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In situ synthesis of $[HRu_3(CO)_{11}]^-$ on the surface of hydroxylated aluminum oxide

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Abstract

The in situ synthesis of supported $[HRu_3(CO)_{11}]^-$ on hydroxylated aluminum oxide from a mononuclear precursor is demonstrated. It is shown by infrared spectroscopy, reaction stoichiometry, and analysis of extracted products that adsorption of $Ru(CO)_3Cl_2(THF)$ onto CATAPAL SB alumina gives initially $Ru^{II}(CO)_3$(ads) which reacts further with CO to give the supported cluster anion, $[HRu_3(CO)_{11}]^-$(ads), rapidly at 25 °C.

Introduction

Metal carbonyls supported on metal oxides have been shown to be catalytically active for a wide range of reactions and to be precursors to highly dispersed metal particles. For these reasons the chemistry during the adsorption of metal carbonyls onto refractory supports has received a great deal of attention in the chemical literature [1–6]. Many of the fundamental transformations of metal carbonyls on oxide surfaces are now recognized [6] but specific synthetic pathways on surfaces are often difficult to design. Here we show that the adsorption of $Ru(CO)_3Cl_2(THF)$ onto hydroxylated alumina yields a mononuclear fragment on the surface which may be transformed quantitatively, as determined by infrared spectroscopy, into a trinuclear species under very mild conditions.

Supported ruthenium carbonyls are reported to yield active catalysts for the reduction of CO and CO_2 when supported on aluminum oxide [3–5]. Depending on the reaction conditions the adsorption of $Ru_3(CO)_{12}$ onto the surface of metal oxides yields the cluster anion, $[HRu_3(CO)_{11}]^-$ (ads) [3,4] ruthenium(II) fragments [4,7,8], $HRu_3(CO)_{11}(Ox)$(ads) [8], or ruthenium carbides [5b,9]. The direct adsorption of $[HRu_3(CO)_{11}]^-$ on metal oxides has been shown to yield an active catalyst for the reduction of CO with enhanced selectivity towards olefins [10]. It is well know that supported rhodium [11] carbonyl clusters may be easily generated from mononuclear precursors. Recently a similar cluster formation reaction has been

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demonstrated for ruthenium at high pressures when a conventional ruthenium catalyst prepared from $RuCl_3$ on MgO is treated at high temperature [12]. When osmium carbonyl chlorides are adsorbed onto magnesium oxide it is suggested that MgO may act as a halide acceptor so that $Os^{II}(CO)_3(ads)$ is formed on the surface. The tricarbonyl fragments however are not observed to form supported clusters even at high temperatures under carbon monoxide [13]. When $H_2Os(CO)_4$ is the osmium carbonyl precursor cluster anions are formed on magnesia [14].

Experimental

The adsorption of $Ru_2(CO)_6Cl_4$ onto hydroxylated alumina was investigated by two different methods. The first was a batch reaction so that extraction of surface species could be performed and evolved gases could be quantitated. The second method was to perform the adsorption on a pressed pellet of alumina so that the reaction could be monitored by in situ infrared spectroscopy without exposure of the sample to air. All experiments were conducted under an atmosphere of either helium (99.999%) or carbon monoxide (99.99%) which had been passed over MnO on SiO_2. The helium flow system used to conduct the batch reactions and the in situ infrared cell have been described previously [15–17]. The aluminium oxide used was CATAPAL SB and was treated as previously described to generate a hydroxylated surface [15].

A typical batch experiment was performed in the following manner. A solution containing approximately 1 mg $Ru_2(CO)_6Cl_4$ in 5 ml of freshly distilled THF was added via syringe to 200 mg of hydroxylated alumina under an atmosphere of helium. In THF solution the dimer is well known to form $Ru(CO)_3Cl_2(THF)$ quantitatively [18]. Helium or carbon monoxide was passed over the support to evaporate the solvent to yield a 0.2% weight loading of metal. At this concentration the hydroxylated alumina completely extracted the ruthenium complex from solution. Attempts to generate higher metal loadings resulted in incomplete removal of the ruthenium complex from solution. Metal loadings were determined by direct current plasma emission spectrometry of selected samples of the prepared materials.

The in situ IR experiments were performed on self supporting aluminum oxide pellets pressed from 20 mg Al_2O_3 at 10.34×10^3 kPa for 5 minutes. These were heated to 100 °C to give a hydroxylated surface. Immersion of the pellet into a 0.01 *M* THF solution of $Ru(CO)_3Cl_2(THF)$ yields the initially adsorbed $Ru(CO)_3Cl_2(THF)$.

Results and discussion

The complex $Ru(CO)_3Cl_2(THF)$ is spontaneously extracted onto hydroxylated alumina from THF solution. During the adsorption less than 0.08 equivalent of CO per equivalent ruthenium is evolved. No additional CO evolution is observed over a 3 h period following adsorption. Attempts to extract the surface species with [PPN]Cl in CH_2Cl_2 does not yield any soluble ruthenium complexes. Thus there are neither weakly adsorbed anionic species or physically adsorbed compounds on the surface. Blank experiments with THF on alumina yield similar quantities of CO thus the adsorption of $Ru(CO)_3Cl_2(THF)$ does not involve loss of CO.

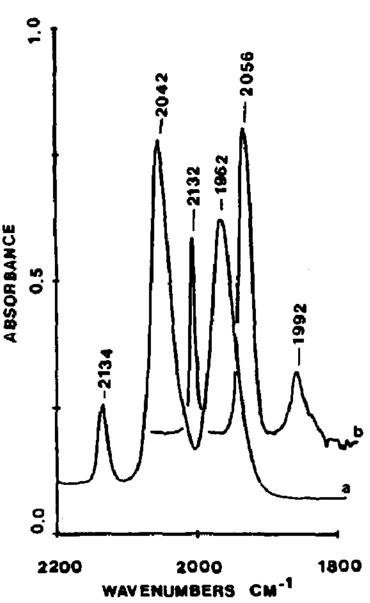

Fig. 1. (a) In situ infrared spectrum of $Ru_2(CO)_6Cl_4$ adsorbed onto hydroxylated alumina. The spectrum remained constant over a 7 h period. (b) Solution infrared spectrum of $Ru_2(CO)_6Cl_4$ in tetrahydrofuran. This spectrum is offset from trace la so that the peak positions can be identified more clearly.

In Fig. 1, trace a shows the in situ infrared spectrum following adsorption of $Ru(CO)_3Cl_2(THF)$ onto hydroxylated alumina. The spectrum shown is that obtained immediately after adsorption; no changes are observed in this spectrum over a 7 h period. Trace b of Fig. 1 shows the infrared spectrum of $Ru(CO)_3Cl_2(THF)$. The bands in the spectrum of the adsorbed species are shifted up to 30 cm^{-1} from the spectrum of $Ru(CO)_3Cl_2(THF)$. Three bands are seen for both species but with different relative intensities. The observation of very little CO evolution during the adsorption process is consistent with retention of a tricarbonyl species on the surface. Furthermore the spontaneous removal of the ruthenium carbonyl chloride from solution implies replacement of either chloride or THF by the surface. Tetrahydrofuran is the better leaving group, thus one possible assignment for the surface species is "$Ru(CO)_3Cl_2(Ox)$", where Ox represents either surface oxide or a hydroxyl group. The small differences in the infrared spectra of $Ru(CO)_3Cl_2(THF)$ and the adsorbed species indicate some structural changes on the surface which may be consistent with the formation of "$Ru^{II}(CO)_3(Ox)_3$". Although the reactivity of the adsorbed species support this assignment (vide infra), a definitive structural assignment to the initially adsorbed species cannot be made. It has been proposed in the literature [8] that a similar species may be formed on SiO_2 from $[Ru(CO)_3Cl_2]_2$; however in that case the infrared spectrum of the adsorbed species is more complex than observed here.

When the adsorption onto hydroxylated alumina is performed under an atmosphere of carbon monoxide or when the surface complex generated above is placed under an atmosphere of carbon monoxide a new reaction takes place. Figure 2 shows the infrared spectra obtained in situ during the adsorption of $Ru(CO)_3Cl_2(THF)$ onto hydroxylated alumina under CO as a function of time. The first spectrum, trace a, represents the sample immediately after adsorption. Initially

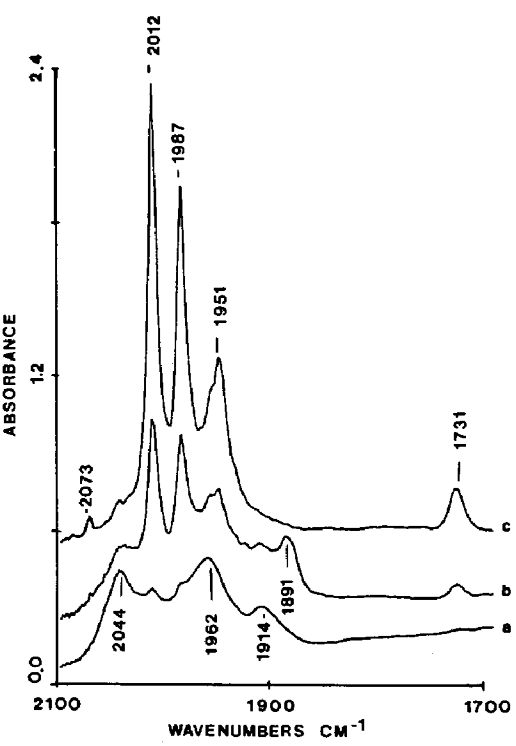

Fig. 2. In situ infrared spectra of $Ru_2(CO)_6Cl_4$ adsorbed onto hydroxylated alumina under an atmosphere of carbon monoxide. The gas phase spectrum of CO has been subtracted from the spectra shown. Trace a, *t* 30 s after adsorption of the ruthenium carbonyl. Trace b, *t* 7 min after adsorption. Trace c, *t* 30 min after adsorption. No further changes were observed in the infrared spectrum after 30 min.

the surface species is "$Ru^{II}(CO)_3(Ox)_3$" which is identified by its major bands at 2044, and 1962 cm^{-1}; with time new bands at 2010, 1998, and 1953 cm^{-1} increase in intensity as the bands due to "$Ru^{II}(CO)_3(Ox)_3$" decrease in intensity. After 30 minutes the bands corresponding to the starting material, ie 2044, and 1962 cm^{-1}, have completely disappeared and major bands at 2010, 1989, 1952, and 1732 cm^{-1} are seen. This spectrum is assigned to $HRu_3(CO)_{11}^-$(ads). The bands for the surface anion generated from the ruthenium carbonyl chloride correspond well to those reported for $[HRu_3(CO)_{11}]^-$ with PPN^+ or NEt_4^+ cations in THF [19]. In solution the position of the bridging carbonyl band is very sensitive to the nature of the cation [19]. The spectra shown by Darensbourg for the supported cluster anion are significantly different than observed here. A well defined bridging carbonyl is not seen by Darensbourg [3] or others [4,9] for $Ru_3(CO)_{12}$ on aluminum oxide. However it should be noted that the solvent used in our work, namely THF, interacts strongly with alumina surfaces and may poison Lewis acid sites. This would prevent any bridging carbonyl from forming a Lewis base–Lewis acid adduct [20] on the surface. Thus when synthesized in the presence of THF on the surface the bridging carbonyl band of $[HRu_3(CO)_{11}]^-$ is readily seen while in the absence of a coordinating solvent the bridging carbonyl band may be shifted to a lower wavenumber. This suggests that $[HRu_3(CO)_{11}]^-$(ads) as synthesized above is only weakly adsorbed.

When $[HRu_3(CO)_{11}]^-$ is generated on the surface from $Ru(CO)_3Cl_2(THF)$ under batch conditions, it is easily extracted from the surface as its PPN^+ salt in CH_2Cl_2.

The extracted cluster anion is identified as $(PPN)[HRu_3(CO)_{11}]$ by infrared spectroscopy and comparison with an authentic sample. Analysis of the support following extraction shows 10% of the total ruthenium remaining on the alumina. Thus the extraction is nearly quantitative. The extraction can be made more quantitative by using the binary solvent system THF/CH_2Cl_2 plus [PPN]Cl. Under these conditions no ruthenium is detected on the alumina following extractions.

It is apparent from the ease of this synthesis that the surface enhances the formation of the cluster anion. The synthesis of ruthenium clusters from carbonyl chloride precursors in solution requires the presence of a chloride acceptor and a reducing agent [21]. At high pressures carbon monoxide serves this role while at low pressure zinc must be used. The probable role of the alumina in the surface reaction is to serve as the chloride acceptor while CO is the only reducing agent available. As noted earlier it has previously been observed that MgO may act as a chloride acceptor during the adsorption of $[Os(CO)_3Cl_2]_2$ [13]. Further evidence for the halide acceptor role of the surface is obtained from a comparison of the reactivity of $Ru(CO)_3Cl_2(THF)$, in solution and adsorbed onto the surface toward $[Co(CO)_4]^-$. In THF solution the cobalt-ruthenium cluster anion, $[RuCo_3(CO)_{12}]^-$, is formed in high yield [22*] while on hydroxylated alumina there is no reaction between the adsorbed ruthenium tricarbonyl and $[Co(CO)_4]^-$. This implies that the surface hydroxyl groups are poor leaving groups for bimetallic cluster synthesis. Work in progress shows that the bimetallic cluster synthesis does proceed on faujasitic zeolites [23].

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