

## HYDRODESULPHURIZATION OF THIOPHENE OVER ZIRCONIA AND ALUMINA SUPPORTED Co-Mo CATALYSTS

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The zirconia supported CoMo catalysts and the commercial sample CoMo/Al<sub>2</sub>O<sub>3</sub> were characterized by XPS measurements and by testing of activity in the HDS of thiophene at 280°C and 1 MPa of total pressure. The XPS measurements revealed the better reducibility of molybdenum, higher sulphidability of cobalt and the absence of surface sulphur oxidation in the presence of zirconia support. The surface atomic concentration ratios S/Mo were 1.2 and 2.2 for zirconia and alumina supported catalysts, respectively. The activity of the zirconia supported CoMo catalyst normalized to the overall amounts of active metals was lower than that of the commercial CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst.

The majority of CoMo hydrorefining catalysts contain aluminium oxide as support. Owing to its distinct acid-base character it strongly interacts with catalyst precursor and influences the properties of resulting active phase such as dispersion, reducibility and intrinsic catalytic activity. Recently, the attention was turned to more inert type of supports, the use of which could overcome some drawbacks of alumina. In the case of active carbon, the lower coke formation and higher HDS activity was achieved and ascribed to the better dispersion of active components<sup>1</sup>.

From this point of view, only little attention has been so far paid to zirconium oxide as starting material for preparation of hydrorefining catalysts. In comparison to alumina, it is less acidic and weaker metal-support interaction could be supposed. For example, it was found that MoO<sub>3</sub> on zirconia can be more easily reduced than that deposited on alumina<sup>2</sup>. The results of oxygen chemisorption on zirconia supported MoO<sub>3</sub> catalyst obtained by Reddy et al.<sup>3</sup> showed higher dispersion of molybdenum achieved in comparison to alumina support. The activities in thiophene HDS and cyclohexene hydrogenation were parallel to oxygen chemisorption and they increased with molybdenum loading up to a monolayer capacity. The results obtained by Daly et al.<sup>4</sup> showed that initial activity of the presulphided CoMo/TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst had more than twofold activity than the commercial CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst HDS-20 in thiophene hydrodesulphurization at 300°C and atmospheric pressure; however, it declined rapidly because of coke formation. The results of ESR study<sup>5</sup> of the sulphided MoO<sub>3</sub>/ZrO<sub>2</sub> catalyst indicated the existence of sulphido-Mo(V) sites involved in HDS.

The aim of the present work was to characterize by XPS measurements the differences in the formation of Co and Mo surface species on zirconia and alumina supports and to compare the activity and selectivity of the zirconia supported Mo and CoMo catalysts in the HDS of thiophene with those of standard hydrorefining CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst.

## EXPERIMENTAL

**Catalysts.** The zirconium oxide was prepared by precipitation of ZrOCl<sub>2</sub> with ammonium hydroxide at 60°C. The precipitate was dried at 120°C and then calcined at 350°C for 3 h. The mixed zirconium–molybdenum oxide (sample 1, 4 mmol of Mo per gram) was obtained from Institute of Nuclear Research (Rež u Prahy, Czechoslovakia). The catalysts 2, 3, and 4 were prepared from these supports (particle size 0.1–0.25 mm) by impregnation with cobalt nitrate and (or) ammonium heptamolybdate water solutions in rotary evaporator under vacuum. The contents of active metals per one gram of catalysts were 1.31 mmol of Co and 2.47 mmol of Mo in the sample 2, 0.66 mmol of Mo in 3, 0.46 mmol of Co and 0.01 mmol of Mo in 4 and 0.41 mmol of Co and 0.58 mmol of Mo in 5. The standard CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst 6 was provided by National Physical Laboratory (Teddington, U.K.). It contained 0.41 mmol of Co and 0.83 mmol of Mo per gram and it was included in the set of catalysts studied for comparison. Before all measurements, the catalysts were sulphided by the mixture H<sub>2</sub>S/H<sub>2</sub> (1 : 10) at 300°C and atmospheric pressure for 1 h. The surface area of sulphided catalysts was determined by N<sub>2</sub> adsorption using the Nielsen–Eggertsen method<sup>6</sup>.

**XPS measurements** were carried out on ESCA 3Mk II VG Scientific apparatus using X-radiation corresponding to Al K<sub>α1,2</sub> line. The spectra were fitted by Gauss functions assuming linear background. Calculations of surface atomic concentrations were based on relation  $c \approx I \sqrt{E_k} / \sigma$ , where  $I$  is the line intensity,  $E_k$  is kinetic energy of photoelectrons and  $\sigma$  is photoionization cross-section<sup>7</sup>. Influence of electric charging of nonconductive samples was eliminated by setting of C 2s line position to the standard value 285 eV. The following XPS lines of all sample components found were recorded and treated: O 1s, S 2p, Al 2p, Zr 3d, Cl 2p (sample 4), Mo 3p and Co 2p.

**HDS activity of catalysts.** The activities of catalysts in the HDS of thiophene were determined at reaction temperature 280°C and 1 MPa of total pressure in the stainless steel flow reactor with fixed bed of catalyst<sup>8</sup>. The apparatus permitted in situ catalyst sulphidation and on-line GC analysis (FID detector) of the feed and reaction products. The feed contained thiophene at the partial pressure 0.6 kPa in hydrogen compressed to 1 MPa. After catalyst presulphidation, the feed was introduced at 280°C and 1 MPa of pressure (0.4 mol per hour). The steady state was usually achieved after 1 h and then the conversion of thiophene in C<sub>4</sub> hydrocarbons were evaluated. The first order rate constants  $k_{\text{HDS}}$  calculated from the conversion data were taken as the measure of the HDS activities.

## RESULTS AND DISCUSSION

The surface concentrations of elements controlling catalyst activity evaluated from the XPS measurements and the HDS activity of catalysts are summarized in Table I.

Two lines of molybdenum were observed in the XPS spectra of most samples. According to the literature<sup>9</sup>, they correspond to the Mo<sup>4+</sup> cation coordinated by S<sup>2-</sup>

anions (394.9 eV) and to the  $\text{Mo}^{6+}$  cation in the neighborhood of  $\text{O}^{2-}$  anions (398.4 eV). The rather broad simple peak at 379.1 eV was found in the spectrum of sample 4 which corresponds probably to the  $\text{Mo}^{5+}$  valency state<sup>9,10</sup>. From comparison of the  $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$  concentrations it follows that roughly 30% of surface molybdenum was reduced to the  $\text{Mo}^{4+}$  species in the  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst. This fraction was much higher on zirconia support where it varied in the range 50–65% confirming the better reducibility of molybdenum deposited on zirconium oxide.

The XPS spectra of cobalt in zirconia supported catalysts differ significantly from those of  $\text{CoMo}-\text{Al}_2\text{O}_3$  catalyst. All cobalt containing samples showed a parent line and broad satellite ( $\text{ZrO}_2$  support: 781.3 eV, +3.4 eV;  $\text{Al}_2\text{O}_3$  support: 781.6 eV, +5.5 eV) which may be clearly ascribed to  $\text{CoO}$  (see ref.<sup>11</sup>). On zirconia one more line at 778.4 eV was observed originating from  $\text{Co}_9\text{S}_8$  species<sup>12–14</sup>. Both oxidic and sulphidic species are known to be present in the sulphided  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalysts, the ratio of which depends on cobalt loading and conditions of sulphidation<sup>15</sup>. In our sample of the  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst we did not find the  $\text{Co}_9\text{S}_8$  species, which we explain by relatively low temperature of sulphidation<sup>15</sup>. Owing to its presence in all other catalysts, we conclude that sulphidation of cobalt proceeds more easily on zirconium oxide than on alumina support.

All the catalysts based on zirconium oxide contain sulphur in the form of sulphide anion<sup>16</sup> (line at 161.8 eV) exclusively. On the other hand, the  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst contains sulphur both in the form of sulphide and of sulphate<sup>16</sup> (162.5 and 168.8 eV) the latter as a consequence of surface oxidation of catalyst during storage. The surface oxidation of the sulphided  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst was often observed earlier<sup>16,17</sup>; the amount of sulphur converted to the sulphate anion reached sometimes

TABLE I

Surface area ( $S$ ), XPS surface atomic concentrations ( $c$ ) and HDS activity ( $k_{\text{HDS}}$ ) of the catalysts

Catalyst	Composition	$S$ $\text{m}^2 \text{g}^{-1}$	$c, \%$					$k_{\text{HDS}}$ $\text{mmol}_{\text{TH}} \text{h}^{-1} \text{mmol}_{\text{metal}}$
			$\text{Co}_{\text{ox}}$	$\text{Co}_{\text{sulph}}$	$\text{Mo}^{4+}$	$\text{Mo}^{6+}$	S	
1	$\text{ZrO}_2-\text{MoO}_3$	18	0	0	13.4	7.2	25.3	0.06 <sup>c</sup>
2	$\text{ZrO}_2-\text{MoO}_3/\text{Co}$	13	7.2	1.5	8.4	5.8	25.7	0.14
3	$\text{ZrO}_2/\text{Mo}$	34	0	0	1.4	1.6	4.3	0.13 <sup>c</sup>
4	$\text{ZrO}_2/\text{CoMo}$	68	2.8	0.5	1.4 <sup>a</sup>	0	2.3	0.22
5	$\text{ZrO}_2/\text{CoMo}$	26	3.2	0.7	2.8	2.1	12.2	0.24
6	$\text{Al}_2\text{O}_3/\text{CoMo}$	200	0.8	0	0.4	0.9	2.9 <sup>b</sup>	1.37

<sup>a</sup> Probably the  $\text{Mo}^{5+}$  valency state, <sup>b</sup> in this sample 35% of sulphur has the form of sulphate anion, <sup>c</sup> small amount of tetrahydrothiophene was present.

up to 50%. Since the prepared catalysts were stored in the same way as the commercial sample, i.e. they were also exposed to air, we deduce that zirconium oxide behaves in respect to this oxidation quite differently than alumina support. Namely it suppresses this transformation completely.

The ratio between sulphur and molybdenum surface concentrations was at about 2.2 in the  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst. This value is in a good agreement with earlier findings<sup>16,18,19</sup> and it confirms the sulphided state of active phase under experimental conditions used. For all catalysts, we have found a clean-cut relation between surface of sulphur and active metals concentrations. Fig. 1 shows the good correlation of sulphur quantity with overall molybdenum and cobalt content using two-parameters least-square fit with respect to Eq. (1).

$$c(\text{S}) = a c(\text{Mo}) + b c(\text{Co}) \quad (1)$$

The coefficients  $a$  and  $b$  reflect the stoichiometry of the sulphidic phase and their values have been estimated to be equal to  $1.2 \pm 0.1$  and  $0.9 \pm 0.3$ , respectively. The coefficient  $b$  for the sulphided cobalt species matches up very well to the theoretical value  $8/9 = 0.89$  corresponding to the compound  $\text{Co}_9\text{S}_8$ . The atomic sulphur/molybdenum ratio  $a$  was somewhat lower than that for the  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst.

The zirconium oxide alone was practically inactive in the HDS of thiophene at our experimental conditions. The sample 1 and 3 containing molybdenum only had the lowest activities and they produced besides the  $\text{C}_4$  hydrocarbons small amount of tetrahydrothiophene (<2%). The impregnation of cobalt caused roughly two-fold increase in activity and significant suppression of tetrahydrothiophene formation. In this respect, zirconium oxide behaves similarly as alumina support.

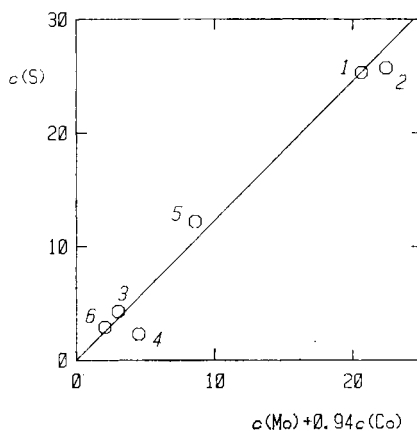


FIG. 1

The dependence of surface concentration of sulphur on surface concentrations of active metals (for designation of catalysts see Table I)

The samples 3,4, and 5 prepared by molybdenum deposition were more active than corresponding samples 1 and 2, in which large fraction of molybdenum is present in unaccessible bulk form. All the catalysts containing zirconium oxide as support displayed the lower HDS activity normalized to the unit amount of active metals than the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst (Table I). From this point of view, the zirconium oxide seems to be worse support for preparation of HDS catalysts than alumina.

The potential use of zirconium oxide could be advantageous in such cases where the better reducibility, easiness of sulphidation of active components and their non-sensitivity toward oxidation is desirable.

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