

# Catalytic activity of CrCo/alumina catalyst in thiophene hydrodesulphurisation

Sari Myllyoja, Jarkko Rätty, Tapani A. Pakkanen\*

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

Received 27 September 1999; accepted 11 January 2000

## Abstract

Cr(CO)<sub>6</sub>/alumina catalysts promoted with Co<sub>2</sub>(CO)<sub>8</sub> were prepared in a fluidised bed reactor by vapour phase adsorption of zero valence metal carbonyls. Catalysts were characterised by diffuse reflectance IR spectroscopy. The catalytic activity was tested in thiophene hydrodesulphurisation (HDS) at 370°C in a batch reactor. Promising HDS results were achieved especially with the reduced bimetallic CrCo/alumina catalyst. The degree of sulphidation was determined after the HDS reaction. The reduction of the catalysts was also investigated by temperature programmed reduction (TPR). TPR and sulphidation results are in agreement with HDS experiments. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrodesulphurisation; HDS; Chromium hexacarbonyl; Cr(CO)<sub>6</sub>; Alumina; Al<sub>2</sub>O<sub>3</sub>; TPR

## 1. Introduction

The removal of sulphur, nitrogen, oxygen and metals from oil by reductive treatment in hydrotreating processes has been of paramount importance ever since oil first came into use as an energy source. Oil and oil products must be purified by hydrotreatment because most of the catalysts used in the further processing of oil products do not tolerate sulphur or metals. A further reason for this cleansing is to diminish the air-polluting emissions of sulphur and nitrogen oxides, which contribute to acid rain [1–4].

Commercial hydrotreatment catalysts generally consist of molybdenum or tungsten sulphides promoted with cobalt or nickel to enhance their activity [5]. In contrast to other group 6 transition metals, only in a few cases has chromium been used in hydrotreating processes, and then especially in hydrodesulphurisation (HDS) [6–10]. Instead, chromium-based catalysts have found wide application in dehydrocyclisation reactions, oxidation processes, the polymerisation of olefins and dehydrogenation reaction of alkanes and alkenes [11–15]. Oxide form CrCo/alumina catalysts are frequently used in heterogeneous oxidation, reduction and synthesis of organic compounds [16]. Chromium oxide supported on silica, also known as Philips catalyst, has been particularly widely studied because of its activity in polymerisation reactions [17–22].

\* Corresponding author. Tel.: +358-13-251-3345; fax: +358-13-251-3344.

*E-mail address:* [tapani.pakkanen@joensuu.fi](mailto:tapani.pakkanen@joensuu.fi) (T.A. Pakkanen).

We have investigated the activity of chromium hexacarbonyl supported on alumina and promoted with dicobalt octacarbonyl in the HDS reaction. Catalysts were prepared in a fluidised bed reactor by vapour phase adsorption of zero valence metal carbonyls. The catalysts were investigated by diffuse reflectance infrared Fourier transform (DRIFT). The HDS tests were made in a batch reactor. The degree of sulphidation was also determined. The reduction of the catalysts was studied by temperature programmed reduction (TPR). A commercial CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst was used as a reference catalyst.

## 2. Experimental

### 2.1. Reagents

Chromium hexacarbonyl (Aldrich Chemical) and dicobalt octacarbonyl (Fluka Chemie) were used as catalyst precursors without further purification. Cr(CO)<sub>6</sub> was vaporised on supports under nitrogen flow (AGA, 99.999%) and Co<sub>2</sub>(CO)<sub>8</sub> under carbon monoxide (Messer 99.997%). Co<sub>2</sub>(CO)<sub>8</sub> was handled inertly because of its air-sensitivity. Alumina oxide supports were  $\gamma$ -alumina of surface area 155 m<sup>2</sup>/g (Aldrich Bockman I) and 195 m<sup>2</sup>/g (Akzo Nobel). Supports were preheated under vacuum for 10 h at 500°C. Pre-treated supports and prepared samples were stored in a glove box.

Before the HDS reaction the catalysts were sulphided with 10% H<sub>2</sub>S/H<sub>2</sub> (AGA). The model sulphur compound was thiophene (> 99%, Aldrich). The HDS reaction was carried out under H<sub>2</sub> pressure (AGA 99.999%). Gases used in gas chromatography were H<sub>2</sub> (99.999%, AGA), CO<sub>2</sub> (99.7%, AGA), air (AGA) and He (99.9996%, AGA). Oxygen (99.999%, AGA) and argon (99.999%, AGA) were used in pulse chemisorption and a 10% H<sub>2</sub>/Ar mixture (AGA) was used in TPR.

### 2.2. Preparation of catalysts

The preparation of the catalysts has been described in Ref. [23] and the fluidised bed reactor has been reported in Ref. [24]. Table 1 summarises the conditions employed in the preparation. Cr(CO)<sub>6</sub>/alumina samples were prepared by the pulse method; chromium hexacarbonyl was vaporised on alumina at 55°C and each vaporisation pulse was followed by decarbonylation for 2 h at 150°C. The vaporisation–decarbonylation cycles were repeated for a total of five cycles in all. In the bimetallic catalysts CrCo, this sequence was followed by the vaporisation of Co<sub>2</sub>(CO)<sub>8</sub> for 5 h at 45°C. Part of the CrCo/Akzo and Cr/Akzo catalysts were furthermore reduced under H<sub>2</sub> flow for 5 h at 300°C. The reduction system has been described in detail in Ref. [25]. The reference CoMo catalyst was a commercial product.

Table 1

Preparation and metal contents of the catalyst samples. One cycle comprises vaporisation (under N<sub>2</sub>, 2 h at 55°C) and decarbonylation (under N<sub>2</sub>, 2 h at 150°)

Catalyst	Vaporisation conditions	Steps in the preparation	Cr (~ wt.%)	Co (~ wt.%)
Cr/Akzo	3 h/55°C	five cycles	1.0 1.5	–
Cr/Aldrich Cr/Akzo	3 h/55°C	five cycles and H <sub>2</sub> reduction (5 h/300°C)	1.0	–
CrCo/Akzo	Cr: 3 h/55°C	five cycles	1.0	0.3
CrCo/Aldrich	Co: 5 h/45°C	one Co pulse	1.5	0.5
CrCo/Akzo	Cr: 3 h/55°C	five cycles	1.0	0.3
	Co: 5 h/45°C	one Cr pulse and H <sub>2</sub> reduction (5 h/300°C)		
CoMo	–	commercial catalyst	Mo av. ~ 10.0	av. ~ 4.0

### 2.3. Characterisation

Metal contents were determined with an energy dispersive X-ray fluorescence spectrometer (ACAX 300 EDXRF). The EDXRF system was equipped with a solid-state Si(Li) detector. Fe(55) radioisotope was used as a source of radiation for Cr measurements and Cd(109) for cobalt. Resolution of the device was 0.15 keV. Measurement time was 100 s.

The amount of sulphur was determined by elemental analysis (EA 1110 CHNS-0) after the HDS experiments. Before analysis, the samples were washed several times with hexane. Heat was applied to remove unreacted thiophene.

Samples were analysed with a Nicolet Impact 400 D Fourier transform infrared spectrometer equipped with a diffuse reflectance device and a mercury–cadmium–tellurium detector. Resolution of the measurements was  $2\text{ cm}^{-1}$ . The spectra reported are difference spectra, from which the pure alumina spectrum has been subtracted. IR spectra were measured under nitrogen atmosphere by DRIFT technique with the DR apparatus enclosed in an IR glovebox with NaCl windows. The DRIFT system has been described in detail elsewhere [26].

Pulse chemisorption of  $\text{O}_2$  ( $\text{PC}(\text{O}_2)$ ) and TPR measurements were carried out in a Micromeritics ASAP 2910 analyser equipped with a thermal conductive detector (TCD). The weights of the samples were 0.5–1.0 g. The carrier gas was Ar in pulse chemisorption of  $\text{O}_2$  and a 10%  $\text{H}_2/\text{Ar}$ -mixture in TPR. During pulse chemisorption, the temperature of the oven was held constant at  $500^\circ\text{C}$ , and during TPR it was linearly ramped at  $10^\circ\text{C}/\text{min}$  to  $500^\circ\text{C}$ . The gas flow was controlled by mass flow controllers. The flow rate of the gases was 10 ml/min.

HDS activity measurements were made in a batch reactor. A detailed description of the batch reactor system can be found elsewhere [27]. The batch reactor system is easy to construct and the amounts of poisonous reactants can be restricted to a low level. The system is also suitable for the pre-tests of new catalyst candidates before

more detailed tests, e.g., by a flow reactor [27]. About 0.5 g of the catalyst sample, except the CoMo catalyst about 0.025 g, was weighed into the reactor vessel, which was closed tightly with a Teflon gasket. After evacuation the reactor was pressurised with 10%  $\text{H}_2\text{S}/\text{H}_2$  ( $\sim 2.0$  bar). The  $\sim$  catalyst was sulphided for 2.5 h at  $370^\circ\text{C}$ , the reactor was cooled and the 10%  $\text{H}_2\text{S}/\text{H}_2$  excess pressure was removed. Thiophene (0.2 ml) was used as the model sulphur compound, added to the reactor by a vacuum and heating method. The HDS reaction was carried out for 2.5 h at  $370^\circ\text{C}$  under  $\text{H}_2$  pressure ( $\sim 4.0$  bar). After the reaction, with the reactor at the temperature of  $150^\circ\text{C}$ , samples were removed for analysis by gas chromatography (HP 5980 Series II). The column was a high performance capillary column HP-1 (length 60 m, film thickness  $1.0\ \mu\text{m}$ , and diameter 0.25 mm), and the detector was a flame ionisation detector (FID).

## 3. Results and discussion

### 3.1. Amount of metals

Metal contents of the catalysts are presented in the Table 1. The way in which the amount of chromium changes during the pulse method has been described in Ref. [23]. After five pulses of chromium hexacarbonyl the amount of chromium deposited was about 1.0 wt.% on Akzo alumina and about 1.5 wt.% on Aldrich alumina. When dicobalt octacarbonyl (one pulse) was added after chromium hexacarbonyl, the amount of cobalt deposited was 0.3 wt.% when the support was Akzo alumina and 0.5 wt.% when it was Aldrich alumina. Although the area of the Akzo alumina was much greater, the amount of chromium supported on it was less than on the Aldrich alumina. Differences in pore structure may affect the degree of adsorption. The metal content of the commercial CoMo has been estimated as the average content of molybdenum (10.0 wt.%) and cobalt (4.0 wt.%).

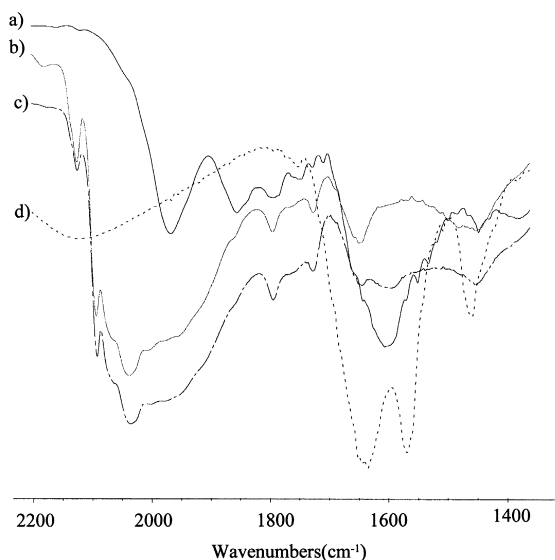


Fig. 1. IR spectra of samples prepared on Akzo alumina: (a)  $\text{Cr}(\text{CO})_6/\text{alumina}$ ; (b)  $\text{Co}_2(\text{CO})_8/\text{alumina}$ ; (c)  $\text{Cr}(\text{CO})_6 + \text{Co}_2(\text{CO})_8/\text{alumina}$ ; (d)  $\text{Cr} + \text{Co}/\text{alumina}$  after HDS reaction.

### 3.2. DRIFT characterisation

IR spectra in Fig. 1 present the carbonyl region after preparation steps of the  $\text{CrCo}/\text{alumina}$  catalyst. An earlier characterisation of the  $\text{Cr}(\text{CO})_6/\text{alumina}$  system is reported in Ref. [23]. There are different  $\text{Cr}(\text{CO})_6$ ,  $\text{Cr}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_4$  species on the alumina surface after the vaporisation step [28–30]. Additional car-

bonate species are formed having bands at  $1232 - 1724 \text{ cm}^{-1}$  [31–33]. The  $\text{Co}_2(\text{CO})_8/\text{alumina}$  spectrum is more complicated because of the many species on the alumina surface. The  $\text{Co}_2(\text{CO})_8/\text{alumina}$  exhibits bands for  $\text{Co}_2(\text{CO})_8$  but most of the bands are attributable to  $\text{Co}_4(\text{CO})_{12}$ . The  $\text{Co}_2(\text{CO})_8$  species is converted to  $\text{Co}_4(\text{CO})_{12}$ . There is also evidence of anionic  $\text{Co}(\text{CO})_4^-$  species [34–36].

### 3.3. HDS activity measurements

Table 2 lists the products (mol%) of the HDS reaction. In all catalyst cases, the main product was *n*-butane. With the  $\text{Cr}/\text{alumina}$  (Akzo) catalyst, 1-butene, *trans*-2-butene and ethyl acetylene were also formed in amounts under 10 mol%. With the  $\text{Cr}/\text{alumina}$  (Aldrich) catalyst, major products besides *n*-butane were *trans*-2-butene ( $\sim 10$  mol%), 1-butene ( $\sim 6$  mol%) and ethyl acetylene ( $\sim 6$  mol%). The amounts of  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_4$  hydrocarbons (mol%) are presented in Table 3. The majority of products were  $\text{C}_4$ -hydrocarbons (isobutane, 1-butene, *n*-butane, *trans*-2-butene, ethyl acetylene). The amounts of  $\text{C}_2$  (ethylene, ethane, acetylene) and  $\text{C}_3$  (propene, propane) were minor and about equal. The amount of hydrocarbons  $> \text{C}_4$  and impurities is small in all catalyst tests. Table 3

Table 2  
Products (mol%) in the HDS reaction (2.5 h, 370°C)

Products (mol%)	Cr/Akzo		Cr/Akzo, $\text{H}_2$ -reduction	CrCo/Akzo		CrCo/Akzo, $\text{H}_2$ -reduction	CoMo, commercial
	Cr/Aldrich			CrCo/Aldrich			
Ethylene	2.1	0.2	0.8	1.1	0.2	1.3	0.2
Ethane	7.4	–	0.5	–	–	–	–
Acetylene	4.7	1.6	5.8	3.8	0.5	2.3	0.5
Propene	3.0	0.3	0.9	0.1	0.5	2.7	0.1
Propane	3.5	0.5	3.6	2.8	–	–	0.3
Isobutane	–	0.1	3.2	3.4	0.1	2.3	–
1-Butene	6.0	3.9	2.5	0.8	1.1	0.2	0.3
<i>n</i> -Butane	12.6	28.6	30.7	61.8	68.3	81.1	90.1
<i>trans</i> -2-butene	10.1	9.5	6.2	2.0	2.8	0.5	1.2
Ethyl acetylene	6.1	6.3	3.7	1.1	1.8	0.3	2.5
Thiophene <sup>a</sup>	44.4	48.9	42.1	22.9	24.7	9.4	4.8

<sup>a</sup>Amount of unreacted thiophene after HDS reaction.

Table 3  
Amounts (mol%) of C<sub>2</sub>-, C<sub>3</sub>- and C<sub>4</sub>-hydrocarbons, the amount of sulphur after HDS and conversion (%) of thiophene

Catalyst	ΣC <sub>2</sub> (mol%)	ΣC <sub>3</sub> (mol%)	ΣC <sub>4</sub> (mol%)	Conversion of thiophene (%)	S (mmol)/metal (mmol) × 10 <sup>-3</sup> after HDS
Cr/Akzo	14.2	6.5	34.8	44.5	0.95
Cr/Aldrich	1.8	0.8	48.4	41.8	1.19
Cr/Akzo, H <sub>2</sub> -reduction	7.1	4.5	46.3	51.1	1.52
CrCo/Akzo	4.9	2.9	69.1	69.2	1.41
CrCo/Aldrich	0.7	0.5	74.1	67.7	0.98
CrCo/Akzo, H <sub>2</sub> -reduction	3.6	2.7	84.4	86.8	2.56

lists also the conversion of thiophene (%). With both Cr/Akzo and Cr/Aldrich, the conversion of thiophene was about 50%. When the sample Cr/Akzo was reduced with H<sub>2</sub> before H<sub>2</sub>S treatment, the activity of the catalyst increased: the amount of *n*-butane was ~ 30 mol%. Chromium and cobalt became oxidised during decarbonylation. Oxidation of metals could be eliminated when samples were treated under H<sub>2</sub> flow before the sulphidation treatment by H<sub>2</sub>S. With the CrCo catalyst, which is chromium hexacarbonyl supported on alumina and promoted with dicobalt octacarbonyl, the amount to *n*-butane increased dramatically: with CrCo/Akzo up to ca. 62 mol% and with CrCo/Aldrich to ca. 68 mol%. The amount of other products was small, while the conversion of thiophene was ca. 75%. When the catalyst CrCo/Akzo was reduced under H<sub>2</sub> flow, the amount of *n*-butane increased dramatically to

about 80 mol%. The reference catalyst was a commercial CoMo used generally in HDS. With the commercial CoMo/alumina catalyst, the amount of *n*-butane was 90 mol%. The amount of thiophene remaining after the HDS reaction was about 5 mol%.

Cr<sub>2</sub>S<sub>3</sub> and Co<sub>9</sub>S<sub>8</sub> species are formed in the case of pure Cr/alumina and Co/alumina during the sulphurisation step [2,9]. The situation becomes more complicated with the bimetallic CrCo/alumina catalyst. Table 3 presents the molar ratios of sulphur to metal. The experimental sulphur/metal ratio is close to the Cr<sub>2</sub>S<sub>3</sub> stoichiometry in the case of the reduced Cr/alumina (Akzo) catalyst. The sulphur to metal ratio is greatest (~ 2.6) in the case of reduced CrCo supported on Akzo alumina. This result agrees well with the HDS activity tests. This also suggests that a different CrCoS phase was formed in the case of the bimetallic CrCo/Akzo

Table 4  
Pulse chemisorption of oxygen (PC(O<sub>2</sub>)) and TPR; Cr, Co, Cr + Co supported on Akzo and Aldrich alumina

Catalyst	Amount of metal (wt.%)	PC(O <sub>2</sub> ) (500°C) total amount of O <sub>2</sub> (ml)/g sample	PC(O <sub>2</sub> ) (500°C) molar ratio: total amount of O <sub>2</sub> /amount of metal	TPR T <sub>max</sub> (°C)	TPR total amount of H <sub>2</sub> (ml)/g sample	TPR molar ratio: total amount of H <sub>2</sub> /amount of metal
Cr/Aldrich	1.5	0.79	0.16	380	1.74	0.25
Cr/Akzo	1.0	1.16	0.17	370	1.85	0.39
Co/Aldrich	0.9	0.47	0.13	320, 500	0.49	0.13
Co/Akzo	0.8	0.65	0.20	225, 500	0.43	0.13
CrCo/Aldrich	1.5/0.5	1.04	0.11	340	2.14	0.24
CrCo/Akzo	1.0/0.3	1.03	0.17	280	2.91	0.49

system when the catalyst was treated under a reductive atmosphere before the sulphidation treatment.

### 3.4. Pulse chemisorption of $O_2$ and TPR

TPR studies were done to determine whether there is a correlation between hydrogen intake

and the hydroprocessing activity of the CrCo/alumina catalyst. Because a part of the catalysts were treated under a hydrogen atmosphere during preparation, no reduction appears without oxidation treatment. The catalysts were oxidised therefore by pulse chemisorption before the reduction treatment. In the pulse chemisorption study, samples were exposed to

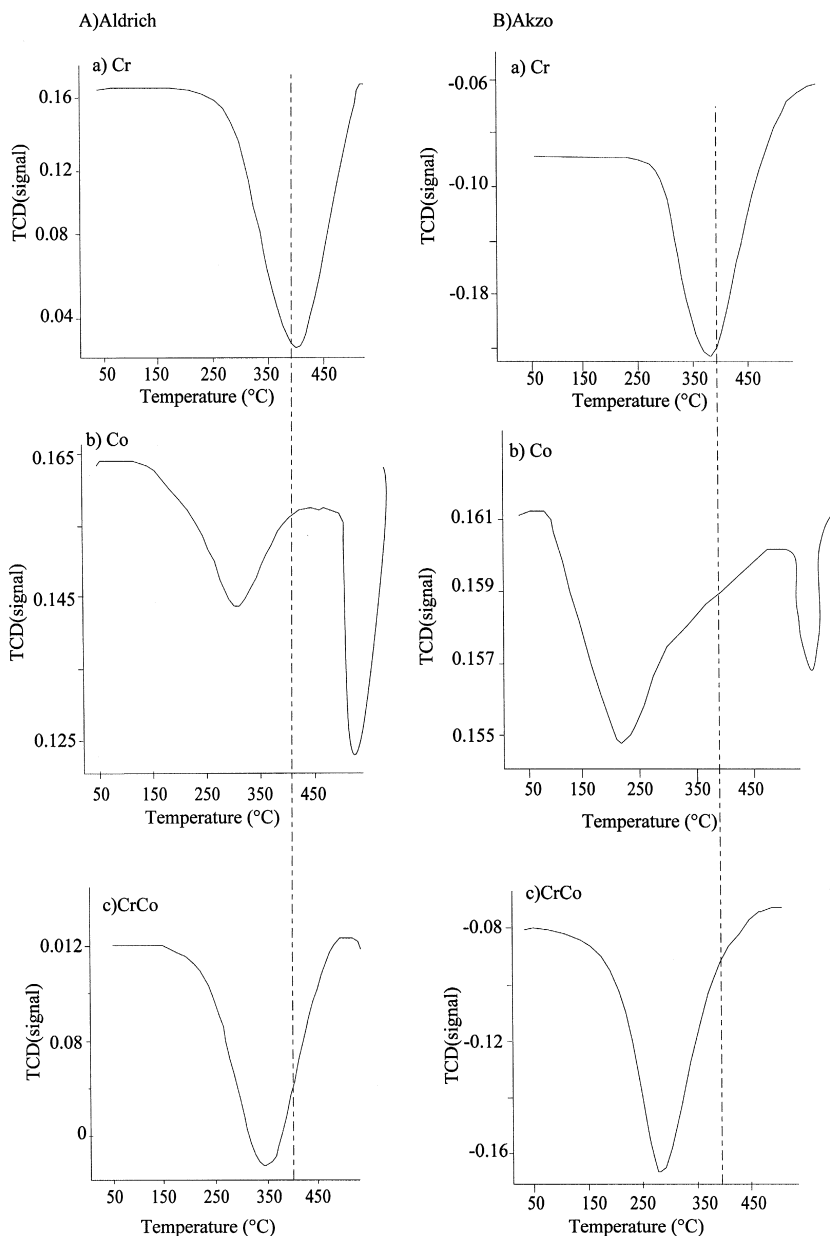


Fig. 2. Profiles recorded in the temperature programmed reduction of catalysts: (a) Cr, (b) Co and (c) Cr + Co supported on (A) Aldrich and (B) Akzo alumina. The temperature of the HDS reaction (370°C) is indicated.

pulses of oxygen and total intake of oxygen was measured as milligram per gram sample (Table 4). The molar ratio (total amount of O<sub>2</sub>/amount of metal) is also presented in Table 4. The molar ratio was the same (~ 0.17) both cases of chromium on alumina. Dicobalt octacarbonyl and bimetallic CrCo supported on the alumina surface adsorbed somewhat more oxygen in the case of the Akzo support. Differences in pore structure in the case of Akzo alumina may affect the consumption of oxygen.

Fig. 2 presents the TPR profiles for the supported catalysts. The HDS reaction temperature (370°C) is indicated. According to the literature, CrO<sub>3</sub>/alumina reduces at 330°C [37–39]. The chromium catalyst supported on alumina required higher temperature for reduction than the other catalysts: the temperature of the reduction was about 370–380°C. This indicates that there are different reduction sites than in the case of CrO<sub>3</sub> supported on alumina. When cobalt was supported on smaller surface area alumina (Aldrich), the temperature of the reduction was 320°C with another maximum at about 500°C. This is higher than for cobalt on higher surface area alumina (Akzo), where the temperatures of reduction were 225°C and 500°C. In the case of bimetallic CrCo catalysts, the temperatures of reduction were 340°C and 280°C, respectively. In every case except for cobalt, there was one reduction maximum, and the temperature of reduction was lower for the Akzo alumina support. The reduction temperature of the bimetallic systems was different from that of the monometallic systems, indicating that the activity sites were different. The consumption of hydrogen indicates also that reduction was different in the case of the bimetallic CrCo/alumina catalyst (Table 4).

#### 4. Conclusions

Chromium hexacarbonyl, promoted by dicobalt octacarbonyl was supported on different alumina by vapour phase adsorption. The metal

contents achieved were relatively low, even though the pulse method was used for preparation. More metal was adsorbed on the lower surface area alumina, indicating differences in the pore structure of the alumina supports.

The catalysis experiments in this work showed that the Cr/alumina system exhibits catalytic activity in HDS. The best results were achieved with the bimetallic CrCo catalyst supported on alumina when samples were reduced before the H<sub>2</sub>S treatment. *n*-Butane was produced as the main product with highest selectivity and the conversion of thiophene is ca. 90%. The sulphur/metal ratio was greatest in the case of the reduced CrCo supported on alumina corresponding to the best HDS activity. This also indicates that different CrCoS phases were formed in the case of the bimetallic CrCo/alumina system when the sample was reduced before the sulphidation step.

In both the monometallic and bimetallic systems, there was as a specific temperature where most of the reduction occurred. The maximum temperature of the reduction was different depending on alumina. The consumption of hydrogen indicates also that reduction was different in the case of the bimetallic CrCo/alumina catalyst.

There is evidence of synergy operating in the bimetallic catalyst, because the sulphidation and TPR results differ from those of the monometallic system. These findings are in agreement with HDS tests. Promising HDS results were achieved especially with the reduced bimetallic CrCo/alumina catalyst.

#### References

- [1] R. Prins, V.H.J. De Beer, G.A. Somorjai, *Catal. Rev. — Sci. Eng.* 31 (1989) 1.
- [2] R.R. Chianelli, *Catal. Rev. — Sci. Eng.* 26 (1984) 361.
- [3] P. Grange, *Catal. Rev. — Sci. Eng.* 21 (1980) 135.
- [4] T.S. Smit, K.H. Johnson, *J. Mol. Catal.* 91 (1994) 207.
- [5] B.T. Carvill, L.T. Thompson, *Appl. Catal.* 75 (1991) 249.
- [6] S. Harris, R.R. Chianelli, *J. Catal.* 98 (1986) 17.
- [7] J.K. Norskov, B.S. Clausen, H. Topsøe, *Catal. Lett.* 13 (1992) 1.

- [8] S. Harris, R.R. Chianelli, *J. Catal.* 86 (1984) 400.
- [9] J.P.R. Vissers, C.K. Groot, E.M. Van Oers, V.H.J. De Beer, R. Prins, *Bull. Chem. Chim. Belg.* 93 (1984) 813.
- [10] M. Sychev, V.H.J. De Beer, A. Kondentsov, E.M. Van Oers, R.A. Van Santen, *J. Catal.* 168 (1997) 245.
- [11] S.J. Schrieka, M. Houalla, A. Proctor, D.M. Hercules, *J. Phys. Chem.* 99 (1995) 1537.
- [12] S. De Rossi, G. Ferraris, S. Fermiotti, E. Garonne, G. Ghiotti, M.C. Campa, V. Indovina, *J. Catal.* 148 (1994) 36.
- [13] F. Cavani, M. Koutyrev, F. Trifiro, A. Barttolini, D. Ghisletti, R. Iezzi, A. Santucci, G. Del Piero, *J. Catal.* 158 (1996) 236.
- [14] F.D. Hardcastle, I.E. Wachs, *J. Mol. Catal.* 46 (1998) 173.
- [15] J.P. Peri, *J. Phys. Chem.* 78 (1974) 588.
- [16] M. Teodorescu, V. Georgescu, I. Sitaru, M.I. Vass, E. Segal, *Thermochimica Acta* 274 (1996) 307.
- [17] C.S. Kim, S.I. Woo, *J. Mol. Catal.* 73 (1992) 249.
- [18] G. Ghiotti, E. Garonne, A. Zecchina, *J. Mol. Catal.* 46 (1988) 61.
- [19] D.S. Kim, I.E. Wachs, *J. Catal.* 142 (1993) 166.
- [20] D.S. Kim, J. Tatibouet, I.E. Wachs, *J. Catal.* 136 (1992) 209.
- [21] J.A. Szymura, P.A. Zielinski, I.G. DallaLana, *Catal. Lett.* 15 (1992) 145.
- [22] M.A. Vuurman, I.E. Wachs, D.J. Stufkens, A. Oskam, *J. Mol. Catal.* 80 (1993) 209.
- [23] S. Myllyoja, T.A. Pakkanen, *J. Mol. Catal. A* 136 (1998) 153.
- [24] S. Suvanto, T.A. Pakkanen, *J. Mol. Catal. A* 125 (1997) 91.
- [25] M. Suvanto, T.A. Pakkanen, *Appl. Catal., A* 166 (1998) 105.
- [26] M. Kurhinen, T. Venäläinen, T.A. Pakkanen, *J. Phys. Chem.* 98 (1994) 10237.
- [27] M. Suvanto, J. Rätty, T.A. Pakkanen, *Appl. Catal., A* 181 (1999) 189.
- [28] A. Kazusaka, R.F. Howe, *J. Mol. Catal.* 9 (1980) 199.
- [29] A. Zecchina, E.E. Platero, C.O. Arean, *Inorg. Chem.* 27 (1988) 102.
- [30] A. Zecchina, C.O. Arean, *Catal. Rev. — Sci. Eng.* 35 (1993) 261.
- [31] A.M. Turek, I.E. Wachs, *J. Phys. Chem.* 96 (1992) 5000.
- [32] A. Brenner, D.A. Hucul, *J. Catal.* 61 (1980) 216.
- [33] A. Brenner, D.A. Hucul, *J. Am. Chem. Soc.* 102 (1980) 2484.
- [34] Y. Iwasawa, M. Yamada, Y. Sato, H. Kuroda, *J. Mol. Catal.* 23 (1984) 95.
- [35] R.L. Sweany, T.L. Brown, *Inorg. Chem.* 16 (1977) 415.
- [36] R.L. Schneider, R.F. Howe, K.L. Watters, *Inorg. Chem.* 23 (1984) 4593.
- [37] A. Rahman, M. Ahmed, in: M. Absi-Halabi (Ed.), *Catalysts in Petroleum Refining and Petrochemical Industries 1995*, Elsevier, 1996, p. 419.
- [38] B.M. Weckhysen, R.A. Schoonheydt, J. Jehng, I.E. Wachs, S.J. Cho, R. Ryoo, S. Kijlstra, E. Poels et al., *J. Chem. Soc., Faraday Trans.* 91 (1995) 3245.
- [39] N.E. Fouad, H. Knözinger, *Z. Phys. Chem.* 186 (1994) 231.