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Group 6 hexacarbonyls supported on alumina: temperature-programmed decomposition and reduction

M. Kurhinen, S. Myllyoja, M. Suvanto, T.A. Pakkanen *

Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland

Abstract

Group 6 hexacarbonyls were supported on aluminas pretreated at three different temperatures. The degree of dehydroxylation was found to affect the temperature-programmed decomposition (TPDE) profile of $Mo(CO)_6$ more than those of $Cr(CO)_6$ and $W(CO)_6$. Different reducible chromium surface species on alumina 500 were suggested: Two reduction maxima appeared when the sample was heated to 200°C and oxidised with pulse chemisorption of oxygen prior to reduction. After heating to 500°C only one broad reduction maximum appeared. Partially oxidised molybdenum on alumina 500 gave a temperature-programmed reduction (TPR) maximum at about 365°C, independent of the decarbonylation conditions. Successive reduction–oxidation cycles showed the irreversibility of partially oxidised molybdenum. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: $Cr(CO)_6$; $Mo(CO)_6$; $W(CO)_6$; Alumina; TPDE; TPR

1. Introduction

Supported group 6 hexacarbonyls are active in disproportionation of olefins [1,2], metathesis [3], hydrogenation [4], Fischer–Tropsch synthesis [5] and in the hydrogenolysis of alkanes [6]. They have also been studied as precursors for hydrodesulphurisation (HDS) catalysts [7–10]. The interaction of $M(CO)_6$ (M = Cr, Mo, W) with the surface of alumina has been studied intensively and various surface species have

been characterised. Temperature-programmed decomposition of $Mo(CO)_6$ and $W(CO)_6$ supported on standard alumina (pretreated at 500°C) shows two temperature maxima indicating decarbonylation in two steps [11–15]. During the first step, three CO ligands are lost and $M(CO)_3(ads)$ species are formed [14]. The last three remaining ligands are removed during further heating. Alumina-supported $Cr(CO)_6$ behaves in a different way, showing only one temperature maximum with a shoulder at a higher temperature [11].

The samples studied here were prepared in a fluidised bed reactor by gas-phase adsorption; the preparation conditions differ from earlier temperature-programmed decomposition (TPDE) studies [11–15]. The aim of this work

* Corresponding author. Tel.: +358-13-2513345; telefax +358-13-2513344.
E-mail address: tapani.pakkanen@joensuu.fi (T.A. Pakkanen).

was to study the decomposition of group 6 hexacarbonyls on aluminas pretreated at three different temperatures to determine the role of the degree of dehydroxylation of the support. A second objective was to study the reducibility of the supported metal and the effect of different pretreatments on reduction. Brenner and Hucul have studied the gaseous products formed during heating under H_2 flow [13], but in the present work we focused on the uptake of hydrogen by the supported metals.

2. Experimental

$Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ were supplied by Aldrich Chemical and used without further purification. γ-Alumina (Brockmann I, standard grade, ∼ 150 mesh, 58 Å, surface area 155 m^2/g, Aldrich) provided the support, and was calcined (about 70 g) at 200°C and 500°C for 10 h under vacuum ($\sim 1.2 \times 10^{-2}$ Torr) and at 800°C for 10 h in air followed by cooling to 500°C in air and further cooling to ambient under vacuum ($\sim 1.2 \times 10^{-2}$ Torr). The pretreated alumina is referred to later in the text as alumina 200, 500 and 800. The calcined supports were stored and packed in a fluidised bed reactor in a glovebox (purity of nitrogen 99.999%). The BET surface areas, measured with ASAP 2010 at liquid nitrogen temperature, and the numbers of OH groups per square nanometer, determined by elemental analysis, are presented in Table 1.

The samples were prepared in a fluidised bed reactor (upper diameter 3.7 cm, lower diameter 1.2 cm, length ∼ 7 cm) by gas-phase adsorption. $M(CO)_6$ (M = Cr, Mo or W) was deposited on alumina at 75°C for 1 h under nitrogen (AGA, 99.999%) flow. The metal contents are presented in Table 1. The carrier gas was circulated via a cold trap at a flow rate of 450–500 ml/min depending on the amount of the sample (5–10 g). Pure gas was added at a flow rate of 30 ml/min, and the normal pressure was retained with a pressure-release mercury bubbler. The $M(CO)_6$/alumina samples were flushed with nitrogen overnight at room temperature in the fluidised bed reactor to remove excess physisorbed species.

TPDE and temperature-programmed reduction (TPR), and the pulse chemisorption of oxygen ($PC(O_2)$) were carried out with a Micromeritics AutoChem 2910 analyser equipped with a thermal conductive detector (TCD). The samples (0.5–0.9 g) were packed in a U-shaped quartz tube in a glovebox, and the sealed tube was attached to the analyser under inert gas flush, the entire treatment carried out in the absence of air.

In TPDE (under helium, purity 99.9999%) and TPR (10%H_2/Ar), the samples were heated to the calcination temperature of the support at a rate of 10 K/min. Oxidations of the samples were carried out by pulse chemisorption of O_2 (purity 99.9999%) at 200°C. The following sequences were used to determine the effects of various pretreatments of the samples on the reducibility of the studied metal.

(i) TPDE to the pretreatment temperature of the supports, PC of oxygen at 200°C, TPR to the pretreatment temperature of the supports,

Table 1
The properties of the supports, the metal loadings and the amount of $M(CO)_6$ per nm^{-2}

Support	BET (m^2/g)	OH/nm^2	$Cr(CO)_6$		$Mo(CO)_6$		$W(CO)_6$	
			wt.%[a]	nm^{-2}	wt.%[a]	nm^{-2}	wt.%[a]	nm^{-2}
Alumina 200	176	10	0.5	0.33	0.7	0.25	0.5	0.09
Alumina 500	187	5	0.9	0.56	1.1	0.37	0.7	0.12
Alumina 800	86	–	0.2	0.54	0.3	0.22	0.3	0.11

[a] The loadings are wt. % of metal.

(ii) PC of oxygen at 200°C, TPR to the pretreatment temperature of the supports. For some of the samples the sequences were continued with a second PC of oxygen at 200°C and a second TPR to the pretreatment temperature of the supports,

(iii) TPR to the pretreatment temperature of the supports, PC of oxygen at 200°C, TPR to the pretreatment temperature of the supports.

The approximate desorption energies for CO and H_2 have been calculated from the temperature maxima obtained from our TPDE profiles according to the Redhead Eq. (1). For a first-order reaction, the temperature maximum is assumed to be related to desorption energy. The E_d value can be approximated as [14,15]

$$E = RT_m \left[\ln(\nu T_m / \beta) - 3.46 \right] \qquad (1)$$

where R is the gas constant, T_m the temperature maximum (K), β the heating rate (K/s) and ν a pre-exponential factor; the value of ν ($\approx kT/h$) has been set at 10^{13} s^{-1}, as in the literature [14,15].

Fig. 1. TPDE profiles of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ on (a) alumina 200, (b) alumina 500 and (c) alumina 800.

3. Results and discussion

3.1. Temperature-programmed decomposition

The decomposition of supported hexacarbonyl compounds was carried out under He flow at a heating rate of 10 K/min. Samples on aluminas 500 and 800 decarbonylated totally during the TPDE, but on alumina 200 part of the CO ligands were left for molybdenum and tungsten carbonyls. A comparison of the TPDE profiles of the different metals on alumina 200 shows (Fig. 1a) that molybdenum loses the three first CO ligands at a lower temperature than tungsten. The T_{max} of chromium is slightly higher than that of tungsten, but this is presumed to be due to the total decarbonylation of $Cr(CO)_6$.

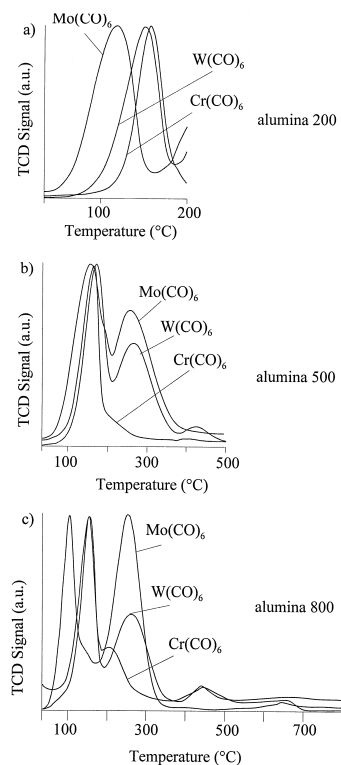When the support is more dehydroxylated, i.e., pretreated at 500°C, the differences in the TPDE profiles of $Mo(CO)_6$ and $W(CO)_6$ diminished. The decarbonylation of $Cr(CO)_6$ occurred in the same temperature region as the first maxima of molybdenum and tungsten. A third maximum was observed for $W(CO)_6$/alumina 500 at around 430°C. The OH groups of the surface oxidise the metal by a redox reaction at high temperature and thus no zero-valent metal species can be achieved [16]. The maximum at 430°C is suggested to be due to a release of hydrogen in accordance with the results of Brenner and Hucul [11]. For chromium, there is a slight change in the TPDE profile at about 405°C, and this could be due to liberated H_2. As these changes appeared after the total decarbonylation of $Cr(CO)_6$ and $W(CO)_6$, they could not be due to the formation of methane. The difference in the thermal conductivity of hydrogen and helium is much smaller than that of CO and He or CO_2 and He. Therefore, the liberation of CO or CO_2 easily disguises the changes

in the TCD signal due to hydrogen. On the other hand, the loading of the hexacarbonyl compounds was lowest for tungsten (0.7 wt.% corresponding to 0.12 tungsten/nm^2); thus, there was less CO to release and the changes due to the liberation of H_2 were clearer than for chromium (0.56 Cr/nm^2).

On alumina 800 the first T_{max} appeared at around 100°C for $Mo(CO)_6$ while for chromium and tungsten the temperature was about 150°C. The second maxima of molybdenum and tungsten were visible at about 255°C (Fig. 1c). There was also a second maximum for chromium at around 205°C. At higher temperatures small maximum for chromium and tungsten appeared at 450°C and at around 650°C for chromium and molybdenum. These weak maxima were proposed to be due to the liberation of H_2 by the oxidation of the metal. The first redox reaction between the carbonyl compound (molybdenum and tungsten) and the surface OH groups were found to occur at the same temperature as the decarbonylation of the last three CO ligands [11–13].

The pretreatment temperature of the support had only a small effect on the decomposition of $Cr(CO)_6$: the temperature maxima appeared at 151–164°C. Decomposition on alumina 800, however, revealed a second maximum. The temperature maxima of CO for supported tungsten hexacarbonyls varied slightly as a function of the degree of dehydroxylation of the alumina: 152–173°C. The pretreatment temperature of the support affected $Mo(CO)_6$ most, the temperature maxima varying from 102°C to 155°C. OH groups assisted the decarbonylation, which could be seen as the lowest T_{max} on alumina 200. The higher pretreatment temperature of the support, 800°C, reduced the T_{max} in comparison to alumina 500. The structure collapsed during the pretreatment of the support, which might have an effect on decarbonylation and thus the TPDE profiles.

Loh et al. have studied the decomposition of $Mo(CO)_6$ on alumina 500 and 800. They found that the loading of molybdenum on alumina 500 affects the TPDE profile. Low loading, 0.14 Mo/nm^2, gave a TPDE profile similar to ours, higher loadings (0.32 or 0.55 Mo/nm^{-2}) yielded profiles that are more complicated [15]. In addition, The TPDE profile of $Mo(CO)_6$/ alumina 800 differed from ours showing three maxima and one intense shoulder. The redox reaction released hydrogen in the same temperature range as in our study. The differences in this work and that of Loh et al. [15] may be due to the sample preparation.

The desorption energies of liberated CO ligands were calculated by the Redhead Eq. (1), and they are presented in Table 2. The E_d values of this work are close to those reported earlier [11]. The first maxima, however, showed a higher desorption energy and the second maxima of molybdenum and tungsten still lower ones when compared to the literature [11].

The desorption energies of hydrogen were about 210 kJ/mol for supported chromium and tungsten samples and about 270 kJ/mol for

Table 2

The temperature maxima (°C) of TPDE profiles and the desorption energies E_d^a for desorption of CO ligands of group 6 hexacarbonyls on alumina pretreated at different temperatures

Support	$Cr(CO)_6$		$Mo(CO)_6$		$W(CO)_6$	
	T_{max} (°C)	E_d (kJ/mol)	T_{max} (°C)	E_d (kJ/mol)	T_{max} (°C)	E_d (kJ/mol)
Alumina 200[b]	158	123	120	112	152	121
Alumina 500[b]	164	125	155, 258	122, 153	173, 283	127, 160
Alumina 800[b]	151, 205	121, 137	102, 254	107, 151	154, 261	122, 153

[a]Calculated according to the Redhead equation.

[b]The pretreatment temperatures of the supports reflect the temperatures to which the samples were heated during TPDE.

supported chromium and molybdenum samples. Earlier TPDE studies of the supported group 6 hexacarbonyls showed a desorption maximum of hydrogen at about the same temperature as the second maximum of liberated CO [11–13]. It seemed that chromium oxidised in two steps, possibly in three. However, chromium exists with several oxidation states, which supports our TPDE results. Molybdenum and tungsten seemed to oxidise in one or possibly two steps. According to our TPDE results, tungsten oxidised by redox reaction with the surface at a much lower temperature than molybdenum did.

3.2. Temperature-programmed reduction

Catalytic activity is often associated with the reduction behaviour of the studied metal. We treated the samples in three different ways prior to reduction: The $M(CO)_6$/alumina samples were decarbonylated during TPDE and oxidised with pulse chemisorption prior to reduction (Sequence i). A pulse chemisorption of oxygen at 200°C was performed for supported $M(CO)_6$ samples prior to the reduction treatments; the CO ligands were removed and metal atoms were possibly oxidised (Sequence ii). Alumina supported $M(CO)_6$ samples were decarbonylated under H_2/Ar flow followed by oxidation at 200°C (Sequence iii).

3.2.1. Alumina 200

Molybdenum and tungsten had CO ligands remaining on alumina 200 after the TPDE was run to 200°C in Sequence i. During the subsequent pulse chemisorption, these ligands were removed and the metal could be oxidised. For chromium, all the CO ligands were removed during the TPDE. The next reduction step, however, showed no distinct maxima for consumption of hydrogen. Neither oxygen (Sequence ii) nor hydrogen–oxygen (Sequence iii) treatments prior to reduction made the supported metal more reducible than in Sequence i. This indicates that 200°C is too low a temperature for any reduction of supported group 6 transition

metals when the decarbonylated samples were oxidised at 200°C prior to TPR runs.

3.2.2. Alumina 500

$Cr(CO)_6$/alumina 500 showed no reduction maxima after TPDE and $PC(O_2)$ (Fig. 2a). In Sequence ii, $Cr(CO)_6$ decarbonylated almost totally during heating to 200°C, the temperature at which pulse chemisorption was carried out. The consumption of oxygen was observed, 0.2 being the molar ratio of O_2/Cr. Some oxygen, however, might be consumed by the oxidation of surface carbonate species. In the subsequent reduction, two maxima can be seen (Fig. 2b) at about 250°C and 360°C. In the following $PC(O_2)$ treatment, the molar ratio of O_2/Cr decreased to 0.03. The subsequent reduction showed only one broad maximum at about 330°C (Fig. 2c) instead of the two separate maxima found in the previous reduction treatment. These results would imply that after the first heating to 200°C there are two different kinds of reducible surface chromium species on alumina. Heating to 500°C changed the surface chromium species, which was seen as changes in the shape of the TPR profile and a slightly increased hydrogen uptake.
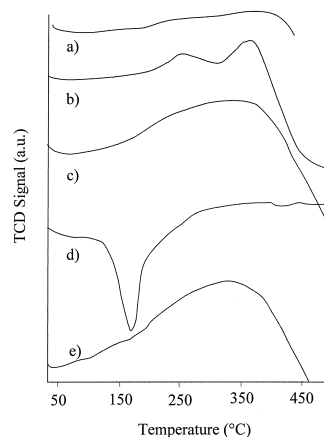

Fig. 2. TPR profiles of Cr/alumina 500. (a) After TPDE and $PC(O_2)$ at 200°C (Sequence i), (b) after $PC(O_2)$ at 200°C (Sequence ii), (c) after $PC(O_2)$ at 200°C, TPR and second $PC(O_2)$ at 200°C (Seq. ii), (d) TPR of $Cr(CO)_6$ on alumina 500 (Sequence iii) and (e) after TPR and $PC(O_2)$ at 200°C (Sequence iii).

The removal of CO ligands of alumina supported chromium under H_2 flow (Sequence iii) gave a TPR profile with one negative signal at about 155°C (Fig. 2d). The TPDE profile showed the T_{max} at the same temperature (Fig. 1) as $Cr(CO)_6$ decarbonylated in one step, so this negative signal can be assigned to the liberation of CO and possibly CH_4 formed by the reaction of H_2 and CO. The second reduction showed a very broad maximum at about 330°C (Fig. 2e). This is in accordance with the discussion above that different chromium species have been formed by heating to 500°C than by heating to 200°C.

Throughout the hydrogen treatments (Sequences i, ii and iii) of molybdenum on alumina 500 the reduction maxima appeared at about 365°C (363–368°C) (Fig. 3). According to these studies, the decarbonylation conditions had only a minor or no effect on the reduction of molybdenum supported on alumina 500.
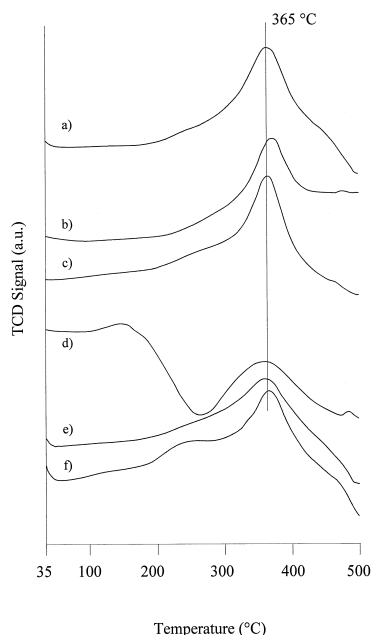

Fig. 3. TPR profiles of Mo/alumina 500. (a) after TPDE and $PC(O_2)$ at 200°C (Sequence i), (b) after $PC(O_2)$ at 200°C (Sequence ii), (c) after $PC(O_2)$ at 200°C, TPR and second $PC(O_2)$ at 200°C (Sequence ii), (d) TPR of $Mo(CO)_6$ on alumina 500 (Sequence iii), (e) after first reduction–oxidation cycle (Sequence iii) and (f) after second reduction–oxidation cycle (Sequence iii).

A case study of three reduction–oxidation cycles (Sequence iii) for $Mo(CO)_6$ on alumina 500 implied that the oxidation and reduction of molybdenum was not reversible. During the first reduction step, the hydrogen consumption was not taken into consideration since side reactions complicated the TPR profile and consumption of hydrogen (Fig. 3d). The second reduction step gave a molar ratio of 0.15 H_2/Mo, and the third one 0.11. The pulse chemisorption of oxygen also showed a decrease in consumption with more treatment steps. The first oxygen treatment gave a molar ratio of oxygen and molybdenum of 0.37. Further heating steps under reductive conditions decreased the consumption of oxygen to about a quarter of the previous oxidation step: the O_2/Mo molar ratios were 0.9 and 0.2 for the second and third oxygen treatments, respectively. The surface species were supposed to be of the same type since the temperature maxima of reduction were not affected by the oxygen treatments; the maxima for the reductions appeared at around 365°C.

The TPO of the decarbonylated Mo/alumina 600 sample yielded an oxidation maximum at 300°C and 1.0 O_2/Mo for the consumed oxygen. The subsequent TPR consumed 1.0 mol hydrogen per 1 mol molybdenum with a reduction maximum at about 400°C [17]. Thus in these reduction–oxidation cycles, molybdenum was not oxidised totally and the reduction maxima appeared at a lower temperature. The partial oxidation of molybdenum in this study might also affect the oxygen and hydrogen uptakes.

The overview of the TPR profiles of $W(CO)_6$/alumina 500 showed no reduction maxima except after the first oxidation (in Sequence ii); a weak maximum appeared at about 250°C. This maximum, however, was lost after the following oxidation step. It should be noted that the loading of tungsten was low (0.12 W atoms/nm^2) in this work, therefore the amount of reducible tungsten surface species was small.

When decarbonylations of molybdenum or tungsten hexacarbonyls were carried out under hydrogen flow, the shape of the TPR profiles

differed from those obtained by heating under helium flow. The release of gaseous products caused the negative signal that appeared in the higher temperature region than the second maxima in TPDE. Brenner and Hucul found a formation of methane during the TPDE of $Mo(CO)_6$/alumina under H_2 flow with T_{max} at about 280°C [13]. The negative signal found in this work was ascribed to the formation of methane.

3.2.3. Alumina 800

Two different reduction behaviours were found for molybdenum supported on alumina 800. The TPR profiles of the Mo/alumina 800, which were (a) decarbonylated during TPDE and oxidised with $PC(O_2)$ or (b) decarbonylated with $PC(O_2)$ treatment prior to reductions, showed very broad maxima at around 480°C. Mo/alumina 800, which was decarbonylated under H_2 flow and oxidised by pulse chemisorption, showed a maximum at about 277°C with shoulders at 140 and about 550°C in the TPR profiles. The amount of hydrogen uptake increased from 0.16 to 0.29 H_2/Mo when decarbonylation was carried out under hydrogen instead of helium. Stronger bonds with the surface might be formed in decarbonylation under helium than under H_2 flow. These species were proposed to reduce in a different way, depending on the interactions with the surface. As discussed above, the changes in the BET surface area of alumina during pretreatment at 800°C might be one explanation for the behaviours of the supported metal species.

The TPR profiles of alumina 800 supported $W(CO)_6$ revealed two maxima at 250°C and 500°C for samples decarbonylated under He and oxidised at 200°C (Sequence i). The lower temperature maximum was also seen in the reduction profiles of Sequences ii and iii. Although the amount of tungsten particles/nm^2 was almost the same on alumina 500 and 800, more reduction maxima in the TPR profiles appeared on alumina 800. This would indicate more re-

ducible tungsten particles on alumina 800 than on alumina 500.

As a summary, the degree of dehydroxylation of the alumina affected the decomposition of $M(CO)_6$ during TPDE. The pretreatment temperature of the support had a smaller effect on decompositions of $Cr(CO)_6$ and $W(CO)_6$ than on the decomposition of $Mo(CO)_6$. The most stable subspecies of the hexacarbonyl compounds were formed on alumina 500 in every group 6 metal.

Samples supported on alumina 200 showed no reduction after the removal of the CO ligands. Different TPR profiles of $Cr(CO)_6$/alumina 500 caused by different heating treatments would indicate changes in the surface chromium species. The three reduction–oxidation cycles of the molybdenum sample implied that oxidation and reduction of surface molybdenum species was not reversible. Molybdenum was only partially oxidised, which was suggested to influence the reactivity of the Mo species.

Molybdenum reduced in two different ways on alumina 800, depending on the decarbonylation conditions. The TPR showed a more complicated profile indicating different surface species of molybdenum from those on alumina 500. The estimation of the reduction behaviour of tungsten hexacarbonyl on alumina was restricted by low metal loadings. However, more reducible tungsten was suggested to form on alumina 800 than on alumina 500.

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