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LETTERS

Intercalation of a Rhodium Carbonyl into the Layered Vanadyl Phosphate $VOPO_4 \cdot 2H_2O$ and Its Catalytic Activity

Arunabha Datta,* Sumit Bhaduri,* Ravindra Y. Kelkar, and Hanif I. Khwaja

Alchemie Research Centre, P.O. Box 155, Thane-Belapur Road, Thane-400 601, Maharashtra, India

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Evidence for the intercalation of a rhodium carbonyl into the layered vanadyl phosphate, $VOPO_4 \cdot 2H_2O$ has been provided from XRD, FTIR, and XPS studies. The incorporated rhodium carbonyl has been found to exhibit catalytic activity and shape selectivity in the hydrogenation of olefinic substrates.

Introduction

Transition metal carbonyls have been supported on various different substrates with the aim of using these discrete molecular metal complexes as tailored metal catalysts. In the past, metal carbonyls have been grafted primarily on oxide surfaces such as alumina, titania, magnesia, and silica, and it has been shown that the starting cluster on interaction with the support may either maintain the original skeleton or aggregate or fragment, perhaps oxidatively.[1] In the more recent past, however, there has been an increasing trend toward anchoring of metal carbonyls on zeolite frameworks[2] since these species exhibit unique catalytic properties in CO hydrogenation based on molecular shape selectivity.

Another potential host for metal carbonyls, which has not yet been explored, is the layered vanadyl phosphates. These compounds are attractive potential hosts both because they themselves are important catalysts[3] and also because they have V═O moieties protruding into the interlayer region which could be expected to be the most likely site for the anchoring of the metal carbonyl. In other words, a vanadyl phosphate host would not only provide an oxidic surface for the carbonyls to anchor on but would also, like the zeolites, keep them confined, in this case, within a specific interlayer spacing. In this context we have recently shown that metal ions incorporated in different ways into a layered vanadyl phosphate not only induce novel structural changes in the host lattice but also exhibit interesting catalytic activity and selectivity.[4].

In the present work therefore we report the first example, to the best of our knowledge, of a metal carbonyl intercalated into a layered vanadium phosphate, and we demonstrate that the incorporated metal carbonyl is catalytically active and exibits shape selectivity for olefin hydrogenation reactions. A rhodium chlorocarbonyl, $Rh_2(CO)_4Cl_2$, was chosen because oxide-supported rhodium is one of the most intriguing heterogeneous catalysts with its ability to catalyze olefin hydrogenation and the conversion of synthesis gas to methanol, higher oxygenates, and hydrocarbons.[5] At the same time, although the intercalation chemistry of the vanadium phosphate $VOPO_4 \cdot 2H_2O$ has been fairly well studied with metal ions and organic molecules having been intercalated,[6] there is no report on the intercalation of a metal carbonyl into this layered compound.

Experimental Section

The vanadium phosphate[7] $VOPO_4 \cdot 2H_2O$ and the rhodium chlorocarbonyl[8] $Rh_2(CO)_4Cl_2$ were prepared by published methods. For the intercalation reaction, 1 g of $VOPO_4 \cdot 2H_2O$ and 50 mg of $Rh_2(CO)_4Cl_2$ in 50 mL of THF were stirred under argon at ambient conditions for 12 days. The solution was then filtered, and the solid was washed repeatedly with THF and hexane and then dried to give a dark green solid coded as **1**.

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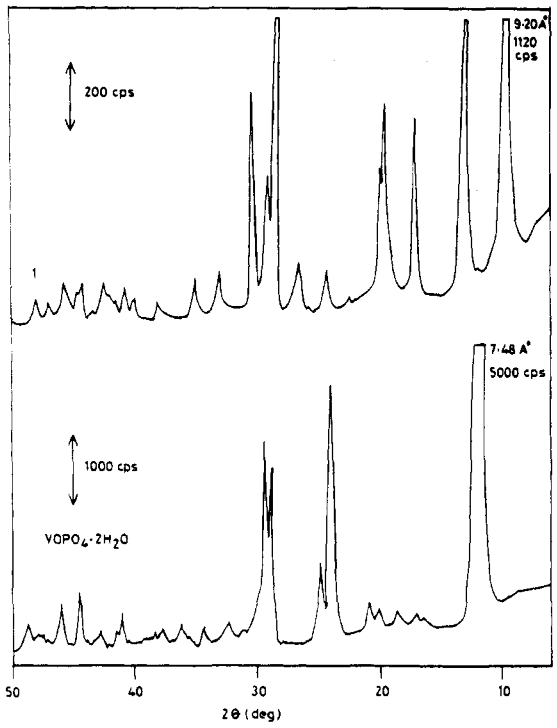

Figure 1. XRD patterns of $VOPO_4{\cdot}2H_2O$ and **1**.

Analysis by atomic absorption spectroscopy showed that **1** contained 0.95% rhodium. For all the catalytic experiments, 10 mg of **1** was magnetically stirred with the olefinic substrate (the substrate:rhodium mole ratio was 300:1) in 20 mL of THF under an atmosphere of hydrogen at 23 °C. Samples taken at regular intervals were analyzed by gas chromatography for conversion and selectivity data. Experiments with Rh/C catalyst were carried out under identical conditions with the same rhodium-to-substrate mole ratio.

The XRD patterns were recorded on a Philips X-ray diffractometer using Cu Kα radiation. The FTIR spectra were recorded on a Nicolet Model 710 spectrometer using an AABSPEC Model 200 multimode FTIR cell for in situ heating of the sample. The sample was heated in a nitrogen atmosphere, at the rate of 10 °C/min, and was maintained at each specified temperature for 30 min. The XPS spectra were recorded on a VG Scientific ESCA-3-MK-2 spectrometer.

Results and Discussion

XRD. It is evident from the XRD patterns (Figure 1) of the parent vanadyl phosphate and the rhodium carbonyl incorporated compound (**1**) that there is an expansion of the interlayer spacing from 7.4 Å in the parent compound to 9.20 Å° in **1**. This is indicative of the incorporation of rhodium carbonyl rather than the metal ion into the interlayer of $VOPO_4{\cdot}2H_2O$ since the presence of metal ions in the interlayer region would have led to a reduction ion the basal spacing.[6d] Also, it is apparent from the drastic reduction in the intensity of the (001) reflection in **1**, compared to the parent compound, that intercalation of rhodium carbonyl leads to a reduction in the interlayer long-range order.

FTIR. The FTIR specrum (Figure 2) of **1** at room temperature shows a broad band with two distinct components centred at 2098 and 2107 cm^{-1}. However, rather surprisingly there are no other bands in the 2060–2000 cm^{-1} region as has been observed in the case of rhodium carbonyls bound to oxide surfaces.[9] On heating to 100 °C and subsequently to 150 °C, the intensity of the 2098 cm^{-1} band is selectively reduced, and it is only on heating to 200 °C that a substantial reduction in the intensity of the 2107 cm^{-1} band is observed. On further heating to 300 °C both the bands disappear almost completely.

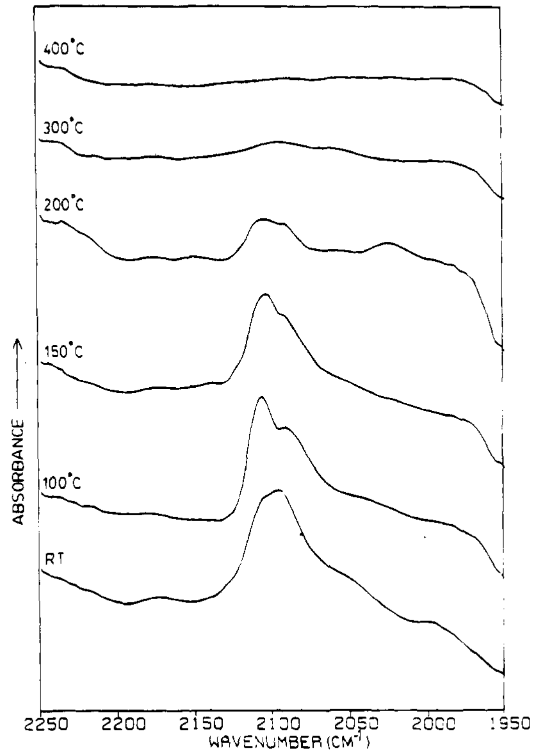

Figure 2. FTIR spectra (CO stretching region) of **1** on heating to different temperatures.

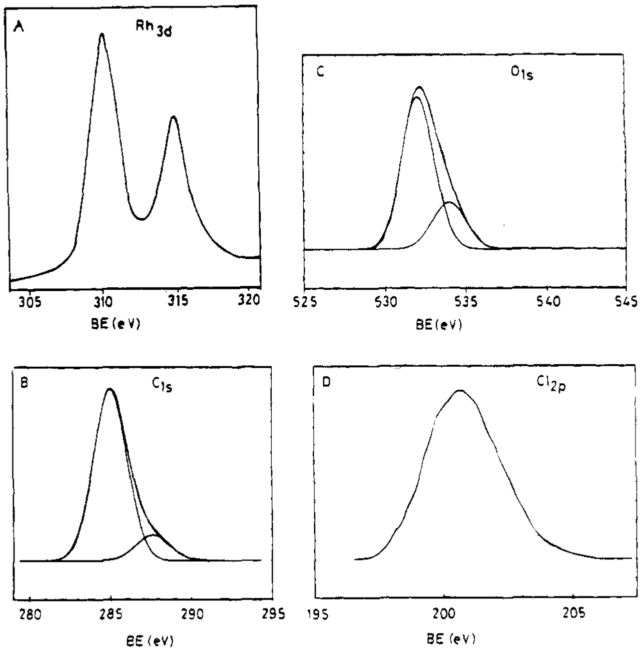

Figure 3. XPS spectra of **1**: (A) Rh_{3d} region, (B) C_{1s} region, (C) O_{1s} region, and (D) Cl_{2p} region.

The position of the two bands is indicative of a Rh(I), rather than a Rh(III), carbonyl species, since in the latter case an absorption at a higher frequency of around 2135 cm^{-1} would be expected.[10] At the same time, the observation of two bands separated by only 9 cm^{-1} with different desorption temperatures suggests the presence of two different carbonyl species in the intercalated compound.

XPS. The XPS (Figure 3) of **1** shows that the binding energy (BE) of the $3d_{5/2}$ state of the intercalated rhodium is 310.3 ±0.2

eV. Although the BE is in the region of Rh(III) compounds, it is known[11] that Rh(I) carbonysl with a formal oxidation state of +1 have a Rh $3d_{5/2}$ BE of around 309.7, which in certain cases could even be as high as 310.2 eV. This is because the σ donation from the 5σ MO of CO to the metal is offset by the π back-bonding from the metal back into the CO $2\pi^*$ MO of the CO, resulting in a net charge transfer away from the metal. Consequently, in the present case, in conjunction with infrared data, the intercalated species can be assumed to be a Rh(I) carbonyl. In addition, the higher BE would also indicate strong interaction between the rhodium and the VPO framework, causing a drain of electrons away from the rhodium and leaving it more positively charged. In the C_{1s} spectrum (Figure 3B), the peak at 287.8 eV is in the region of the C_{1s} BE of a terminal carbonyl group[11] while the major peak at 285.0 eV is the C_{1s} BE of the contaminant hydrocarbon to which all the other BE's have been referenced. In the O_{1s} spectrum (Figure 3C), the peak at 534.1 eV is once again due to the oxygen of a terminal carbonyl group[11] while the major peak at 532.0 eV is due to the oxygen of the parent $VOPO_4 \cdot 2H_2O$. In addition, a broad (fwhm = 3.2 eV) unresolved peak (Figure 3D) centered at 200.7 eV due to chloride was observed in the XPS spectrum. In rhodium chlorocarbonyl, the chloride peak appears as a doublet[11] in the XPS spectrum with a spin−orbit splitting of 1.6 eV and a $2p_{3/2}$:$2p_{1/2}$ ratio of 1.8. In the present case, therefore, the broad unresolved peak in the XPS spectrum is indicative of the presence of more than one type of chloride species. This is in agreement with the observation of infrared bands due to two different carbonyl species.

Catalytic Activity. The catalytic activity and selectivity of **1** for olefin hydrogenation reactions have been studied and compared with that of a conventional rhodium (5%) on carbon catalyst. Under identical conditions, with 2-cyclohexen-1-one as the substrate, the catalytic activity of Rh/C is about 5 times that of **1**. The turnover numbers under these conditions are 0.1 and 0.02 s^{-1}, respectively. To explore the comparative selectivities, both of these catalysts have been tested for the hydrogenation of α,β-unsaturated cyclic ketones differing mainly in steric bulk. Hydrogenation of the carbon oxygen double bond was not observed in any of the cases. However, the size and shape of the olefinic substrate have observable effects on the rates of hydrogenation for both the catalysts with the effect being clearly far more pronounced in the case of **1** than in the case of the conventional Rh/C catalyst. Thus, with **1** as the catalyst, the ratio of initial rates of hydrogenation of 2-cyclohexen-1-one and 3-methyl-2-cyclohexen-1-one is 10:1, whereas under identical conditions with Rh/C as catalyst the ratio is 4:1. Furthermore, while **1** does not catalyze the hydrogenation of 3,5-dimethyl-2-cyclohexen-1-one *at all*, Rh/C shows only a slightly reduced rate. With the latter catalyst the ratio of the initial rates for 2-cyclohex-en-1-one and 3,5-dimethyl-2-cyclohexen-1-one is 6:1. For all the catalytic reactions, a blank experiment using only the parent compound $VOPO_4 \cdot 2H_2O$ was done, and no hydrogenation activity was observed in any of the cases.

The infrared spectra of the samples recorded after the catalytic experiments did not show any of the ν_{CO} bands at 2107 and 2098 cm^{-1}. It would appear therefore that the active catalyst is a decarbonylated rhodium species, indicating decomposition of the intercalated carbonyl species during the catalytic reaction. The observed shape selectivity in the case of the intercalated compound compared to Rh/C is therefore most likely due to the active rhodium species being confined within the layers of the parent vanadyl phosphate. This is interesting because steric effects leading to high selectivity are well documented in homogeneous catalysis,[12] but its occurrence in heterogeneous catalysis is confined mainly to zeolites.[1,13] It is, however, evident from our studies that intercalated layered materials can also exhibit some of the characteristics of a shape-selective catalyst.

Conclusions

It is shown in the present work that a rhodium carbonyl can be intercalated into the layered vanadyl phosphate without the rhodium species getting oxidized by the V^{5+} centers present in the parent compound. The incorporated species appears to be different from those anchored on oxides or zeolites. Also, the catalytic activity and shape selectivity exhibited by the rhodium carbonyl species intercalated into a host compound with oxidation centers raises the very attractive possibility of such intercalated carbonyl species acting as novel catalysts.

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