

## THE EFFECT OF $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> AND ZrO<sub>2</sub> SUPPORTS ON HYDRODESULFURIZATION ACTIVITY OF TRANSITION-METAL SULFIDES

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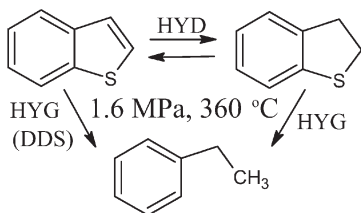
The transition metals V, Cr, Mn, Fe, Co, Ni, Mo, Ru, Rh, Pd, W, Re, Os, Ir and Pt were deposited from aqueous solutions of their salts onto conventional  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and unconventional TiO<sub>2</sub> and ZrO<sub>2</sub> supports by vacuum impregnation and characterized in their sulfided form by a model reaction of benzothiophene hydrodesulfurization. It was found that the TiO<sub>2</sub> and ZrO<sub>2</sub> supports influenced predominantly positively the resulting activity of relatively low-active metals (V, Cr, Mn, Fe, Co, Ni, Mo, Ru, W and Os), whereas the highly active metals (Rh, Pd, Ir, Pt and Re) were influenced slightly negatively or not at all by those supports compared with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported system. A significant effect of the supports on the hydrodesulfurization-activity ranking of the transition-metal sulfides studied was ascertained.

**Keywords:** Hydrodesulfurization; Transition-metal sulfides; Sulfide catalysts;  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; TiO<sub>2</sub>; ZrO<sub>2</sub>.

The industrially used catalytic systems for hydrodesulfurization (HDS) are CoMoS<sub>x</sub>, NiMoS<sub>x</sub> and NiWS<sub>x</sub> phases supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>1</sup>. Because of the continuous demand for the improvement of hydrodesulfurization catalysts, new supports and new active phases have been recently investigated. The effects of supports such as MgO, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, zeolites, mesoporous materials, activated carbon, and clays on HDS activities of the conventional phases have been summarized in the reviews<sup>2,3</sup>. Among them, TiO<sub>2</sub> and ZrO<sub>2</sub> supports exhibited promising features. Their textural properties such as specific surface area have been significantly improved in the last decade<sup>4-7</sup> and, nowadays, are not so far from those of traditional  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Furthermore, the HDS activities of the TiO<sub>2</sub>- and ZrO<sub>2</sub>-supported Mo sulfide species were more than twice as high as that of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> counterparts<sup>7-11</sup>. Taking into account that those supports exhibit practi-

cally the same acid-base properties as  $\text{Al}_2\text{O}_3$ <sup>2,12</sup>, whereas the MgO (silica)-based materials are significantly more basic (acidic) than alumina, the systematic research into the influence of the  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  supports on HDS activity of transition-metal sulfides is of great interest.

Nevertheless, the HDS activities of other than conventional transition metals were studied only to a limited extent: in the case of dibenzothiophene<sup>13</sup> (unsupported metals), thiophene<sup>14,15</sup> and 1-benzothiophene<sup>16</sup> (supported on activated carbons), thiophene<sup>17</sup> (supported on alumina), and a petroleum-based feed<sup>18</sup> (supported on alumina and silica). The purpose of the present work is to compare the activities of transition metals supported on commercially available  $\text{TiO}_2$  and  $\text{ZrO}_2$  with their  $\text{Al}_2\text{O}_3$ -supported counterparts. The hydrodesulfurization of 1-benzothiophene at elevated pressure was selected as a model test reaction (Scheme 1), because the reaction makes it possible to reflect on selectivity C–S hydrogenolysis/C=C hydrogenation. The aim was to study the influence of the supports on HDS activity ranking.



SCHEME 1

## EXPERIMENTAL

The extrudates of  $\text{Al}_2\text{O}_3$  (Akzo Chemicals HDS-000-1.5, Netherlands),  $\text{TiO}_2$  (Alfa Aesar, Product No. 44429, Germany) and  $\text{ZrO}_2$  (Alfa Aesar, Product No. 43815, Germany) were crushed and sieved to a particle size fraction of 0.16–0.32 mm. An amount of 5 g of the grains were impregnated from 10 ml of an aqueous solution of a transition metal (Me) precursor to deposit 0.215 mmol Me per gram of catalyst. The slurry of the support and impregnation solution was stirred with shaking for 1 h, then dried in a rotary vacuum evaporator at 95 °C and calcined in an air stream at 400 °C for 1 h with the temperature ramp 15 °C min<sup>-1</sup>.

The following metal precursors were used for the impregnation: (i) Aldrich, Germany:  $\text{Mn}(\text{NO}_3)_2$  (Product No. 203742),  $\text{OsCl}_3$  (Product No. 209066); (ii) Fluka AG, Germany:  $\text{NH}_4\text{VO}_3$  (Product No. 10030),  $(\text{NH}_4)_{10}\text{H}_2\text{W}_{12}\text{O}_{42}$  (Product No. 10040),  $\text{RuCl}_3$  (Product No. 84050); (iii) Lachema, Czech Republic:  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (purum),  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (purum),  $\text{Fe}(\text{NO}_3)_3$  (Product No. 1161),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (min. 99%, p.a.),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (purum); (iv) Safina Vestec, Czech Republic:  $\text{RhCl}_3$  (Product No. 160/D/66/53-Š041185),  $\text{PdCl}_2$  (Product No. 160/D/66/113-Š/21/85),  $\text{IrCl}_4$  (solution 69.8 g l<sup>-1</sup>),  $\text{H}_2\text{PtCl}_6$  (Product No.

160/D/66/112-Š6/85, solution 250 g l<sup>-3</sup>); (v) BDH, Great Britain: RuCl<sub>3</sub> (Product No. 30032); (vi) Schuchardt München, Germany: NH<sub>4</sub>ReO<sub>4</sub>.

N<sub>2</sub> adsorption isotherms were measured using a Micromeritics ASAP 2010M instrument over samples evacuated at 350 °C for 12 h. Specific surface area, S<sub>BET</sub>, were determined by the common Brunauer–Emmett–Teller (BET) procedure. The X-ray diffraction data were collected on a Philips X'Pert MPD system using CuKα radiation (40 kV, 40 mA) and a secondary graphite monochromator. The data were collected in the range of 10–70° 2θ, with the rate of measurement being 0.03° per 3 s.

1-Benzothiophene (BT) HDS was carried out in the gas phase in an integral fixed-bed tubular-flow reactor (i.d. 3 mm) at the total pressure 1.6 MPa. The composition of the starting reaction mixture was kept constant; the partial pressures of BT, decane and hydrogen were 16, 200 and 1384 kPa, respectively. The catalyst charge, *W*, varied from 0.02 to 1.2 g, depending on its activity. The reaction was run at 360 °C at three feed rates of BT, *F*<sub>BT</sub>: 7.7, 10.3 and 15.5 mmol h<sup>-1</sup>. A steady state was reached in 30 min after a change of the feed rate, and deactivation of the catalysts was not observed. The reaction mixture was analyzed on a Hewlett–Packard gas chromatograph (6890 Series) equipped with a capillary column HP-5 (30 m, 0.53 mm, 1.5 μm). The reaction products were dihydrobenzothiophene (DHBT) and ethylbenzene (EB). The following parameters were determined: relative composition of the reaction mixture, *a<sub>i</sub>* (*a*<sub>BT</sub> = *n*<sub>BT</sub>/*n*<sup>0</sup><sub>BT</sub>, *a*<sub>DHBT</sub> = *n*<sub>DHBT</sub>/*n*<sup>0</sup><sub>BT</sub>, *a*<sub>EB</sub> = *n*<sub>EB</sub>/*n*<sup>0</sup><sub>BT</sub>); or conversion, *x<sub>p</sub>*, overall conversion of BT (*x*<sub>BT</sub> = 1 - *a*<sub>BT</sub>); conversion of BT to DHBT (*x*<sub>DHBT</sub> = *a*<sub>DHBT</sub>) and conversion of BT to EB (*x*<sub>EB</sub> = *a*<sub>EB</sub>), where *n*<sup>0</sup> and *n* were the initial and final numbers of moles, respectively. The relative compositions *a*<sub>EB</sub> in the range 0.1–0.9 were taken for the determination of HDS activities (see Results and Discussion). Prior to the measurements, the catalysts were presulfided in situ in a H<sub>2</sub>S/H<sub>2</sub> flow (1:10) at a temperature ramp of 10 °C min<sup>-1</sup> to 400 °C and a dwell time of 1 h. The following industrial alumina-supported catalysts were used for comparing HDS activities: Mo (M8-30, BASF, Germany, 15.0 wt.% MoO<sub>3</sub>, 1.042 mmol Mo per gram of catalyst), CoMo (KF 756, Akzo Nobel, Netherlands, 3.2 wt.% CoO, 15.5 wt.% MoO<sub>3</sub>, 1.505 mmol Co + Mo per gram of catalyst) and NiMo (KF 846, Akzo Nobel, Netherlands, 3.1 wt.% NiO, 20.7 wt.% MoO<sub>3</sub>, 1.853 mmol Ni + Mo per gram of catalyst).

## RESULTS AND DISCUSSION

The N<sub>2</sub> adsorption-desorption isotherms and X-ray diffraction patterns of the supports studied are shown in Figs 1 and 2, respectively. It was found that all the supports exhibited similar N<sub>2</sub> adsorption isotherms of type IV<sup>19</sup>, which is typical for materials containing mesopores. However, the supports differed in S<sub>BET</sub>, which were 262, 140, and 108 m<sup>2</sup> g<sup>-1</sup> for Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>, respectively. For that reason, relatively low loadings of transition metals, presumably significantly below the maximal dispersion capacity of all the supports towards the transition metals selected, were chosen. The Me content of 0.215 mmol g<sup>-1</sup>, for example, corresponded to MoO<sub>3</sub> loading 3 wt.%, which was, as we previously found, 6.1, 3.5 and 2.5 times lower than the saturated loading was over Al<sub>2</sub>O<sub>3</sub><sup>20</sup>, TiO<sub>2</sub><sup>21</sup> and ZrO<sub>2</sub><sup>7</sup>, respectively, needed for maximum HDS activity.

The  $\text{Al}_2\text{O}_3$  was found to be a  $\gamma$  (cubic) modification, which is a typical HDS support<sup>1</sup>. The commercial  $\text{TiO}_2$  and  $\text{ZrO}_2$  were tetragonal (anatase) and monoclinic (baddeleyite), respectively.

The HDS activity was expressed as a formal rate constant of ethylbenzene formation,  $k_{\text{EB}}$ , which was acquired by non-linear fitting of the dependence  $a_{\text{EB}}$  on  $W/F_{\text{BT}}$  using the equation  $a_{\text{EB}} = 1 - \exp(-k_{\text{EB}} W/F_{\text{BT}})$ . An example of

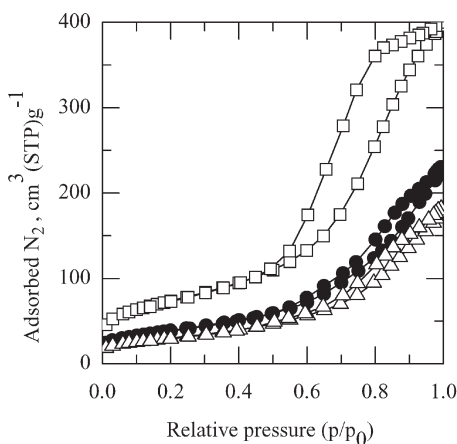


FIG. 1  
 $\text{N}_2$  adsorption-desorption isotherms of  $\gamma\text{-Al}_2\text{O}_3$  ( $\square$ ),  $\text{TiO}_2$  ( $\bullet$ ) and  $\text{ZrO}_2$  ( $\triangle$ ) supports

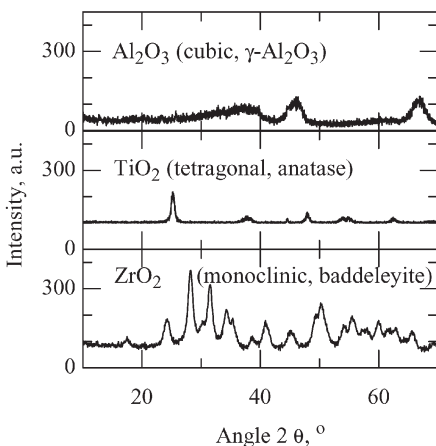


FIG. 2  
 X-ray diffraction patterns of the supports

the fitting and the  $k_{\text{EB}}$ s obtained are shown in Fig. 3 and Table I, respectively.

It was found that the resulting HDS activity differed by 3 orders of magnitude, depending on the supported transition-metal sulfide. In specific cases, the support also influenced the resulting activity. To consider the periodic trends of the activities and the contribution of the supports, the transition-metal sulfides are systematically compared in Fig. 4, and the ratio of  $k_{\text{EB}}$  of  $\text{TiO}_2$ - or  $\text{ZrO}_2$ -supported catalysts to  $k_{\text{EB}}$  of the  $\text{Al}_2\text{O}_3$ -supported counterpart is quantified in Table II.

First, the sulfides of the first-row transition metals exhibited only little influence of the HDS activity on the position in the periodic table (manifested by V-shaped curves with Mn at the valleys with highly active Ni/ $\text{TiO}_2$  being an exception) unless the second- and third-row transition metals. The highest activities were recorded over Rh-, Pd-, Ir- and Pt-supported sulfides. Second, it was found that the positive effect of both unconventional supports on the activity was almost systematically pronounced in the first-row transition-metal sulfides, with the exception of Co supported on  $\text{ZrO}_2$ , whereas in the second and third rows only over Mo, Ru, W and Os. The other metal sulfides studied were either not influenced by the unconventional supports at all or the influence was negative. Third, the activity

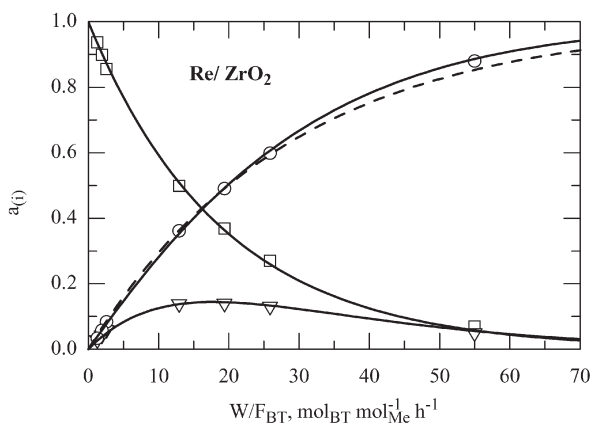


FIG. 3

The dependence of the relative composition ( $a_i$ ) of the reaction mixture on space time ( $W/F_{\text{BT}}$ ) in benzothiophene HDS. Solid lines: fitting with four pseudo-first-order constant reaction schemes ( $\text{BT} \rightarrow \text{DHBT}$ ,  $\text{DHBT} \rightarrow \text{BT}$ ,  $\text{DHBT} \rightarrow \text{EB}$  and  $\text{BT} \rightarrow \text{EB}$ ) to determine the ratio  $x_{\text{EB}}/x_{\text{DHBT}}$  at  $x_{\text{BT}} = 0.5$ . Dashed line: the formal first-order equation of EB formation (for details see the text) to fit  $k_{\text{EB}}$ . BT ( $\square$ ), DHBT ( $\nabla$ ), EB ( $\circ$ )

higher than  $160 \text{ mol}_{\text{EB}} \text{ mol}_{\text{Me}}^{-1} \text{ h}^{-1}$ , again with the exception of Ni supported on  $\text{TiO}_2$ , was not accompanied by an explicitly positive contribution of the  $\text{TiO}_2$  and  $\text{ZrO}_2$  support.

In general, the hydrodesulfurization of sulfur-containing heteroaromatics proceeded in two ways: (i) direct desulfurization (DDS) – sulfur is removed from the heteroaromatics while aromatic C=C bonds remain unsaturated (direct C–S hydrogenolysis, HYG) and (ii) hydrogenation (HYD) – C=C bonds are hydrogenated prior to sulfur removal. For example, in the case of

TABLE I

The activity in the HDS of 1-benzothiophene ( $k_{\text{EB}}$ ) and HYG/HYD selectivity ( $x_{\text{EB}}/x_{\text{DHBT}}$ ) of the prepared and reference industrial catalysts

Me	$k_{\text{EB}}, \text{mol}_{\text{EB}} \text{ mol}_{\text{Me}}^{-1} \text{ h}^{-1}$			$x_{\text{EB}}/x_{\text{DHBT}}$		
	$\text{Al}_2\text{O}_3$	$\text{TiO}_2$	$\text{ZrO}_2$	$\text{Al}_2\text{O}_3$	$\text{TiO}_2$	$\text{ZrO}_2$
V	12	76	60	2.4	1.9	1.8
Cr	13	69	38	2.0	1.3	1.9
Mn	–	37	–	–	1.3	–
Fe	8	56	27	2.2	2.6	2.9
Co	50	80	29	2.8	3.1	3.5
Ni	34	164	42	8.0	4.0	6.1
Mo	43	101	81	1.3	0.8	1.1
Ru	12	58	59	1.3	1.4	1.7
Rh	320	247	488	6.1	1.5	2.9
Pd	676	237	225	2.0	3.2	1.2
W	8	55	16	–	1.0	1.9
Re	186	179	162	2.6	1.4	2.6
Os	4	38	10	4.3	2.6	1.5
Ir	321	362	413	1.6	1.1	1.3
Pt	540	604	613	4.6	2.8	4.3
Reference catalyst						
Mo	27			1.2		
CoMo	282			8.6		
NiMo	235			25.3		

TABLE II  
The relative contribution of the  $\text{TiO}_2$  and  $\text{ZrO}_2$  supports on the HDS activities of the deposited transition-metal sulfides

Me	$k_{\text{EB}}(\text{TiO}_2)/k_{\text{EB}}(\text{Al}_2\text{O}_3)$	$k_{\text{EB}}(\text{ZrO}_2)/k_{\text{EB}}(\text{Al}_2\text{O}_3)$
V	6.3	5.0
Cr	5.4	2.9
Fe	6.6	3.2
Co	1.6	0.6
Ni	4.8	1.2
Mo	2.4	1.9
Ru	4.9	5.0
Rh	0.8	1.5
Pd	0.4	0.3
W	12.7	3.7
Re	1.0	0.9
Os	9.6	2.4
Ir	1.1	1.3
Pt	1.1	1.1

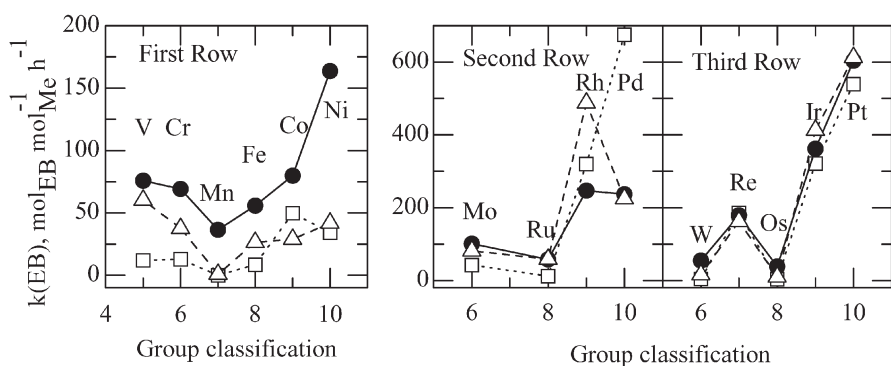


FIG. 4

The periodic trends of the transition-metal sulfides studied in HDS and the influence of the supports:  $\gamma\text{-Al}_2\text{O}_3$  ( $\square$ , dotted lines),  $\text{TiO}_2$  ( $\bullet$ , solid lines) and  $\text{ZrO}_2$  ( $\triangle$ , dashed lines)

dibenzothiophene HDS<sup>22-25</sup>, the DDS pathway manifests itself by the presence of biphenyl in the final products while the HYD pathway by the presence of tetrahydrodibenzothiophene as the intermediate and cyclohexylbenzene as the final product. In the case of benzothiophene HDS, the relative increase in the yield of the dihydrobenzothiophene intermediate is reflected in the HYD pathway, and it is believed that the selectivity HYG/HYD is reflected in the quality on the active sites<sup>7,26</sup>. Due to the fact that the HDS activity over the prepared catalysts differed by 3 orders of magnitude, the HYG/HYD selectivity was expressed as the ratio  $x_{EB}/x_{DHBT}$  at  $x_{BT} = 0.5$  to assess the prepared active phase quantitatively. The HYG/HYD index was taken from the graph fitting dependence of relative composition on  $W/F_{BT}$  by a scheme of four pseudo-first-order reactions. An example is given in Fig. 3.

The HYG/HYD selectivity is summarized in Table I. It was found that the HYG/HYD selectivity index over the prepared catalysts varied from 0.8 to 8.0 without any correlation with the HDS activity or the support used. It could be concluded that the  $x_{EB}/x_{DHBT}$  remained within the same order of magnitude for all the monometallic catalysts studied. The high value of the HYG/HYD selectivity seemed to be an inherent property of bimetallic phases Co-Mo-S and Ni-Mo-S supported on  $\gamma\text{-Al}_2\text{O}_3$ , which is demonstrated in Table I by the industrial reference catalysts.

The transition-metal sulfides studied might be divided into two groups according to their catalytic performance. The first group, i.e. Pt, Ir, Pd, Rh and Re, exhibited two following important features: (i) the highest HDS activities and (ii) neutral (Pt, Ir, Rh, Re) or negative (only Pd) influence of the  $\text{TiO}_2$  and  $\text{ZrO}_2$  supports on the resulting activity. More precisely, the activity decreased in the following order: Pd > Pt > Ir  $\approx$  Rh > Re over  $\gamma\text{-Al}_2\text{O}_3$ ; Pt > Ir > Rh  $\approx$  Pd > Re over  $\text{TiO}_2$ ; and Pt > Rh > Ir > Pd > Re over  $\text{ZrO}_2$ . The second group, i.e. V, Cr, Mn, Fe, Co, Ni, Mo, Ru, W and Os, exhibited low activity and a positive influence of the  $\text{TiO}_2$  and  $\text{ZrO}_2$  supports on the resulting activity (Ni and Co on  $\text{ZrO}_2$  might be considered an exception). To specify further, the lowest activities were achieved over Fe, W, Os and Mn; the supports did not change the activity order Fe > W > Os > Mn. The activity order over other sulfides depended on the support used and was the following: Co > Mo > Ni > Ru  $\approx$  V  $\approx$  Cr over  $\gamma\text{-Al}_2\text{O}_3$ ; Ni > Mo > Co > V > Cr > Ru over  $\text{TiO}_2$ ; and Mo > V > Ru > Ni > Cr > Co over  $\text{ZrO}_2$ . Clearly, the industrially-used catalytic systems Co, Ni, Mo and W belong to the second group, in which high synergism between Co(Ni) and Mo(W) in HDS activity were observed (see a reference in ref.<sup>17</sup>). In the second group, the posi-



tive effect of the  $\text{TiO}_2$  and  $\text{ZrO}_2$  support on the resulting activity could also be considered as promotional. The supports themselves did not exhibit HDS activity but significantly promoted the activity of a deposited transition-metal sulfide.

The comparison of the HDS activity of unsupported transition-metal sulfides<sup>13</sup> and sulfides supported on the studied oxidic supports is shown in Fig. 5. The HDS activities fairly correlated, but Ru and Os significantly differed. The research into unsupported sulfides<sup>13</sup> reported that Ru and Os showed the peak activities in the HDS of dibenzothiophene while in the present study Os was practically inactive and Ru was far from being as active as Mo, for example. In the studies into activated-carbon-supported sulfides<sup>14,15</sup>, Os and Ru exhibited comparable activities in HDS of thiophene, which were more than 2.5 higher than the activity of Mo but not as high as that/those of Ir and Rh, for instance. Our recent study<sup>27</sup> into the effect of the support on the activity of Ru in the HDS of thiophene has shown that the highest activities were obtained over activated-carbon-supported species followed by  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$ . It seems that the main factor influencing the HDS activity over the unsupported sulfides was the transition

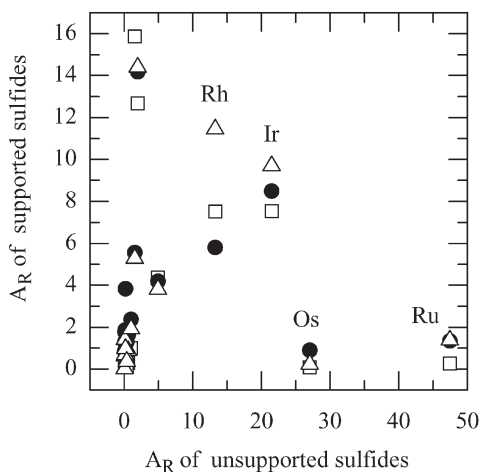


FIG. 5

A comparison of the relative activities ( $A_R$ ) of bulk transition-metal sulfides in the HDS of dibenzothiophene (the data were taken from ref. <sup>13</sup>) and the relative activities of the studied supported sulfides in benzothiophene HDS. The relative activities  $A_R$  were calculated as a ratio of the activity index of transition-metal sulfide to the activity index of Mo catalyst in each series. Supports:  $\gamma\text{-Al}_2\text{O}_3$  (□),  $\text{TiO}_2$  (●) and  $\text{ZrO}_2$  (△)

metal itself, i.e. an electronic factor<sup>13</sup>. That factor presumably was not the only one to govern the activity of supported transition-metal species. Activated carbons, often considered as inert supports, changed the activity order only slightly while the studied oxidic supports influenced the HDS activity significantly, presumably because of the specific interaction of the support with a transition-metal species. Detailed generalization concerning the HDS-activity ranking of the transition-metal sulfides remains a challenge.

The present study covered the transition-metal sulfides, the HDS activity of which was affected by the TiO<sub>2</sub> and ZrO<sub>2</sub> support. From a practical point of view, this might be interesting, for example, in the case of V, which is a typical metal present in petroleum-based HDS feedstocks<sup>28,29</sup>. Vanadium-containing feeds form vanadium-sulfide deposits over HDS catalysts, which are thus poisoned. Vanadium-containing catalysts were studied in the patent literature<sup>30,31</sup> as a protection of the conventional HDS catalysts. In the present study, it was found that the TiO<sub>2</sub> and ZrO<sub>2</sub> supports increased the activity of V species more than five times. It is expected that V supported on TiO<sub>2</sub> or ZrO<sub>2</sub> could serve as hydrodemetalizers to protect conventional HDS catalysts downstream and would possess, at the same time, a significantly higher HDS activity than the alumina-supported counterpart.

## CONCLUSIONS

It was concluded that the TiO<sub>2</sub> and ZrO<sub>2</sub> supports significantly increased the HDS activity of the sulfided species of the first-row transition metals studied, Mo, Ru, W and Os, in comparison with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. However, the HDS activities of all those species were still quite below the activity of the Rh-, Pd-, Ir-, Pt- and Re-sulfided species, which were hardly at all or negatively influenced by the TiO<sub>2</sub> and ZrO<sub>2</sub> supports. Furthermore, neither the type of transition metal nor the support affected the relative selectivity C-S HYG/C=C HYD to the extent typical for the conventional bimetallic phases. The supports influenced the HDS activity ranking of the sulfided transition metal as follows: (i)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: Pd > Pt > Ir  $\approx$  Rh > Re >> Co > Mo > Ni > Ru  $\approx$  V  $\approx$  Cr > Fe > W > Os; (ii) TiO<sub>2</sub>: Pt > Ir > Rh  $\approx$  Pd > Re  $\approx$  Ni > Mo > Co > V > Cr > Ru  $\approx$  Fe  $\approx$  W > Os  $\approx$  Mn; (iii) ZrO<sub>2</sub>: Pt > Rh > Ir > Pd > Re > Mo > V > Ru > Ni > Cr > Co  $\approx$  Fe > W > Os.

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