

SUPPORTED MOLECULAR CATALYSTS FOR CO HYDROGENATION

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INTRODUCTION

The metal-oxide support is known to exert a strong influence on the activity and selectivity of heterogeneous CO hydrogenation catalysts (1). Ichikawa demonstrated that catalysts derived from $[\text{Rh}_4(\text{CO})_{12}]$ deposited on basic MgO produced methanol from CO + H₂ with >95% selectivity, whereas $[\text{Rh}_4(\text{CO})_{12}]$ -derived catalysts supported on more acidic metal oxides such as $\gamma\text{-Al}_2\text{O}_3$ and SiO₂ produced chiefly methane with only traces of oxygenated products being formed (2). Only limited data is currently available relating these differences in catalytic performance to differences in catalyst structure (3). However, it was recently demonstrated that under high-temperature CO hydrogenation conditions (275°C, 10 atm) anionic osmium carbonyl clusters (e.g., $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$) are formed on MgO from adsorbed $[\text{H}_2\text{Os}(\text{CO})_4]$ (4). This finding is in contrast to the cluster fragmentation and Os(II) subcarbonyl formation observed under similar conditions for osmium clusters adsorbed on $\gamma\text{-Al}_2\text{O}_3$ and SiO₂ (5); the nature of the support dictates the surface organometallic chemistry.

Here we present the results of an investigation confirming the presence of $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ on the surfaces of conventional MgO-supported CO hydrogenation catalysts prepared by aqueous impregnation with $[\text{H}_2\text{OsCl}_6]$ (6). The carbido carbonyl cluster is synthesized in high yield from Os(IV) on MgO exposed to CO hydrogenation conditions.

EXPERIMENTAL

The MgO support (MX-65-1 powder, MCB reagents) was contacted with an aqueous solution of $[\text{H}_2\text{OsCl}_6]$ having sufficient volume (~2 ml/g) to yield a heavy paste. The material was dried at 70°C in vacuum, and the resultant light-blue powder was analyzed by X-ray fluorescence (XRF) spectroscopy and found to contain 1.3 wt % Os.

Samples (0.30 g) of MgO impregnated with $[\text{H}_2\text{OsCl}_6]$ were treated with H₂ or a H₂ + CO mixture in a tubular flow reactor. The samples were thoroughly dried by pretreatment in flowing He for 1 h at 150°C. Conventional Os/MgO catalysts (7) resulted from reduction with H₂ at 275°C and 1 atm for 10 h. These catalysts were subsequently exposed *in-situ* to H₂ + CO (equimolar) at 275°C and 1 or 10 atm for 8 h. A sample of $[\text{H}_2\text{OsCl}_6]$ and MgO was treated directly with H₂ + CO (equimolar) at 275°C and 1 atm for 5 h. In each case the sealed reactor tube was unloaded in a dry box. The H₂-reduced materials were metallic gray after exposure to CO hydrogenation conditions; the sample exposed directly to H₂ + CO was reddish-pink. The gases employed were Matheson UHP grade and were further purified by passage over activated 5A molecular sieve and supported Cu₂O (H₂ and He only).

$[\text{Et}_4\text{N}]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$ was synthesized following the procedure of Hayward and Shapley (8). The metal cluster was adsorbed on MgO (pretreated in vacuum at 400°C) from dry tetrahydrofuran (THF) solution. The resultant reddish-pink solid was recovered by filtration, washed with fresh THF, and dried in flowing nitrogen.

Acetone solutions of $[\text{PPN}][\text{Cl}]$ ($\text{PPN}^+ = \text{N}(\text{PPh}_3)_2^+$) were used to extract $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ from the catalyst surfaces by ion exchange. $[\text{PPN}]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$ in the extract solutions was detected by infrared spectroscopy.

Infrared spectra were obtained with a Nicolet 7199 Fourier transform spectrometer. Powders were pressed, forming self-supporting wafers which were loaded (without exposure to air) into a leak-tight glass cell fitted with NaCl windows. The thermostated cell could be connected to a manifold for evacuation or gas treatments.

Ultraviolet-visible spectra of powders under N_2 were recorded with a Cary 219 spectrophotometer equipped with a diffuse reflectance attachment.

Extended X-ray absorption fine structure (EXAFS) measurements were conducted at the Cornell High Energy Synchrotron Source (CHESS). $[Os_{10}C(CO)_{24}]^{2-}/MgO$ formed by the $H_2 + CO$ reduction of Os(IV) on MgO and a sample of $[Et_4N]_2[Os_{10}C(CO)_{24}]$ and MgO were examined.

RESULTS AND DISCUSSION

In the presence of CO or an equimolar mixture of $H_2 + CO$ at 275°C and 1 atm, Os(IV) on MgO is reduced and carbonylated to yield $[Os_{10}C(CO)_{24}]^{2-}$ ionically bound to the MgO surface. The formation of $[Os_{10}C(CO)_{24}]^{2-}$ under these conditions has been confirmed by IR, UV-Vis, and EXAFS spectroscopies, in addition to the isolation of $[PPN]_2[Os_{10}C(CO)_{24}]$ from the surface by cation metathesis with $[PPN][Cl]$ in acetone.

Treatment of MgO impregnated with $[H_2OsCl_6]$ in $H_2 + CO$ (equimolar) at 275°C and 1 atm for 5 h in a flow reactor, resulted in a change in color of the solid from light blue to reddish pink, indicative of the formation of $[Os_{10}C(CO)_{24}]^{2-}$. The UV-Vis diffuse reflectance spectrum (200-800 nm) of the product is in excellent agreement with that of $[Et_4N]_2[Os_{10}C(CO)_{24}]$ deposited on MgO from THF. Extraction of a portion of the material with $[PPN][Cl]$ in acetone resulted in a white solid and a brownish-red solution. The infrared spectrum of the solution contains only strong bands assigned to $[PPN]_2[Os_{10}C(CO)_{24}]$ (Table 1).

The synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ on the MgO surface was also monitored by in-situ infrared spectroscopy. Slowly heating a wafer of $[H_2OsCl_6]$ and MgO to 275°C in flowing $H_2 + CO$ at atmospheric pressure, first produced Os(II) subcarbonyls ($\nu_{CO} = 2105(m), 2030(s), 1936(s) \text{ cm}^{-1}$) on MgO (9). However, near 275°C there was a dramatic increase in absorption in the carbonyl stretching region, and after 1.5 h under these conditions strong bands assigned to $[Os_{10}C(CO)_{24}]^{2-}/MgO$ (Table 1) were present. A similar experiment conducted using pure CO instead of $H_2 + CO$ also resulted in the formation of the carbido carbonyl cluster in high yield.

TABLE 1

Molecular Cluster	$\nu_{CO} \text{ (cm}^{-1}\text{)}$	Ref.
$[PPN]_2[Os_{10}C(CO)_{24}]$	2034(s), 1992(s) (acetone)	(8)
$[Et_4N]_2[Os_{10}C(CO)_{24}]$ and MgO	2079(vw), 2062(w), 2030(s), 1998(sh), 1986(sh), 1975(vs), 1966(sh)	This work
$[Os_{10}C(CO)_{24}]^{2-}$ from Os(IV) on MgO	2104(vw), 2080(w), 2040(s), 1998(sh) 1989(s), 1979(sh), 1963(sh)	This work

Confirmation of the identity of the surface species was obtained from EXAFS spectroscopy. The reduction and carbonylation were again effected in-situ and comparison made to the spectrum of $[Et_4N]_2[Os_{10}C(CO)_{24}]$ deposited on MgO. Close agreement was found for the EXAFS oscillations above the Os L_{III} edge over the range of the wavevector from $k = 3$ to 12 \AA^{-1} . A final structure determination awaits detailed analysis of the data.

Even reduction of MgO impregnated with $[H_2OsCl_6]$ with H_2 to yield supported Os aggregates (7) did not completely inhibit the formation of $[Os_{10}C(CO)_{24}]^{2-}$. The highly stable molecular cluster was isolated in low yields by ion exchange of H_2 -reduced samples exposed to $H_2 + CO$ at 275°C and 1 or 10 atm for 8 h. The presence of the cluster in the lightly colored extract solutions was confirmed by infrared spectroscopy. In addition, Deeba *et al.* have reported that MgO-supported catalysts derived from the decomposition of adsorbed $Os_3(CO)_{12}$ gave evidence for the presence of molecular clusters following use in CO hydrogenation to produce C_1 - C_4 hydrocarbons at 300°C and 7 atm (10). Comparing the infrared data reported for their used catalysts ($\nu_{CO} = 2080(m), 2048(sh), 2039(s), 2010(sh), 1986(vs), 1950(sh) cm^{-1}$), with those of $[Os_{10}C(CO)_{24}]^{2-}/MgO$, we infer that this molecular cluster was formed on these catalysts as well.

In summary, $[Os_{10}C(CO)_{24}]^{2-}$ represents an extremely stable molecular structure on the surfaces of Os/MgO CO hydrogenation catalysts. The basicity of the MgO support appears to be essential; analogous structures do not form on the more acidic $\gamma-Al_2O_3$ and SiO_2 surfaces (4), and the surface-mediated synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ parallels the syntheses of high-nuclearity Group VIII - metal clusters in basic solution (11). What direct role this metal cluster has in the catalysis remains to be elucidated.

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