

Controlled deposition of chromium hexacarbonyl on silica surfaces in a fluidised bed reactor

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Abstract

Cr(CO)₆/silica samples were prepared in a fluidised bed reactor by vapor phase adsorption of zerovalent chromium hexacarbonyl under N₂ flow. Two different preparation methods were used; a vaporisation method without decarbonylation step and a pulse method in which a sample was decarbonylated after vaporisation, followed by repeated vaporisation–decarbonylation cycles. The chromium content can be controlled and weakly adsorbed chromium species can also be removed from the silica surface using the pulse method. The chromium carbonyl/silica interactions were characterised using diffuse reflectance Fourier transform IR spectroscopy (DRIFT). ²⁹Si cross-polarisation magic-angle spinning (CP MAS) NMR studies indicated that chromium hexacarbonyl interacts with single silanols of the silica surface even though the interaction is either physisorption or weak chemisorption. Samples were also characterised by temperature programmed techniques. The preoxidation temperature influences to the reduction of the samples. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Chromium hexacarbonyl; Silica; DRIFT; TPD; ²⁹Si CP MAS NMR; TPR

1. Introduction

Chromium-based catalysts have found a wide range of applications in many important industrial reactions, especially those in the petrochemical industry. These catalysts are usually composed of chromium oxides supported on inorganic oxides, such as silica, alumina and zeolites. Chromium on silica is the famous Phillips catalyst for the polymerisation of ethy-

lene [1,2]. Another common chromium-based polymerisation catalyst is the Union Carbide catalyst, which is chromocene supported on a silica surface [3]. Chromium hexacarbonyls have also been used as polymerisation catalyst precursors, while supported on alumina or silica–alumina, for the polymerisation of ethylene. Chromium hexacarbonyl supported on alumina can be used to hydrogenate propene [4]. Chromium-based catalysts on different supports are also active in dehydrogenation reactions of alkenes and alkanes, oxidation processes and dehydrocyclisation reactions [5–10].

There is current interest on supported transition metal carbonyls as heterogeneous catalysts

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or catalyst precursors. It is believed that such systems can potentially combine advantages from both homogeneous and heterogeneous catalysis. They also provide a convenient route to highly dispersed low-valence metals, without the need for strong reduction treatments [11,12]. Decarbonylation of metal carbonyl anchored on the surface of various supports may offer convenient routes to this goal. Immobilised carbonyls are also useful in the investigation of ligand substitution reactions and catalytic reactions [13–15].

Impregnation and sublimation in vacuum are convenient preparation methods in the case of chromium carbonyl supported on silica [16,17]. In the present work we have used a fluidised bed reactor system in which the catalytic precursor, zerovalent chromium hexacarbonyl, can be evenly vaporised on the silica surface. Samples can be prepared and preparation can be observed in stages. The use of a solvent can also be eliminated in contrast to the impregnation method, for example. In this work, the preparation steps of the $\text{Cr}(\text{CO})_6/\text{SiO}_2$ system were characterised by DRIFT (diffuse reflectance Fourier transform IR spectroscopy), ^{29}Si CP MAS (cross-polarisation magnetic angle spinning) NMR spectroscopy and by different temperature programmed techniques.

2. Experimental

2.1. Reagents

Chromium hexacarbonyl (Aldrich Chemical) was used as a catalyst precursor without further purification. $\text{Cr}(\text{CO})_6$ was vaporised on a silica (S 432, Grace Davison) support under nitrogen flow (AGA, 99.999%). Silica was preheated under vacuum for 10 h at 300°C and 500°C (designated sil300 and sil500, respectively) to remove physisorbed water and to control the amount of OH species on the surface of silica. The surface area of different pre-treated silicas

(untreated, sil300 and sil500) were measured by adsorption of N_2 (ASAP 2010). These experiments were carried out at the temperature of liquid nitrogen (-196°C). Silica surface area was about 320 m^2/g (pH ~ 7). After pre-treatment it was stored in a glove-box under N_2 , and from there packed into the fluidised bed reactor, without being exposed to air.

2.2. Equipment

$\text{Cr}(\text{CO})_6/\text{silica}$ samples were prepared in a fluidised bed reactor system. The reactor has been described in detail by Suvanto et al. [18]. Chromium hexacarbonyl was deposited under N_2 flow. The vaporisation temperature for $\text{Cr}(\text{CO})_6$ was 55°C and at the same time the temperature of the reactor was 65°C [19]. The samples were decarbonylated at 150°C. In the pulse method, the samples were decarbonylated after vaporisation. The entire reaction sequence was carried out under a nitrogen atmosphere without exposure to air or moisture.

The chromium content was estimated with an energy dispersive X-ray fluorescence spectrometer (ACAX 300 EDXRF). Fe(55) radioisotope was used as the source of radiation for Cr measurements [19].

The infrared (IR) spectra were recorded with a Nicolet Impact 400 D Fourier transform IR spectrometer equipped with a diffuse reflectance device and a mercury–cadmium–tellurium detector. Resolution of the measurements was 2 cm^{-1} . The spectra presented here are those recorded spectra from which the pure silica spectrum has been subtracted. IR spectras were measured under nitrogen atmosphere by the DRIFT technique with the diffuse reflectance apparatus enclosed in an IR glove-box with NaCl windows [20].

The solid state ^{29}Si NMR spectra were obtained at 79.49 MHz with a Bruker AM-400 spectrometer under conditions of ^1H – ^{29}Si CP and magnetic spinning (MS). Samples were spun at 8 kHz spinning rate in a zirconium oxide

rotor. Spectra were obtained by using a contact time of 4.5 ms, a pulse repetition time of 4 s and acquisition time of 129 ms.

Temperature-programmed desorption (TPD), pulse chemisorption of O₂ and temperature-programmed reduction (TPR) measurements were carried out in a Micromeritics ASAP 2910 analyser equipped with a thermal conductive detector (TCD). The outlet from TPD analysis was connected to HP 5971 quadruple mass spectrometer. The mass of the sample was 0.5–1.0 g. The carrier gas was helium in TPD, argon in pulse chemisorption of O₂, and 10% H₂/Ar-mixture in TPR. During pulse chemisorption the temperature of the oven was held constant at 200, 300 or 500°C, and during TPD and TPR it was linearly ramped at 10°C/min to the temperature of different pre-treated silicas (300°C or

500°C). Gas flow (10 ml/min) was controlled by mass flow controllers.

3. Results and discussion

3.1. Chromium content

Fig. 1A shows the chromium content of the sample during vaporisation from 1 to 15 h. The amount of chromium was about 0.07 wt.% between 1 and 15 h vaporisation in a both cases, sil300 and sil500. The pre-treatment of support (sil300 and sil500) did not affect the amount of chromium deposited. It can be assumed that the silica surface still has free adsorption places. Steric hindrance of CO groups on the silica surface is not a problem after decarbonylation.

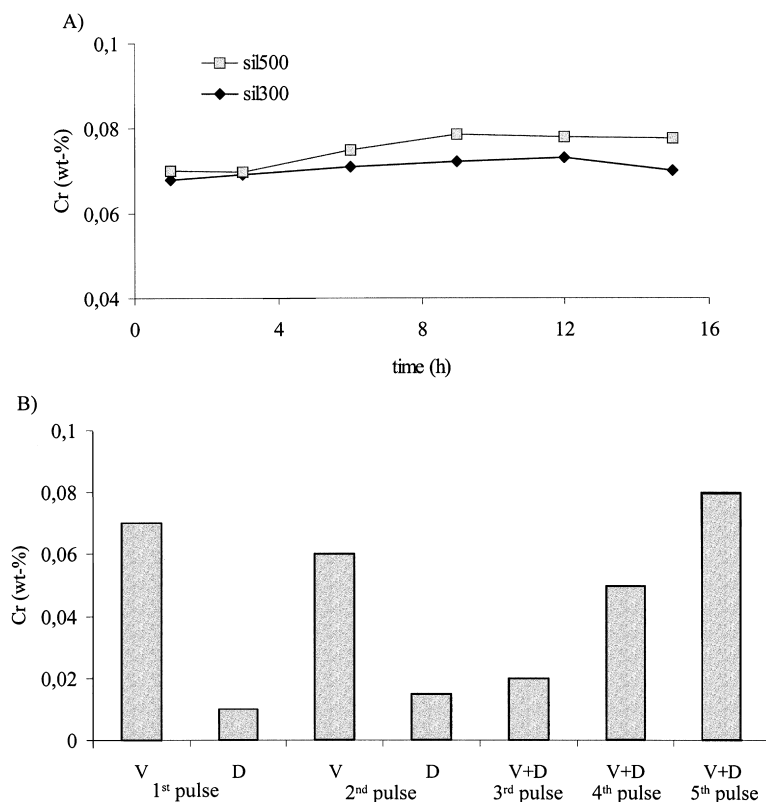


Fig. 1. The amount of chromium (wt.%) during (A) deposition at 55°C and (B) pulse technique, V = vaporisation (2 h at 55°C), D = decarbonylation (2 h at 150°C).

It can be supposed that $\text{Cr}(\text{CO})_6/\text{silica}$ interactions are very weak and adsorption energy is very low.

Fig. 1B presents results from a pulse method in which the sample has been decarbonylated, after the vaporisation step followed by repeated vaporisation–decarbonylation cycles. After the first vaporisation step the chromium content is about 0.07 wt.%, yet after the sample was decarbonylated, the amount of chromium decreased dramatically. This indicates that $\text{Cr}(\text{CO})_6/\text{silica}$ interaction is very weak and that during decarbonylation most of the chromium desorbs from the silica surface. The situation is also the same after the second pulse. The chromium content achieved was not stable in the case of vaporisation without decarbonylation. Heating the sample caused the chromium content to decrease. Chromium content increased slowly as more vaporisation–decarbonylation cycles were performed and after the fifth pulse the amount of chromium was

about 0.08 wt.%. The chromium content obtained was rather low even though the pulse method was used. Commercial polymerisation catalysts usually contain 0.5–1.0 wt.% Cr, but only a fraction of this, 10–20%, or even less, is actually active for polymerisation [21].

3.2. IR and ^{29}Si CP MAS NMR characterisation

3.2.1. CO region

Fig. 2A presents the IR spectra of $\text{Cr}(\text{CO})_6$ supported on sil500 after 0.5, 2 and 15 h of vaporisation (spectra a–c) and five pulses (spectrum d) and on sil300 after five pulses (spectrum e). The same peaks are visible in the spectra after 0.5 h of vaporisation as appear after five pulses. The same characteristic appears in the spectra of both supports, so it can be concluded that the pre-treatment of silica has no influence on the adsorption of chromium hexacarbonyl. In this study there were bands at 2112 (w), 2023 (w) and 1998 (s) cm^{-1} .

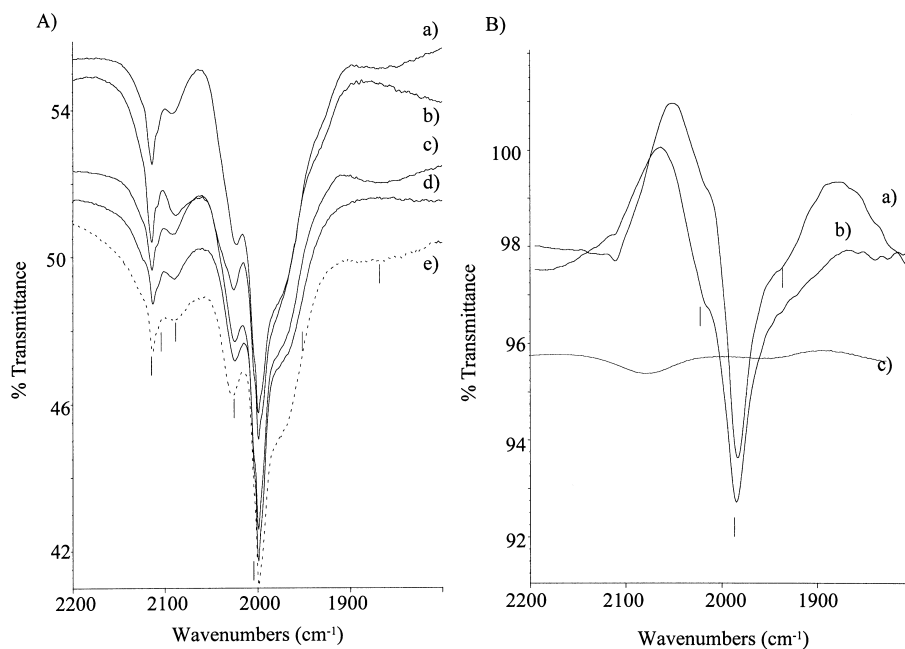


Fig. 2. IR spectra of $\text{Cr}(\text{CO})_6$ supported on silica. (A) After (a) 0.5 h vaporisation at 55°C, (b) 2 h vaporisation at 55°C, (c) 15 h vaporisation at 55°C, (d) five pulses (sil500) and (e) five pulses (sil300). (B) After (a) 0.5 h decarbonylation at 100°C, (b) 2 h decarbonylation at 100°C and (c) 2 h decarbonylation at 150°C.

Gugliemotti [16] assigned the bands at 1990 (vs) and 2015 (w) cm^{-1} for physisorbed $\text{Cr}(\text{CO})_6$ on silica to the T_{1u} and E_g modes. The additional band at 2112 (w) cm^{-1} for $\text{Cr}(\text{CO})_6$ in solution was due to the A_{1g} mode [16]. In the gas phase, the octahedral $\text{Cr}(\text{CO})_6$ molecule (O_h) exhibits a single IR active mode (T_{1u}) at about 2000 cm^{-1} corresponding to C–O vibrations of the ligands. The two Raman active modes, A_{1g} and E_g become slightly active in solution or if $\text{Cr}(\text{CO})_6$ is physisorbed [11,12,15,22]. This could also be seen in this study.

There were also other frequencies already after 0.5 h of vaporisation at 2107 (sh), 2086 (w) 1968 (sh) and 1846 (vw) cm^{-1} . According to Hunter et al. [17], bands at 2038, 2003 and 1924 cm^{-1} in the spectra, after removal of more weakly bound species, are ascribed to $\text{Cr}(\text{CO})_6$ molecules interacting with the sil500 surface via one carbonyl ligand. Similar assignments have been given for adsorption on an H–Y zeolite at 1960 cm^{-1} [17]. There was also a vibration at the frequency 2089 cm^{-1} and when the chromium hexacarbonyl was supported on zeolite. The band at this frequency is O-bonded $\text{Cr}(\text{CO})_6$ [15]. In this study, the frequencies that belong to weak chemisorbed interaction were at 2086 (w) and 1968 (sh) cm^{-1} .

Fig. 2B presents the results after decarbonylation treatment at different temperatures. There were still three IR-frequencies in the wavenumbers 2023 (sh), 1987 (s) and 1938 (sh) after 30-min decarbonylation at 100°C, and all these frequencies can still be seen in the IR spectra (Fig. 2B) after 2-h decarbonylation at 100°C. Very weakly adsorbed chromium species desorb from silica surface at 100°C. The oxidation state of zero-valent chromium changes to some low valence state during decarbonylation, as evidenced by a colour change of the sample. TPR studies revealed the presence of Cr^{2+} , especially on silica surfaces with low chromium loadings [23]. There were no carbonyl species on the silica surface when the sample had been decarbonylated for 2 h at 150°C (Fig. 2B, c). $\text{Cr}(\text{CO})_6$ decomposes by losing CO groups and

forms very small metal agglomerates. Adsorption of chromium hexacarbonyl on such samples led to both physisorbed and weakly chemisorbed species. In this study, frequencies of chemisorbed species were observed at 2107 (sh) and 1846 (vw) cm^{-1} . According to the literature, these chemisorbed species have IR bands at 2125, 2055, 2020 and 1875–1835 cm^{-1} [16].

3.2.2. OH region

The surface species on silica have been characterised in great detail by analytical methods such as IR [24,25] and solid state NMR spectroscopy, as well as both ^{29}Si CP MAS [26,27] and ^1H MAS [28,29]. In this study, IR and ^{29}Si CP MAS spectroscopy measurements have been used to analyse silica surfaces.

Fig. 3A shows the OH region (3400–3500 cm^{-1}) of three silica samples (untreated sil300 and sil500). Changes can be clearly seen when molecularly adsorbed water is removed during pre-treatment. Fig. 3 shows the silica surface with free (3746 cm^{-1}) and geminal (3742 cm^{-1}) OH groups. There is overlap of band in the OH region. Interaction with chromium hexacarbonyl and silica was quite weak, and also the amount of adsorbed chromium hexacarbonyl was rather small. Therefore, changes in the OH region are very slight (Fig. 3B). Hunter et al. [17] have reported that these bands are not attributable to $\text{Cr}(\text{CO})_6$ molecules interacting with surface silanol groups via hydrogen bonds, because the IR band at 3750 cm^{-1} due to silanol groups was unaffected by the adsorption process. Adsorption may occur at strained siloxane bridge sites, which involve silicon atoms exhibiting electron-accepting properties, and which are formed by surface dehydroxylation at higher temperatures [17].

NMR characterisation (Fig. 4a) indicates that on the silica surface there are geminal silanols (–91 ppm), single silanols (–101 ppm) and siloxane bridges (–111 ppm). In NMR characterisation the intensity ratio of single silanols and siloxane bridges can be compared. The

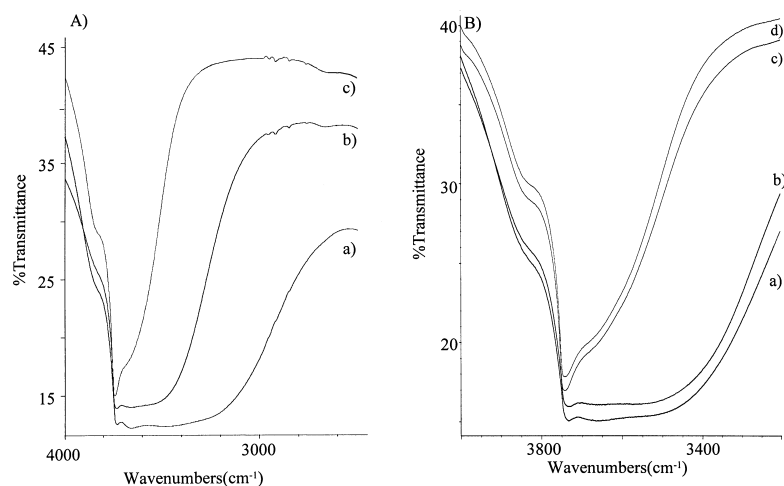


Fig. 3. IR spectra of $\text{Cr}(\text{CO})_6$ supported on silica. (A) (a) Untreated silica, (b) sil300, (c) sil500. (B) (a) Sil300, (b) sil300 after five pulses, (c) sil500 and (d) sil500 after five pulses.

increase in pre-treatment temperature (Fig. 4a, b and d) decreased the amount of single silanols compared to siloxane bridges. There is a change in the NMR peaks after vaporisation of $\text{Cr}(\text{CO})_6$. Changes can also be seen in Fig. 4b sil300 compared to Fig. 4c $\text{Cr}(\text{CO})_6$ supported on

sil300. The intensity ratio of single silanols and siloxane bridges was compared and found to be smaller after $\text{Cr}(\text{CO})_6$ was adsorbed on the silica surface than before adsorption. On the basis of NMR spectroscopy, it can be deduced that chromium carbonyls interact with OH groups,

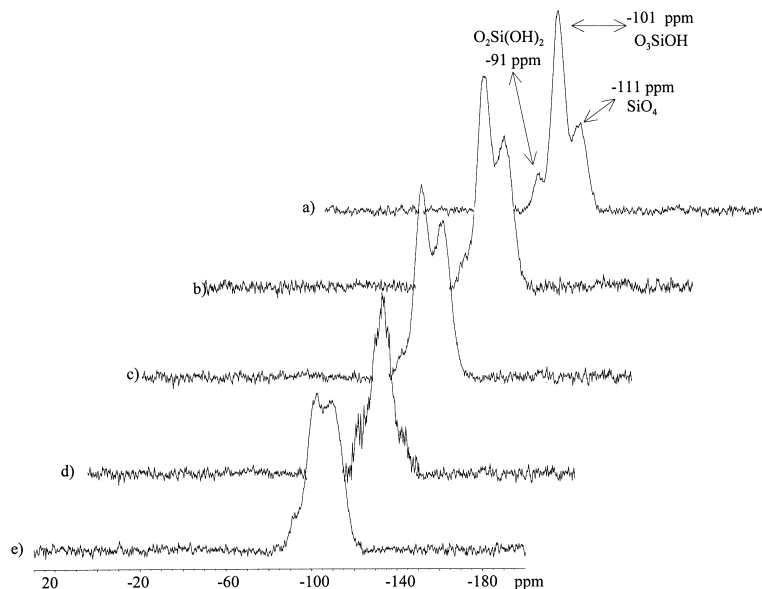


Fig. 4. ^{29}Si CP MAS NMR spectra of $\text{Cr}(\text{CO})_6$ supported on silica. (a) Untreated silica, (b) sil300, (c) sil300 + $\text{Cr}(\text{CO})_6$, (d) sil500 and (e) sil500 + $\text{Cr}(\text{CO})_6$.

single silanols of the silica surface, because the relationship of single silanols and siloxane bridges, as mentioned above decreased when chromium hexacarbonyl had been supported on the silica surface.

3.3. TPD, pulse chemisorption of O_2 and TPR

3.3.1. TPD

Fig. 5 presents the TPD spectra of $Cr(CO)_6$ /silica system under argon flow analysed by mass spectrometer. One sharp maximum at about $150^\circ C$ can be seen in the TPD spectra (Fig. 5A). Fig. 5B shows the abundance of desorbed groups from the silica surface as a function of time during TPD. Most of desorbed species were CO groups and some methane was also formed. In the IR spectra, physisorbed CO_2 can be observed at 2346 cm^{-1} on silica [30], which was also noted in this study at 2379 cm^{-1} . The formation of CO_2 , is described in literature by means of CO and surface O^{2-} interaction. The hydrogen has been shown to arise from a redox reaction between surface hydroxyl groups and the metal. The formation

of H_2 indicates an oxidation of the original zerovalent $Cr(CO)_6$ [31].

3.3.2. Pulse chemisorption of O_2 and TPR

Chromium hexacarbonyl/silica system was also examined by oxidation and reduction treatments. In this work, samples were reduced directly without decarbonylation as well as after decarbonylation. A preoxidation was done at $200^\circ C$ and $500^\circ C$ in the case of sil500, and at $300^\circ C$ in the case of sil300. The maximum temperature both in pulse chemisorption of oxygen and TPR was the preheated temperature of silica. There was not a distinct reduction maximum when the sample was reduced without oxidation in the case of sil300 (Fig. 6A, a). H_2 consumption decreased at $\sim 150^\circ C$, but then increased when the decarbonylated and preoxidised sample was reduced (Fig. 6A, b). Desorption occurs from silica surface when consumption of H_2 decreases.

A reduction maximum was observed at about $470^\circ C$ in the case of sil500 (Fig. 6B, a/not oxidised) CO groups desorbed from silica surface at $150^\circ C$ when the sample had not been decarbonylated (Fig. 6B, a and c). There were two desorption peaks at $150^\circ C$ and $250^\circ C$ where the consumption of hydrogen decreased. Between these temperatures hydrogen consumption increased when the sample had been preoxidised at $200^\circ C$. There was also, in this case, a distinct maximum at $470^\circ C$, and the shape of the TPR spectra before and after decarbonylation were similar. There was only one temperature maximum at $470^\circ C$ when the sample had been preoxidised at $500^\circ C$ (Fig. 6B, c). Differing reduction places were observed when comparing the sil500 sample preoxidised at $200^\circ C$ with the sample preoxidised at $500^\circ C$ (Fig. 6B, b and c).

Ellison et al. [32,33] have reported that different chromium species have specific reduction temperatures, e.g., CrO_3 has a reduction T_{max} in the range of $355\text{--}365^\circ C$ and $395\text{--}405^\circ C$, chromate like $450\text{--}480^\circ C$ and dichromate like $505\text{--}515^\circ C$. Two different species are also formed at

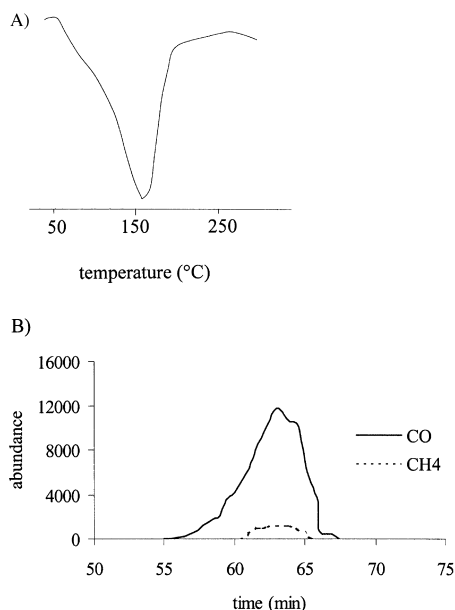


Fig. 5. (A) TPD spectra of $Cr(CO)_6$ supported on silica and (B) desorbed species during TPD characterised by mass spectrometer.

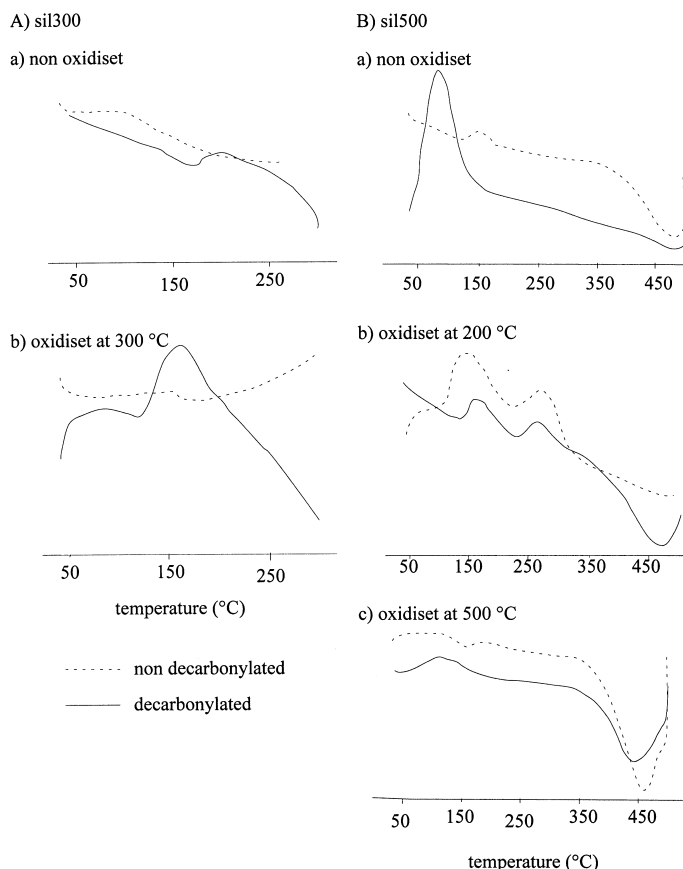


Fig. 6. TPR spectra of $\text{Cr}(\text{CO})_6$ supported on silica (A) sil300 and (B) sil500 (a) without oxidation, (b) after oxidation at 200°C (sil500) and at 300°C (sil300) and (c) after oxidation at 500°C (sil500).

550–560°C and 650–660°C [32,33]. EPR (electron paramagnetic repulsion) spectra of silica-supported $\text{Cr}(\text{CO})_6$ closely resemble the spectra-supported chromium catalysts prepared by either reduction of CrO_3 or impregnation with solutions of Cr^{2+} or Cr^{3+} salts [33]. Cr^{3+} is the most stable oxidation state and has been studied extensively. The oxidation states Cr^{5+} and Cr^{4+} are rather unstable and Cr^{5+} is easily disproportionate to Cr^{3+} and Cr^{6+} . The Cr^{2+} ions are strongly reductive and are only stable in the absence of oxygen [1]. The EPR spectra indicate that activation of silica-supported $\text{Cr}(\text{CO})_6$ in vacuum produces only chromium with low oxidation states, probably mostly Cr^{2+} , which has been shown to be stable on silica in the absence of oxygen. Exposure to oxygen

results in oxidation to Cr^{5+} , and ultimately to Cr^{6+} [34].

4. Conclusions

$\text{Cr}(\text{CO})_6/\text{silica}$ samples were prepared in a fluidised bed reactor by vapor phase adsorption of chromium hexacarbonyl. Two different preparation methods were used; a vaporisation method without the decarbonylation step and a pulse method where a sample was decarbonylated after vaporisation followed by repeated vaporisation–decarbonylation cycles. The chromium content achieved was about 0.1 wt.% in both cases. The chromium content decreases dramatically when the sample is decarbony-

lated. This indicates that chromium carbonyl/silica interaction is weak. $\text{Cr}(\text{CO})_6$ /silica samples can be prepared under controlled conditions by the pulse method. Chromium content increases evenly after each pulse. Weakly adsorbed chromium carbonyl species can be eliminated from the silica surface when the pulse method is used.

Chromium carbonyl supported on silica has physisorbed and weakly chemisorbed species. Changes of OH region are very small in the IR spectra. On ground of ^{29}Si CP MAS NMR, it can be clearly seen that $\text{Cr}(\text{CO})_6$ interacts with hydroxyl groups on the silica surface; the intensity ratio of single silanols and siloxane bridges differs after chromium hexacarbonyl is deposited on the silica, as can be seen when the spectra of pure silica, are compared to those of $\text{Cr}(\text{CO})_6$ /silica. The interaction between single silanols and chromium carbonyl is evident.

Chromium hexacarbonyl supported on silica without preoxidation has only one temperature maximum at about 470°C in the TPR spectra. Preoxidation temperatures influence the reduction temperatures. For chromium carbonyl supported on sil500 in which the sample is preoxidised at 200°C, chromium has at least three different reduction sites. There is also one reduction maximum at 470°C when higher preoxidation temperature (500°C) is used. These findings indicate that, e.g., chromate, CrO_3 or dichromate [32,33] like species may form during reduction treatment after different preoxidation treatments.

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