

## ACTIVITY AND SELECTIVITY OF CARBON-SUPPORTED TRANSITION METAL SULFIDES IN SIMULTANEOUS HYDRODEAROMATIZATION AND HYDRODESULFURIZATION

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Hydrodesulfurization (HDS) and hydrodearomatization (HYD) activities of carbon-supported sulfides of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ru, Rh, Pd, W, Re, Ir, and Pt, and of the commercial Co-Mo/Al<sub>2</sub>O<sub>3</sub> and Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts were evaluated. Simultaneous hydrodesulfurization of benzothiophene and hydrogenation of naphthalene to tetralin at pressure of 2 MPa were used as the model reactions. Platinum group metal sulfides and Re sulfide exhibited the highest HDS activity and Pd and Rh sulfides reached the activity of a good commercial Ni-Mo catalyst. The catalysts strongly differed in the selectivity of dihydrobenzothiophene formation during HDS; up to 55% of dihydrobenzothiophene was obtained over W sulfide, while Rh, Ni, Co-Mo and Ni-Mo catalysts produced less than 8% of it. The highest HYD activity exhibited platinum group metal sulfides; the best were Ir and Pt sulfides which were four times and three times more active than the commercial Ni-Mo catalyst, respectively. The selectivity HDA/HDS depended strongly on the type of transition metal. The sulfides of W, Ir and Pt were much more selective for HYD than the Ni-Mo catalyst, and the Co-Mo sample showed by far the lowest HDA/HDS selectivity.

Hydrogenation of aromatic hydrocarbons in the presence of sulfur is still a problem. A number of transition metal catalysts are active in the hydrogenation at low temperature and pressure but they are highly sensitive to sulfur poisoning<sup>1</sup>.

Two ways are used industrially to reduce the content of aromatic hydrocarbons in sulfur-containing feedstocks by hydrogenation. The two-stage process consists of separate hydrodesulfurization of the first step, followed by hydrogenation of aromatic hydrocarbons over more active but sulfur-sensitive metallic catalysts.

The second possibility is one-step hydrogenation process using sulfidic Co-Mo, Ni-Mo or Ni-W catalysts. However, these catalysts require the temperatures above 300°C which are unfavourable for the equilibrium and the effect of high temperature must be compensated by increased hydrogen pressure<sup>2</sup>.

The need for hydrodearomatization catalysts active in the presence of sulfur under mild conditions seems to grow recently. Two important applications can be mentioned. The synthetic crudes from coal or oil sands are highly aromatic and must be partially hydrogenated before they can be used as the feed in usual refineries<sup>3-5</sup>. There are proposals to lower the limit of aromatics in diesel fuel in order to reduce the smoke emissions<sup>6,7</sup>. These targets are not achievable with the current generation of the industrial hydrorefining Co-Mo, Ni-Mo and Ni-W catalysts at the pressure below 4 MPa.

The catalytic properties of the conventional sulfidic systems Co-Mo, Ni-Mo and Ni-W are well described in the literature. The catalysts Ni-Mo and Ni-W possess higher hydrodearomatization activity and higher HDA/HDS selectivity than the Co-Mo system<sup>8-11</sup>. It was also reported that the hydrodearomatization activity of the Ni-Mo catalyst is improved by the addition of P (ref.<sup>12</sup>), or F (ref.<sup>13</sup>). It was concluded that the Ni-W system is still not fully optimized<sup>14</sup>; the activity of this catalyst is also promoted by F (ref.<sup>15</sup>).

It is usually believed that the hydrogenation activity of platinum group metals is poisoned by sulfur. However, some literature data suggest that this poisoning is by far not complete at higher hydrogen pressures and at increased temperature, and that the sulfur tolerance of these metals can be improved by a proper carrier. For instance, platinum metals on a special support exhibited a reasonable activity at 5.6 MPa and 320°C up to the content of sulfur in the feed of about 200 ppm (ref.<sup>16</sup>); benzene containing 1 000 ppm of sulfur was hydrogenated over a Pd/alumina catalyst at 10 MPa and 270°C (ref.<sup>17</sup>).

The recent work on the hydrodearomatization of synthetic distillates<sup>18</sup> reports on the application of large pore Ni/silica-alumina catalysts containing about 50% of nickel. However, this is a special approach not concerning the steady state activity. The high capacity of the catalysts to adsorb sulfur and the low content of sulfur in the feed (69 ppm) allowed to retain the high degree of dearomatization for several hundreds hours on stream; the eventual saturation of the catalyst bed by sulfur led to the complete poisoning at the conditions used (3.5 MPa, 200–300°C).

The purpose of the present work was to study the catalytic properties of a broad series of transition metal sulfides in simultaneous hydrodearomatization and hydrodesulfurization. Such information is not available in the literature. The prime aim was to compare unmodified sulfides; active carbon was chosen as a support in order to avoid specific interactions with a more active carriers. The hydrodesulfurization of benzothiophene and the hydrogenation of naphthalene to tetralin were chosen as the model reactions. The comparison included 15 carbon-supported transition metal catalysts and also commercial Ni-Mo/Al<sub>2</sub>O<sub>3</sub> and Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. The interest was concentrated more on the HDA/HDS selectivity and less on activity features because the selectivity depends less on details of preparation of the catalyst than activity and can consequently be more easily generalized.

## EXPERIMENTAL

*Catalysts.* Carbon-supported catalysts Me-S/C contained 0.83 mmol of the active metal Me per gram of catalyst. They were prepared by the impregnation of the active carbon GA-1, produced by Slovenské lučobné závody, Czechoslovakia, with the BET surface area 960 m<sup>2</sup> g<sup>-1</sup>. The carbon was crushed and sieved to the particle size fraction 0.2–0.3 mm. The metal compounds used for the impregnation were (crystal water omitted): NH<sub>4</sub>VO<sub>3</sub>, Cr(NO<sub>3</sub>)<sub>3</sub>, MnCl<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, NbCl<sub>5</sub>, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, RuCl<sub>3</sub>, RhCl<sub>3</sub>, PdCl<sub>2</sub>, (NH<sub>4</sub>)<sub>10</sub>.H<sub>2</sub>(W<sub>2</sub>O<sub>7</sub>)<sub>6</sub>, NH<sub>4</sub>ReO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>IrCl<sub>6</sub>, H<sub>2</sub>PtCl<sub>6</sub>. The slurry of the carrier with the water solution of the metal salt was dried at 80°C in a rotary vacuum evaporator. The samples were not calcined and were sulfided in situ at atmospheric pressure by the mixture of 10 vol. % of H<sub>2</sub>S in H<sub>2</sub>; the temperature was gradually increased during 1 h to 400°C and kept constant 1 h at 400°C.

The commercial bimetallic catalysts were Shell 324, Ni-Mo/Al<sub>2</sub>O<sub>3</sub> containing 1.66 mmol of metals (Ni + Mo) per gram of catalyst, and Cherox 3601, Co-Mo/Al<sub>2</sub>O<sub>3</sub> containing 1.50 mmol

of metals (Co + Mo) per gram of catalyst. They were crushed and sieved to the particle size fraction 0.16–0.35 mm and were sulphided in the same way as the carbon-supported samples.

*Apparatus.* The catalytic properties were measured in a tubular flow reactor with 4 mm i.d. at the total pressure of 2 MPa. The composition of the liquid feed was in mole %: decane 92, durene 2, benzothiophene 3, and naphthalene 3. The liquid part of the reaction product was frozen out at  $-20^{\circ}\text{C}$ ; the efficiency of the condenser was checked by blank experiments without the catalyst in the reactor. The liquid samples were taken out in 10 min intervals and were analyzed by GLC under the following conditions: column length 3.5 m, temperature  $200^{\circ}\text{C}$  and packing 5% Carbowax 20M on Chezasorb. The following acronyms are used in this paper: benzothiophene BT, dihydrobenzothiophene DHBT, hydrogen sulfide HS, naphthalene NA, tetralin TE.

*Procedure.* The integral data  $x = f(W/F)$  were measured, where  $x$  is conversion,  $W$  catalyst weight, and  $F$  feed rate. The range of conversions was 0.05–0.95 and the definition of them was as follows: the overall conversion of BT to DHBT and hydrogen sulfide HS,  $x(\text{BT}) = (n^0(\text{BT}) - n(\text{BT}))/n^0(\text{BT})$ ; the conversion of BT to DHBT,  $x(\text{DHBT}) = n(\text{DHBT})/n^0(\text{BT})$ ; the conversion of NA to TE,  $x(\text{TE}) = n(\text{TE})/n^0(\text{NA})$ , where  $n$  and  $n^0$  were the final and initial number of moles, respectively. The hydrogenation of durene and tetralin was negligible (the conversions were lower than 0.03) at all conditions used. The reactivity of BT was much higher than that of NA and it was not possible to determine HDS and HYD activities at the same temperature. The catalyst charge,  $W$  (mmol (Me)), was presulfided *in situ* and the temperature was decreased from  $400^{\circ}\text{C}$  to  $300^{\circ}\text{C}$  in the flow of the  $\text{H}_2\text{S}/\text{H}_2$  mixture at atmospheric pressure. The sulfiding mixture was exchanged for hydrogen ( $0.3 \text{ mol h}^{-1}$ ), the pressure was increased to 2 MPa, and the feed of the reaction mixture started in such a rate that  $F(\text{BT}) = 2.3 \text{ mmol}(\text{BT}) \cdot \text{h}^{-1}$ . The conversions  $x(\text{BT})$  and  $x(\text{DHBT})$  were determined;  $x(\text{NA})$  was always lower than 0.03 at this temperature. Then the temperature was increased to  $350^{\circ}\text{C}$  and the feed rate of the liquid was decreased to  $F(\text{NA}) = 0.6 \text{ mmol h}^{-1}$ . The conversion  $x(\text{TE})$  was determined;  $x(\text{BT})$  was always higher than 0.97 at this temperature (the only exception was the Mn/C catalyst which exhibited very low activity). The value  $W/F$  was varied using different charges of catalyst  $W$ . The steady-state conversions were achieved after 10–20 min of the feeding at any conditions used.

## RESULTS

The conditions of the measurement are summarized in Table I. Seventy runs with different charges of various catalysts were made, which means that the integral kinetic curve for each reaction and for each catalyst was determined by 3–5 points in the range of conversions  $x(\text{BT})$  and  $x(\text{NA})$  0.05–0.95. An example of the curves for the Co/C catalyst is shown in Fig. 1.

The extent of the formation of dihydrobenzothiophene intermediate during the reaction of benzothiophene was dependent on the type of catalyst; the maximum value of observed  $x(\text{DHBT})$  varied from about 0.02 for the Ni–Mo/ $\text{Al}_2\text{O}_3$  catalyst up to 0.55 for the W/C sample.

The hydrodesulfurization activity of the catalysts was evaluated from the dependences  $x(\text{HS}) = f(W/F(\text{BT}))$ . The experimental points were well fitted by the equation

$$x(\text{HS}) = 1 - \exp(-k(\text{HDS}) W/F(\text{BT})), \quad (1)$$

where  $k(\text{HDS})$  is the apparent rate constant, characterizing the HDS efficiency of the catalyst. The quality of the fit is illustrated in Fig. 1 for the catalyst  $\text{Co/C}$  and was similar for all other catalysts.

The extent of the formation of intermediate dihydrobenzothiophene during the hydrodesulfurization of benzothiophene was characterized by the integral selectivity parameter  $I(\text{DHBT})$ , defined by the equation

$$I(\text{DHBT}) = \int_0^1 x(\text{DHBT}) d(x(\text{BT})), \quad (2)$$

TABLE I  
The reaction conditions

Reaction	Initial partial pressure, kPa					Temperature °C
	H <sub>2</sub>	BT	NA	DU	DE	
Hydrodesulfurization of benzothiophene	1 587	12	12	8	381	300
Hydrogenation of naphthalene	1 871	4	4	3	118	350

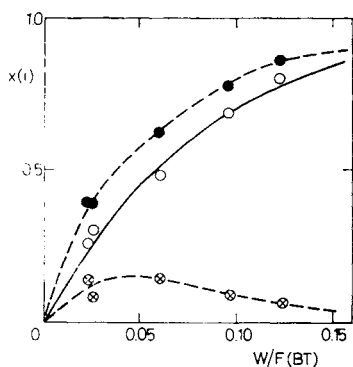


FIG. 1  
Hydrodesulfurization of benzothiophene over  $\text{Co/C}$  catalyst. ●  $x(\text{BT})$ , ○  $x(\text{HS})$ , ⊗  $x(\text{DHBT})$ ; — calculated according to the Eq. (1) and  $k(\text{HDS})$  in Table II, --- graphical interpretation; the dimension of  $W/F$  is  $\text{mmol}(\text{Me}) \text{ h} (\text{mmol}(\text{BT}))^{-1}$

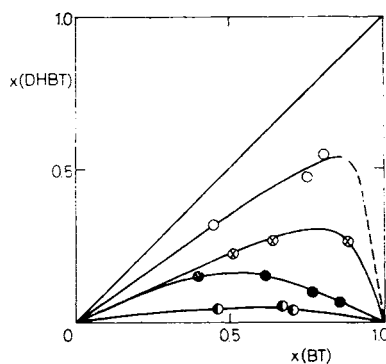


FIG. 2  
The examples of the curves used for graphical evaluation of the integral selectivity of DHBT formation; the value of  $I(\text{DHBT})$  is given by the area under the curve. ○  $\text{W/C}$ , ⊗  $\text{Mo/C}$ , ●  $\text{Co/C}$ , ●  $\text{Rh/C}$

and the meaning of it is illustrated in Fig. 2. It is seen that this parameter can theoretically vary in the range 0–0.5. No dihydrobenzothiophene is desorbed during the hydrodesulfurization of benzothiophene over the catalyst with  $I(\text{DHBT}) = 0$ . On the other hand, during the reaction over the catalyst with  $I(\text{DHBT}) = 0.5$ , all benzothiophene in the feed is hydrogenated to dihydrobenzothiophene before any hydrogen sulfide appears in the gas phase.

The activity of the catalyst in the hydrogenation of naphthalene to tetralin was evaluated by the fitting the experimental points  $x(\text{TE}) - W/F(\text{NA})$  to the equation

$$x(\text{TE}) = 1 - \exp(-k(\text{HYD}) W/F(\text{NA})), \quad (3)$$

where  $k(\text{HYD})$  is the apparent rate constant characterizing the hydrodearomatization efficiency. It should be recalled that the consecutive hydrogenation of tetralin to decaline was negligible under all conditions used.

The obtained catalytic parameters are summarized in Table II.

TABLE II

Activity and selectivity properties of sulfide catalysts in hydrodesulfurization of benzothiophene and hydrogenation of naphthalene

Metal	Activity <sup>a</sup>		Selectivity <sup>b</sup>	
	$k(\text{HDS})$	$k(\text{HYD})$	$I(\text{DHBT})$	$k(\text{HYD})/k(\text{HDS})$
V	6	1.2	0.15	0.20
Cr	4	1.4	0.16	0.35
Mn	1	0.2	0.11	0.20
Fe	3	0.6	0.13	0.20
Co	12	1.7	0.09	0.14
Ni	5	0.7	0.05	0.14
Nb	3	0.5	0.14	0.17
Mo	12	2.5	0.18	0.21
Ru	12	6.1	0.07	0.51
Rh	58	18.1	0.03	0.31
Pd	71	13.8	0.10	0.19
W	2	2.3	0.32	1.15
Re	29	5.3	0.13	0.18
Ir	42	35.0	0.15	0.83
Pt	35	27.2	0.09	0.78
Ni-Mo/Al <sub>2</sub> O <sub>3</sub>	79	9.3	0.01	0.13
Co-Mo/Al <sub>2</sub> O <sub>3</sub>	34	1.2	0.03	0.04

<sup>a</sup> Activity parameters are in  $(\text{mmol h}^{-1} (\text{mmol}(\text{Me}))^{-1})$ ; <sup>b</sup> selectivity parameters are dimensionless.

## DISCUSSION

The main purpose of the present work was the relative evaluation of the selectivity properties of transition metal sulfides. The selectivity is much less dependent on the method of catalysts preparation and on the conditions of testing than the relative order of activity. Only the most pronounced features of the activity will be discussed here.

*Hydrodesulfurization activity.* Several previous comparative studies on transition metal sulfides dealing only with HDS but not with HYD activities have been summarized elsewhere<sup>11</sup>. The sulfides were divided into three, although not sharply separated groups: a) the platinum group metal sulfides and Re sulfide, with high activity, b) the sulfides of Fe, Co, Ni, Cr, Mo, and W, with medium activity, and c) the sulfides of Ti, V, Mn, Zr, Nb, and Ta, with low activity. Our data in Table II agree with this classification.

However, a more detailed order of the activities is not possible to arrange. For instance, two previous studies on HDS of thiophene at atmospheric pressure over carbon-supported catalysts reported different sequences of the activity of platinum group metal sulfides: Ir > Rh > Ru > Pt > Pd (ref.<sup>19</sup>), and Rh > Ir ≫ Ru > Pd > Pt (ref.<sup>20</sup>). Our data in Table II obtained with benzothiophene at increased pressure give another sequence: Pd > Rh > Ir > Pt > Ru.

In contradistinction to previous comparative studies on carbon-supported sulfides, the specific feature of our work was that it included the commercial bimetallic alumina-supported samples. The results in Table II show that the activity of Pd/C and Rh/C catalysts is of the same rank as the activity on the Ni-Mo Shell 324 catalyst, which is considered to belong to the best commercial products. Our results on carbon-supported catalysts thus agree with the generalization of data on catalysts with other supports, that platinum group metal sulfides and also rhenium sulfide are the only monometallic sulfides which have HDS activities similar to, or higher, than the bimetallic commercial systems<sup>11</sup>.

*Hydrodearomatization activity in the presence of sulfur.* There is only one recent comparative study of the hydrodearomatization activity of transition metal sulfides<sup>21</sup>. It used alumina-supported catalysts with the loading 0.25 mmol(Me) g<sup>-1</sup> and the parallel hydrogenation of naphthalene and hydrodeoxygenation of diphenyl ether in the liquid phase at 14 MPa and 350°C. The results of that study are compared in Fig. 3 with our data from Table II. The only possible conclusion is the classification of sulfides into broad groups, similarly as it was made above in the case of the hydrodesulfurization activity: the platinum group metal sulfides and Re sulfide possess the high activity, and the sulfides of Fe, Co, Ni, Cr, and Mo possess the medium hydrodearomatization activity. The only exception to this rule is the low activity of Ru sulfide found by Shabtai and coworkers<sup>21</sup>.

The remarkable result seen in Table II is very high activity of Pt, Ir, Pd, and Ru sulfides as compared with the commercial bimetallic catalysts. This shows that the habitual opinion in the literature on the hydrodearomatization in the presence of sulfur over platinum metals is often incorrect. For instance, the recent discussion on the partial hydrodearomatization of diesel fuel<sup>7</sup> misquotes: "The very best (hydrodearomatization catalysts) that are noble metal catalysts are, in fact, sulfur poisoned". This statement is only valid for the mild conditions of low temperature and pressure. Our data in Table II prove that at the more severe conditions typically used for bimetallic Ni-Mo, Co-Mo and Ni-W systems, some platinum metal sulfides should be classified as the best catalysts known.

*Selectivity of the DHBT formation during HDS of BT.* The extent of the formation of dihydrobenzothiophene during the hydrodesulfurization of benzothiophene is characterized by the parameter  $I(\text{DHBT})$  in Table II. The theoretically possible limits of it are 0 and 0.5. Table II shows that the catalysts differed very strongly in this respect. The very low selectivity  $I(\text{DHBT})$  exhibited sulfides of Rh and Ni, the highest  $x(\text{DHBT})$  was about 0.04–0.08. On the other hand, tungsten sulfide was very selective for the DHBT formation, the maximum  $x(\text{DHBT})$  on it was about 0.55. The thermodynamic data on the partial equilibrium  $\text{BT-DHBT-H}_2$  at the temperature of our measurement of 300°C are not available in the literature. However, the equilibrium data<sup>22,23</sup> at 270°C suggest, that this partial equilibrium was attained over tungsten catalyst in the present work.

The commercial bimetallic Ni-Mo and Co-Mo catalysts exhibited practically no formation of DHBT under given conditions and their selectivity  $I(\text{DHBT})$  was considerably lower than that of monometallic catalysts. The decrease of the selectivity accompanying the mixing of Ni or Co sulfides with Mo sulfide is connected with the synergistic effect in these bimetallic systems and is discussed elsewhere<sup>11,22,24</sup>.

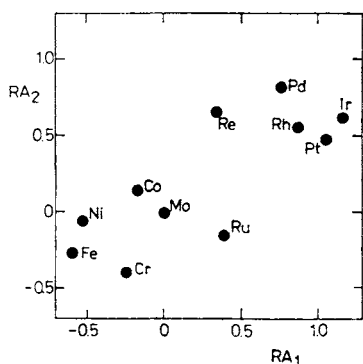


FIG. 3

Comparison of the relative activities,  $RA$ , of sulfided catalysts in hydrogenation of naphthalene to tetralin, found in the present work and reported in ref.<sup>21</sup>.  $RA_1 = \log . . (k(\text{HYD}, i)/k(\text{HYD}, \text{Mo}))$ ,  $k(\text{HYD})$  are from Table II;  $RA_2 = \log (k_2(i)/k_2(\text{Mo}))$ ,  $k_2(i)$  are from ref.<sup>21</sup>; all constants are normalized to  $\text{mmol}(\text{Me})$

*Selectivity HDA/HDS.* This selectivity was defined here as the ratio of the rate parameters obtained at different temperatures (HDA at 350°C and HDS at 300°C). The reason for it was the well known difficulty of the measurement of the HDA and HDS activities at the same temperature (for the experience of other authors see e.g.<sup>2,5</sup>). However, our non-isothermal index  $k(\text{HDA})/k(\text{HDS})$  is equally justifiable as the ratio of rate constants for the same temperature; the evaluation of the selectivity is temperature dependent in both cases.

The Ni-Mo catalyst is known to have higher HDA/HDS selectivity than the Co-Mo system<sup>11</sup>. Our data in Table II are in full agreement with this generally proven fact. However, the data in Table II further show that the selectivity changes with the type of transition metal in the much broader range than is the difference between Co-Mo and Ni-Mo catalysts. The Co-Mo catalyst seems to represent the lower limit of the HDA/HDS selectivity achievable with any type of catalyst; no other catalyst in Table II was more selective to HDS. On the other hand, the HDA/HDS selectivity of the Ni-Mo catalyst is clearly far from the upper limit of the selectivity; this upper limit is represented by tungsten sulfide according to Table II.

The high HDA/HDS selectivity of tungsten sulfide occurred at the relatively low level of activity. Iridium and platinum sulfides exhibited more interesting properties because the high selectivity to HDA occurred here at very high level of activity. The high selectivity was not a common property of all platinum group metals because palladium and also rhodium were very non-selective. The selectivity mostly increased from the 1st to the 3rd row metal sulfides; however, rhodium sulfide deviated strongly from this trend. No regularity was observed in selectivity changes in each row of Periodic Table.

The selectivity  $k(\text{HYD})/k(\text{HDS})$  did not correlate with the extent of DHBT formation given by  $I(\text{DHBT})$ . The behaviour of tungsten sulfide was unique in this respect because it had by far the highest values of both parameters simultaneously. However, Ir and Pt sulfides were very selective for HDA but formed only small quantities of DHBT. Molybdenum sulfide, on the other hand, was selective for DHBT but non-selective for HDA.

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