekerdt, J. G.; Deutsch, S.; Gates, B. C., unpublished results.