

Deposition of chromium hexacarbonyl on alumina in a fluidized bed reactor

Sari Myllyoja ^{*}, Tapani A. Pakkanen

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

Received 14 November 1997; accepted 13 January 1998

Abstract

Cr(CO)₆/Al₂O₃ samples were prepared in a fluidized bed reactor by vapour phase adsorption of chromium hexacarbonyl under nitrogen flow. The preparation of the samples were followed by diffuse reflectance IR spectroscopy and the chromium content was determined by EDXRF. Deposition and pulse techniques were used to vaporize the hexacarbonyl on the alumina surface. The pulse technique proved to be very effective when higher chromium contents were desired. The temperature of the calcination (500°C/300°C) also had a significant effect on the amount of chromium adsorbed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Chromium hexacarbonyl; Cr(CO)₆; Alumina; Al₂O₃; Fluidized bed reactor; DRIFT

1. Introduction

Chromium based catalysts have found wide application in industrial reactions, especially reactions in the petrochemicals industry. They are active in dehydrocyclization reactions, oxidation processes, the polymerization of olefins and dehydrogenation reactions of alkenes and alkanes [1–9]. Studies have mostly focused on chromium oxide supported on silica, alumina and other supports. CrO₃/SiO₂, also known as Philips catalyst, has been particularly widely studied because of its activity in polymerization reactions [4,5,10–22].

The chemistry of transition metal carbonyl complexes, M(CO)₆ (M = Cr, Mo or W), sup-

ported on metal oxide surfaces has also attracted attention in recent years, in part because catalysts of high activity at low temperature can be generated [23]. Among the transition metal carbonyls, chromium hexacarbonyl has only rarely been used as catalytic precursor on alumina support [24–31], and only occasionally on silica [32–34] and zeolite [35,36]. Since metal carbonyls possess high symmetry, they are excellent models for complex systems [27,28]. They also provide a convenient route to highly dispersed low-valent metals without the need for strong reducing conditions. The use of supported transition metal carbonyls as heterogeneous catalysts or catalyst precursors has excited interest because such a system under the right conditions combines the advantages of heterogeneous and homogeneous catalysis while avoiding their disadvantages, especially those related to sepa-

^{*} Corresponding author. Fax: +358-13-2513390; e-mail: Sari.Myllyoja@joensuu.fi

ration of the catalysts from its products [28,31,37].

Catalysts have usually been prepared by solution phase methods, e.g., precipitation, adsorption, ion exchange and impregnation [38]. If gas phase methods such as dry mixing or PVD or CVD technique are used instead, interference from the solvent and other disadvantages are eliminated. In the work described here, we used a fluidized bed reactor system in which the catalytic precursor can be evenly vaporized and deposited on alumina under controlled conditions. The advantage of the fluidized bed system was investigated for the deposition of $\text{Cr}(\text{CO})_6$ by normal deposition and pulse techniques on alumina calcined at different temperatures. The progress of the sample preparation was followed by IR spectroscopy and the chromium content was determined by EDXRF.

2. Experimental

2.1. Reagents

Chromium hexacarbonyl supplied by Aldrich Chemical was used as catalytic precursor and was used without further purification. Nitrogen (99.999%) was the carrier gas. Alumina (Aldrich Bockman I) of surface area $155 \text{ m}^2/\text{g}$ and granular size 150 mesh supplied the support. Alumina was calcined under vacuum for 10 h at 300°C and 500°C (designated alu300 and alu500, respectively). The calcined supports were stored in a glove box.

2.2. Equipment

Samples were prepared in a fluidized bed reactor system [39] consisting of two parts: the reactor vessel, which is placed in an oven, and the vaporization system, which is surrounded by a water bath. The reactor vessel can be loaded with the support in a glove box and then connected to the reactor system. If the catalytic

precursor is an air-sensitive reagent it, too, can be loaded in the glove box. The fluidized bed reactor system is evacuated and flushed with N_2 three times before the reaction is started. If necessary, the reaction can be interrupted and the reactor vessel stored in the glove box. The reactor setup is suitable for the preparation of heterogeneous catalysts if the catalytic precursor can be vaporized at temperatures $\leq 100^\circ\text{C}$. A particular advantage of the system is that the temperature can be controlled separately for the vaporization and the reactor units.

Samples were analysed with a Nicolet Impact 400 D Fourier Transform infrared spectrometer equipped with an MCT (mercury–cadmium–tellurium) detector. The resolution of the spectrometer is 2 cm^{-1} . Spectra reported here are difference spectra, from which the pure alumina spectrum has been subtracted. IR spectra were measured under N_2 atmosphere by diffuse reflectance (DR) technique with the DR apparatus in an IR-glove box with NaCl windows [40].

Chromium content was determined from measurements with an energy dispersive X-ray fluorescence spectrometer (ACAX 300 EDXRF), and for a few reference samples by AAS (lithium tetraborate frit). Note that the results should be considered as only approximate since the samples were powders. The AAS results, together with the EDXRF results for the same samples, were used in calculating the chromium contents of samples measured only by EDXRF.

3. Results

Suitable vaporization and reactor temperatures were determined before the experiments were begun. A suitable vaporization temperature for the $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ system was between 50°C and 55°C , and a suitable difference between the temperatures of the reactor vessel and the vaporization cell was 10°C . Under these conditions the amount of chromium hexacarbonyl was sufficient for 5 h reaction, and the

amount of chromium hexacarbonyl in a cold finger (not attached to the surface of the alumina) was insignificant.

3.1. Chromium content

If it is assumed that one chromium atom binds to one OH-group, and if the surface area of alumina and the temperature of the calcination are known, it can be calculated how much chromium will theoretically adsorb. The values will only be approximate, however, since the surface of the alumina is in reality relatively complex. Various OH-groups, with differing adsorption capacity, are present on the alumina surface [41–47]. Once the adsorbed chromium concentration reaches a certain point, hindrance of the adsorbed species begins to limit further adsorption. Fig. 1 shows, for both alu500 and alu300, how the chromium content increases with the deposition time until a saturation level is achieved. In the ideal situation, a monomolecular chromium hexacarbonyl layer is formed on the surface. In our case it can be assumed that a monomolecular layer was formed since the chromium content became constant. If the chromium content were to continue increasing, formation of more than one layer could be assumed. About 0.9 wt.% chromium content was achieved with the alu500 support and a deposition temperature of 55°C. With lower de-

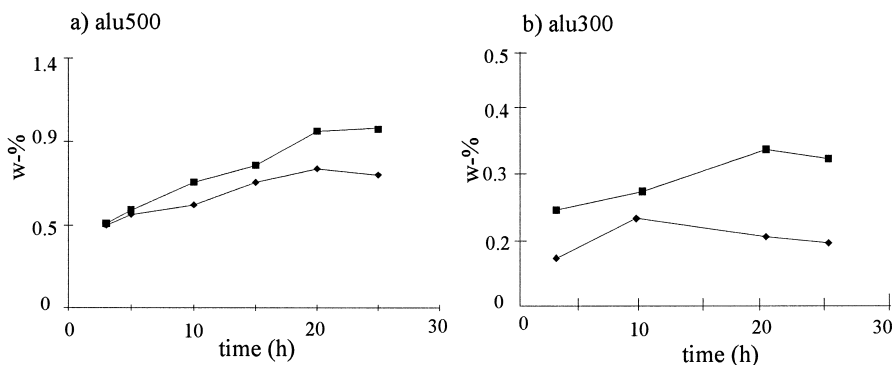


Fig. 1. Deposition of $\text{Cr}(\text{CO})_6$ on alumina temperature of deposition 50°C (—■—), temperature of deposition 55°C (—◆—). (a) alu500 = alumina calcined in vacuum 10 h at 500°C; (b) alu300 = alumina calcined in vacuum 10 h at 300°C.

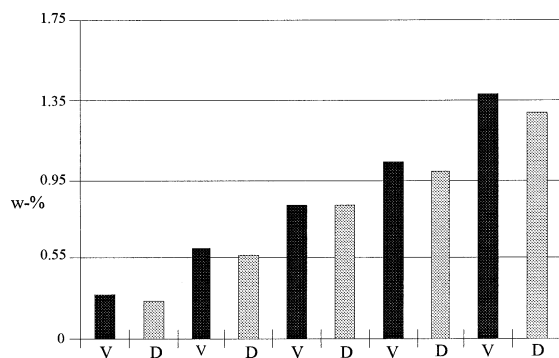


Fig. 2. Deposition of $\text{Cr}(\text{CO})_6$ on alumina with the five cycles. V = 5 h deposition (55°C); D = 2 h decarbonylation (150°C).

position temperature (50°C) the chromium content was a little lower because of the lower vapour pressure of the chromium hexacarbonyl. Considerably lower chromium content was obtained with alu300: at the higher vaporization temperature the total chromium content was only about 0.3 wt.%. Although there are more OH-groups on the surface of alu300, the alu500 support adsorbs more chromium hexacarbonyl, presumably because greater numbers of active adsorption sites, octahedral or tetrahedral Al^{3+} , are formed at the higher calcination temperature [24].

If higher chromium content is desired, a pulse technique can be applied and samples can be decarbonylated after each deposition cycle. For

the decarbonylation of $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$, the sample was heated in the fluidized bed reactor at 100–200°C. The vaporization–decarbonylation can be repeated several times. Fig. 2 shows the trend in the chromium content when the $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ sample was prepared by the pulse technique. The chromium content increased after each pulse, and was about 1.3

wt.% after the fifth pulse. Since, reportedly, the maximum chromium loading that can be achieved by the vaporization technique is only 0.03–0.05 wt.% [24], the chromium content can be increased dramatically with the pulse technique. Evidently, only monomeric subcarbonyls are present in the $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ system. Since there are no bridging carbonyl bands, it is diffi-

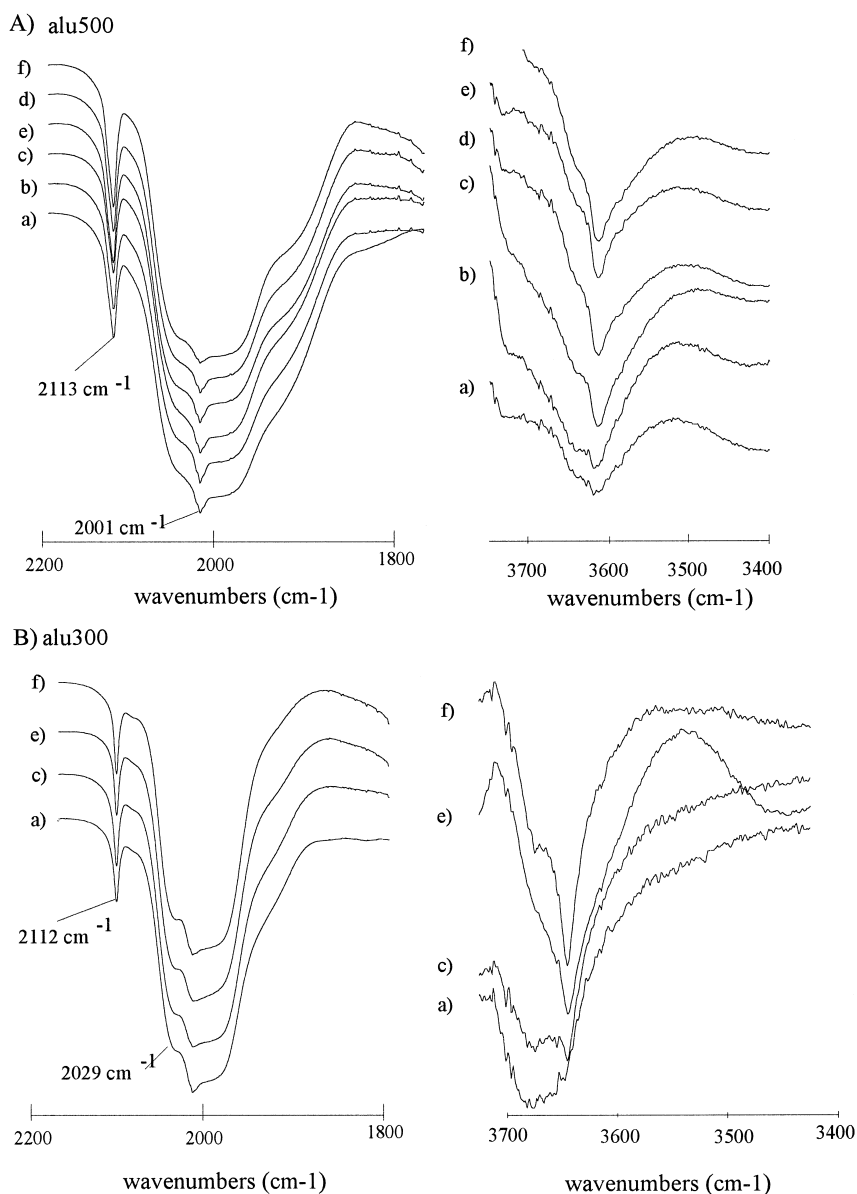


Fig. 3. IR spectra of $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ where the support is (A) alu500 and (B) alu300, after (a) 3 h deposition, (b) 5 h deposition, (c) 10 h deposition, (d) 15 h deposition, (e) 20 h deposition, (f) 25 h deposition.

cult to obtain high loadings of chromium on the alumina support [24] even with decarbonylation.

3.2. IR characterization

Diffuse reflectance Fourier transform infrared (DRIFT) spectra provide useful information on the nature and concentrations of the carbonyl, hydroxyl, carbonate and bicarbonate species present on the surface of the alumina support after vaporization and decarbonylation of the $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ samples.

Zecchina and Arean [26] and Zecchina et al. [48] have described how group VI metal carbonyls $[\text{M}(\text{CO})_6]$, where $\text{M} = \text{Cr}, \text{Mo}$ or W] adsorb onto γ -alumina. In gas phase, the octahedral $\text{Cr}(\text{CO})_6$ molecule shows a single IR-active band at about 2000 cm^{-1} . The A_{1g} and E_g modes, being only Raman active, are not observed. In solution these modes become slightly active, so that in the ideal situation the IR spectrum shows three IR-active bands, at 2112 – 2118 , 2018 – 2010 and 1984 – 1976 cm^{-1} . The same spectrum is also expected for physically adsorbed $\text{Cr}(\text{CO})_6$, where slight interaction with the support causes only a weak perturbation of the CO stretching modes. Hydrogen bonding to Brønsted acid sites, with consequent formation of $(\text{CO})_5\text{Cr}-\text{CO} \cdots \text{H}^+$ adducts, decreases the bridged CO frequency by about 50 cm^{-1} , while the vibrations of the $-\text{Cr}(\text{CO})_5$ moiety are only

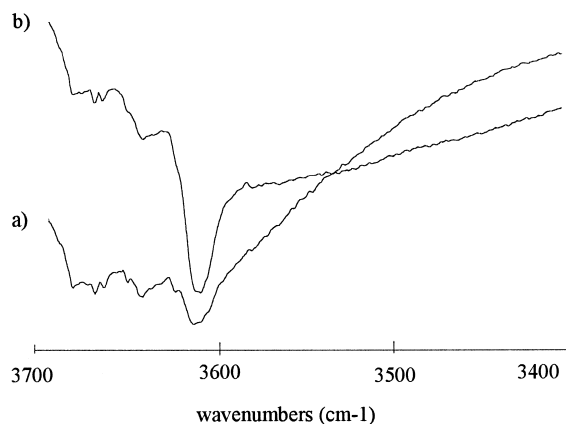


Fig. 4. (a) Vaporization of $\text{Cr}(\text{CO})_6$ on alu500 (5 h deposition at 55°C). (b) Sample (a) decarbonylated 2 h at 150°C .

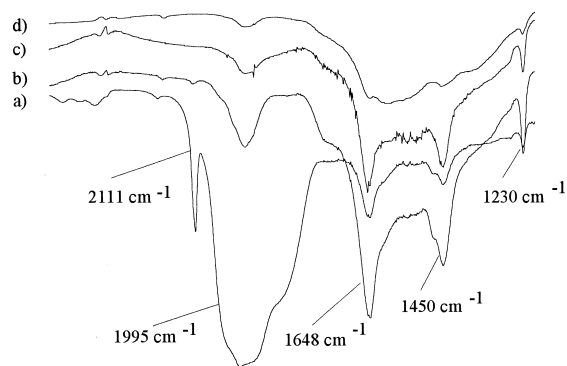


Fig. 5. IR spectra of $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ (alu500) after (a) 15 h deposition at 55°C and sample (a) after (b) 3 h decarbonylation at 100°C , (c) 3 h decarbonylation at 150°C , (d) 1 h decarbonylation at 200°C .

slightly affected and fall at nearly the same frequency as the physically adsorbed carbonyl. O-bonding to coordinatively unsaturated cations leads to the appearance of a low-frequency band (1770 – 1780 cm^{-1}) due to O-bonded CO-group, and to a parallel increase of the remaining CO stretching frequencies [26,48].

Fig. 3 shows how the IR spectra change with time of deposition. The area of the CO frequencies increases, while the area of the OH frequencies decreases. Alu300 has more OH-groups on the surface, but it adsorbs less chromium hexacarbonyl than alu500. In both cases there are free OH-groups after 25 h deposition, but there is so much steric hindrance on the surface of alu300 that effectively there are no more sites available for adsorption. Free adsorption sites, OH-groups, become accessible during decarbonylation (Fig. 4). Fig. 5 shows how the IR spectra change with the temperature of the decarbonylation.

A closer inspection of the area of the CO frequencies reveals what kinds of groups exist on the surface. The various vibrations that have been observed in the $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ system are listed in Table 1. According to Kazusaka and Howe [24], the first interaction between chromium hexacarbonyl and alumina is physisorption and the amount of chemisorbed species is small. In our spectra, bands at ~ 2114 and $\sim 2000\text{ cm}^{-1}$ dominate the IR-spectra, in-

Table 1

IR frequencies of carbonyl species on the surface of a $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ sample

Adsorption site/support	IR (cm^{-1}) (this study, support alu500)	IR (cm^{-1}) (literature)	Literature, various supports	References
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{oct}}^{3+}$	2142 (w)	2142(w)	γ -alu800	[26,48]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{tet}}^{3+}$	2122 (w)	2130 (w)	γ -alu800	[26,48]
$\text{Cr}(\text{CO})$ (physisorption)	2000 (s)	2120, 2000	alu450	[45]
$A_{1g}; \text{Cr}(\text{CO})_6$ (physisorption)	2117 (s)	2120 (w)	γ -alu	[26,49]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{oct}}^{3+}$	a	2090 (w)	γ -alu800	[26,48]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{oct}}^{3+}$	a	2040 (w)	γ -alu800	[26,48]
$\text{Cr}(\text{CO})_5$ (physisorption)	a	2080	alu450	[24]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{surf}}^{3+}$	a	2075 (vw)	γ -alu800	[48]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{tet}}^{3+}$	a	2075 (w)	γ -alu800	[26,48]
$E_g; \text{Cr}(\text{CO})_6$ (physisorption)	2029 (sh)	2015 (sh)	γ -alu	[48,49]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{surf}}^{3+}$	a	2010 (sh)	γ -alu800	[48]
$\text{Cr}(\text{CO})_4$ (physisorption)	2000	2000	alu450	[24]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{tet}}^{3+}$	2000 (s)	2000 (s)	γ -alu800	[26,48]
$T_{1u}; \text{Cr}(\text{CO})_6$ (physisorption)	1980 (s)	1980 (s)	γ -alu	[48,49]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{surf}}^{3+}$	a	1922 (w)	γ -alu800	[48]
$(\text{CO})_5\text{Cr}-\text{Al}^{3+}$ -site	1874	1880		[24]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{tet}}^{3+}$	1859 (m)	1850–1875 (m)	γ -alu800	[26,48]
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{oct}}^{3+}$	1795 (w)	1770–1780 (w)	γ -alu800	[26,48]
$(\text{CO})_4\text{Cr}-\text{Al}^{3+}$ -site	b	1760		[24]
$(\text{CO})_5\text{Cr}(\text{CO})$ -strong	b	1670 (w)	γ -alu800	[26]
Lewis acid plac				
$(\text{CO})_5\text{Cr}(\text{CO})-\text{Al}_{\text{surf}}^{3+}$	b	1605 (w)	γ -alu800	[26]
$\text{Cr}(\text{CO})_{6-x}$	b	1530 (w)	γ -alu800	[26]

vw = very weak.

w = weak.

sh = shoulders.

m = medium.

s = strong.

a = get covered.

b = not observed.

dicating the presence on the surface at least of $\text{Cr}(\text{CO})_4$ and $\text{Cr}(\text{CO})_5$ species. The $\text{Cr}(\text{CO})_4$ seen at $\sim 2000 \text{ cm}^{-1}$ is adsorbed by weak

physisorption interaction. The band expected at 1760 cm^{-1} due to chemisorption of $\text{Cr}(\text{CO})_4$ is covered with the carbonate signal. As Fig. 6

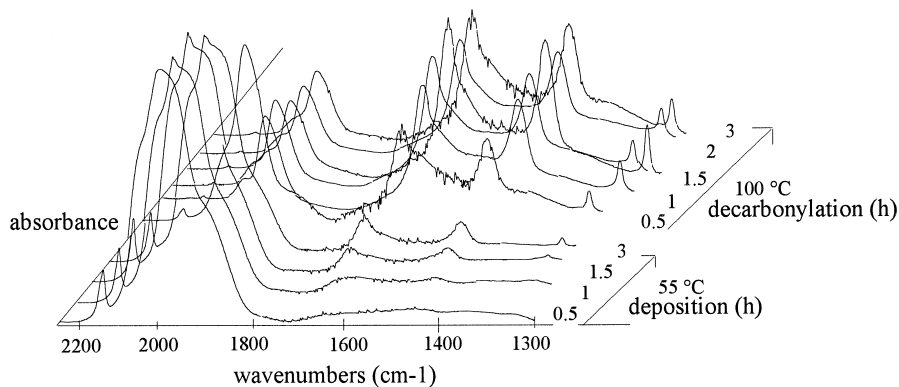


Fig. 6. Chromium hexacarbonyl supported on alumina (alu500): deposition–decarbonylation.

Table 2

IR frequencies of carbonate species on the surface of a decarbonylated $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ sample

Carbonate species	IR (cm^{-1}), in the literature [50]	IR (cm^{-1}), in this study
Unidentate	1530 (ν_{as}) 1370 (ν_{s})	1535
Bidentate	1730–1660 (ν_{as}) 1270–1230 (ν_{s})	1229
Bridged	1900–1750 (ν_{as}) 1180 (ν_{s})	not observed
Bicarbonate	3610–3605 (γ_{OH}) 1650–1639 (ν_{as}) 1490–1440 (ν_{s}) 1236–1226 (δ_{OH})	1649 1445 1229

shows, it is not clear exactly what happens in the $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ system during vaporization and decarbonylation, even though the reaction was observed at 0.5 h intervals.

Various carbonate species appear on the support when the $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ sample is decarbonylated, and the number of the vibrations is increased with time and temperature of deposition or decarbonylation. Table 2 lists the vibrations observed. As the carbonate region is relatively broad, it is not easy to decide to which carbonate species the vibrations belong. At first bicarbonate species were recognized at frequencies ~ 1649 , 1445 and 1226 cm^{-1} , and unidentate and bidentate carbonates at frequencies 1535 and 1229 cm^{-1} . No bridged carbonate species were observed. Following Brenner and Hucul [51,52], the carbonate species are due to the formation of CO_2 form in the reaction of two CO molecules on the alumina surface via the Boudouard mechanism. A somewhat different proposal, by Brown [53], is that CO_2 forms in a surface reaction between the support and the carbonyl precursor, with decarbonylation occurring as a competing reaction. A reaction between the decarbonylated CO-group and surface oxo group has also been proposed [54]. In a fluidized bed reactor system like ours, the carbonates are more likely to form as we describe, because in the fluidized system N_2 gas is cycled by the pump, and not all decarbonylated CO groups are removed by the bubbler. We have also observed that the alumina support affects

the amount of carbonates formed in the reaction.

4. Conclusions

There are many advantages to preparing $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ catalyst in a fluidized bed reactor. An even temperature can be achieved because the alumina particles are in constant motion in the reaction vessel and the large common area of the gas and solid particles ensures that the heat transfer rate is fast. The reaction can be scrutinized visually all the time since the reactor vessel and the vaporization system are made of glass. Constant observation is necessary to confirm that the fluidization is occurring evenly. The amount of catalyst prepared is relatively large (about 10 g), so several experimental tests can be carried out if necessary. Decarbonylation, which is used in the pulse technique to achieve higher chromium content, is easily done in the same reactor system. The whole reaction, including DRIFT analysis, can be carried out under N_2 atmosphere, so the system is suitable for air-sensitive reagents.

High chromium contents (about 1.3 wt.%) were achieved when the pulse technique was used with our fluidized bed reactor system. What happened during the reaction was easily followed with DRIFT spectra, and other analytical methods could have been applied for more detailed study. DRIFT spectra showed the pres-

ence on the surface of alumina at least of $\text{Cr}(\text{CO})_5$ and $\text{Cr}(\text{CO})_4$ species and physisorbed chromium hexacarbonyl. Alumina calcined for 10 h at 500°C adsorbed more chromium than alumina calcined for 10 h at 300°C . It can be assumed that favourable Al^{3+} adsorption sites are formed at the higher calcination temperature, allowing the chromium content to increase. Evidently, a monomolecular $\text{Cr}(\text{CO})_{6-x}$ ($x = 6-0$) forms on the surface of the alumina because the chromium content reaches a maximum during deposition. However, further study is required to confirm this.

References

- [1] S.J. Strieka, M. Houalla, A. Proctor, D.M. Hercules, *J. Phys. Chem.* 99 (1995) 1537.
- [2] M.A. Vuurman, F.D. Hardcastle, I. Wachs, *J. Mol. Catal.* 84 (1993) 193.
- [3] J.B. Peri, *J. Phys. Chem.* 78 (1974) 588.
- [4] M.A. Vuurman, I.A. Wachs, D.J. Stufkens, A. Oskam, *J. Mol. Catal.* 80 (1993) 209.
- [5] F.D. Hardcastle, I.E. Wachs, *J. Mol. Catal.* 46 (1988) 173.
- [6] F. Cavani, M. Koutyrev, F. Trifino, A. Bartolini, D. Ghisletti, R. Iezzi, A. Santucci, G. Del Piero, *J. Catal.* 158 (1996) 236.
- [7] S. De Rossi, G. Ferraris, S. Fermiotti, E. Garronne, G. Ghiotti, M.C. Campa, V. Indovina, *J. Catal.* 148 (1994) 36.
- [8] B.M. Weckhysen, I.E. Wachs, R.A. Schoonheydt, *Preparation of Catalysts VI*, 1995, p. 151.
- [9] S.J. Schrieka, M. Houalla, A. Proctor, D.M. Hercules, *J. Phys. Chem.* 99 (1995) 1537.
- [10] G. Ghiotti, E. Garronne, A. Zecchina, *J. Mol. Catal.* 46 (1988) 61.
- [11] N.E. Fouad, H. Knözinger, H.M. Ismail, M. Zaki, *Z. Phys. Chem.* 173 (1991) 201.
- [12] B. Rebenstorf, *Acta Chem. Scand.* 45 (1991) 1012.
- [13] D.S. Kim, I.E. Wachs, *J. Catal.* 142 (1993) 166.
- [14] H.L. Krauss, *J. Mol. Catal.* 46 (1988) 97.
- [15] J.A. Szymura, P.A. Zielinski, I.B. Dalla Lana, *Catal. Lett.* 15 (1992) 145.
- [16] R. Blom, A. Follestad, O. Noel, *J. Mol. Catal.* 91 (1994) 237.
- [17] B. Rebenstorf, *J. Mol. Catal.* 56 (1989) 170.
- [18] D.S. Kim, J. Tatibouet, I.E. Wachs, *J. Catal.* 136 (1992) 203.
- [19] C.S. Kim, I.H. Seong, *J. Mol. Catal.* 73 (1992) 249.
- [20] A. Ellison, T.A. Overton, *J. Mol. Catal.* 90 (1994) 81.
- [21] C.S. Kim, S.I. Woo, *J. Mol. Catal.* 73 (1992) 249.
- [22] C.S. Kim, S.I. Woo, D.J. Jeong, J.S. Oh, *Polym. Bull.* 29 (1992) 205.
- [23] K.P. Reddy, T.L. Brown, *J. Am. Chem. Soc.* 117 (1995) 2845.
- [24] A. Kazusaka, R.F. Howe, *J. Mol. Catal.* 9 (1980) 199.
- [25] Y. Iwasawa, *Tailored Metal Catalysts*, Reidel, Dordrecht, Holland, 1986.
- [26] A. Zecchina, C.O. Arean, *Catal. Rev.* 35 (1993) 261.
- [27] I.M. Baibich, J.H.Z. Dos Santos, *Can. J. Appl. Spectrosc.* 39 (1994) 18.
- [28] I.M. Baibich, F.C. Stedile, I.J.R. Baumvol, J.H.Z. Dos Santos, V.E. Santarosa, *Phys. Status Solidi* 192 (1995) 519.
- [29] W.M. Shirley, N. Abdul-Manan, J.S. Frye, *Inorg. Chem.* 27 (1988) 3846.
- [30] A. Kazusaka, R.F. Howe, *J. Catal.* 63 (1980) 447.
- [31] E.E. Platero, C.O. Arean, D. Scarano, G. Spoto, A. Zecchina, *Mater. Chem. Phys.* 29 (1991) 347.
- [32] E. Guglielminotti, *J. Mol. Catal.* 13 (1981) 207.
- [33] S.D. Kohler, J.G. Ekerdt, *J. Phys. Chem.* 98 (1994) 4336.
- [34] A. Brenner, D.A. Hucul, S.J. Hardwick, *Inorg. Chem.* 18 (1979) 1478.
- [35] H. Ang, K. Chan, G. Chuah, S. Jeanicke, S. Neo, *J. Chem. Dalton Trans.* (1995) p. 3753.
- [36] A. Zecchina, K.M. Rao, S. Coluccia, *J. Mol. Catal.* 53 (1989) 397.
- [37] E. Platero, M.P. Mentrut, *Inorg. Chem.* 33 (1994) 1506.
- [38] J.T. Richardson, *Principles of Catalysts Development*, Plenum, New York, 1989, p. 95.
- [39] S. Suvanto, T.A. Pakkanen, *J. Mol. Catal. A*, in press.
- [40] M. Kurhinen, T. Venäläinen, T.A. Pakkanen, *J. Phys. Chem.* 98 (1994) 10237.
- [41] H.H. Lamb, B.C. Gates, H. Knözinger, *Angew. Chem.* 27 (1988) 1127.
- [42] D.H. Lee, R.A. Condrate Sr., *Mater. Lett.* 23 (1995) 241.
- [43] C. Morterra, G. Magnacca, *Catal. Today* 27 (1996) 497.
- [44] A.A. Tsyganenko, P.P. Mardilovich, *J. Chem. Soc., Faraday Trans.* 92 (1996) 4843.
- [45] K. Smith (Ed.), *Solid Supports and Catalysis in Organic Synthesis*, 2nd edn., Ellis Horwood, Prentice Hall, New York, 1992.
- [46] C. Morterra, C. Emanuel, G. Cerrato, G. Magnacca, *J. Chem. Soc., Faraday Trans.* 88 (1992) 339.
- [47] H. Knözinger, P. Rantanmasy, *Catal. Rev. Sci.* 17 (1978) 31.
- [48] A. Zecchina, E.E. Platero, C.O. Arean, *Inorg. Chem.* 27 (1988) 102.
- [49] R.F. Howe, *Inorg. Chem.* 15 (1976) 486.
- [50] A.M. Turek, I.E. Wachs, E. De Canio, *J. Phys. Chem.* 96 (1992) 5000.
- [51] A. Brenner, D.A. Hucul, *J. Catal.* 61 (1980) 216.
- [52] A. Brenner, D.A. Hucul, *J. Am. Chem. Soc.* 102 (1980) 2484.
- [53] T.L. Brown, *J. Mol. Catal.* 12 (1981) 41.
- [54] V.E. Henrich, P.A. Cox, *The Surface Science of Metal Oxides*, Cambridge Univ. Press, 1994, p. 269.