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CATALYSIS OF THIOPHENE HYDROGENOLYSIS BY BIMETALLIC SULFIDE CATALYSTS OF DIFFERENT COMPOSITIONS

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The activity of sulfide catalysts M_I/SiO_2, M_I/WS_2, $(M_I,W)/SiO_2$ and $(Ni,M_{II})/SiO_2$ (M_I is a first row transition metal, and M_{II} = Nb, Mo, W or Re) in the thiophene hydrogenolysis reaction has been studied. Activities of mono- and bimetallic catalysts are found to change in the same manner depending upon the nature of M_I. The formation of a sulfide bimetallic species (SBMS) is suggested.

Изучена активность в реакции гидрогенолиза тиофена сульфидных катализаторов M_I/SiO_2, M_I/WS_2, $(M_I,W)/SiO_2$ и $(Ni,M_{II})/SiO_2$, где M_I - металл первого переходного ряда, а M_{II} - Nb, Mo, W, Re. Обнаружено симбатное изменение активности моно- и биметаллических катализаторов в зависимости от природы металла M_I. Предполагается образование сульфидного биметаллического соединения.

In recent years, the structure of the active component of sulfide catalysts of HDS has been decoded [1,2]. The active component is a sulfide bimetallic species (SBMS) having the structure of a MoS_2 (WS_2) slab with Ni(Co) atoms localized in its edge plane (10$\bar{1}$0) [2,3]. Thus, the question arises whether structural analogs of the SBMS involving other transition metal ions are active in the reaction under consideration. It is known,

for example, that NbS_2 [4] and ReS_2 [5] are stabilized in the MoS_2 structure; for this reason we used Ni for anchoring on its surface. Besides, first row transition metals were supported on WS_2 and WS_2/SiO_2 by methods described in [6,7].

EXPERIMENTAL

Synthesis of catalysts. Bulky catalysts were obtained by treating commercial WS_2 (S_{BET} = 7.6 m^2/g) with an alcohol solution of acetylacetonate (acac) complexes of first row transition metals $M_I(acac)_2$. After metal supporting, the catalyst was washed off with alcohol and dried under vacuum. The catalysts so obtained contained ca. 0.05 wt.% of the supported metal.

Supported catalysts were obtained in several stages. First, SiO_2 (S_{BET} = 220 m^2/g) was treated with a WCl_6 or $NbCl_5$ solution in CCl_4. When washed off with a pure solvent, SiO_2 was treated with ethanol, dried under vacuum and then treated with H_2S at 400°C. In the second stage an $M_{II}S_2$-containing support was treated with a $M_I(acac)_2$ solution in benzene, chloroform or alcohol. Ti in the form of tetrabenzyltitanium was supported from solution in heptane. After washing off with a pure solvent the catalyst was dried under vacuum and sulfurized. For comparison, monometallic sulfide catalysts M_I/SiO_2 were also prepared under identical conditions. Re catalysts were obtained via $Re(OC_2H_5)_3$.

Conditions for sulfurization, determination of catalytic properties and registration of X-ray photoelectron spectra (XPS) were as described in [6,7].

RESULTS AND DISCUSSION

Activities of sulfide catalysts M_I/SiO_2, M_I/WS_2 and $(M_I,W)/SiO_2$ changed in the same manner producing two maxima at Cr and (Co, Ni) (Fig. 1). Similar dependences of activity on the nature of the first row transition metal have been reported for reactions of synthesis and conversion of S-containing molecules and C-S, C-O and C-N bond hydrogenolysis [8-12].

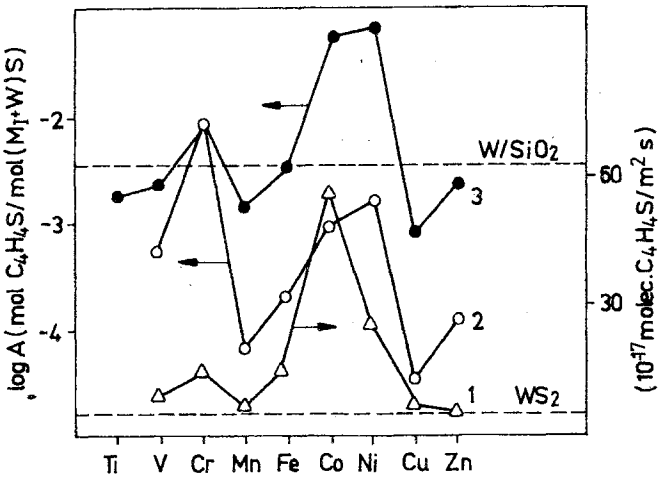

Fig. 1. Activity of supported sulfide catalysts M_I/WS_2 (c. 1), M_I/SiO_2 (c. 2) and $(M_I-W)/SiO_2$ (c. 3) vs. metal nature. Atomic ratio $\lambda = M_I/M_I+W$ in $(M_I,W)/SiO_2$ catalysts is close to 0.3

A salient feature of the SBMS is an increase in binding energy of M_I $2p_{3/2}$ on Ni(Co) atoms in comparison with NiS (Co_9S_8) [13-15]. Incorporation of Ni(Co) atoms into the edge plane $(10\bar{1}0)$ of the MoS_2 (WS_2) slab compensates an excess negative charge of terminal sulfur atoms, thus making the entire fragment electroneutral [16]. An analogous situation seems to occur upon addition of Ni, Co or Cu to WS_2, and also Ni to ReS_2, since XP-spectra indicate an increase in BE of M_I $2p_{3/2}$ (Table 1) in comparison with binary sulfides of these metals. Nonetheless, the tendencies in catalyst activity changes are opposite, i.e., Ni and Co increase the activity of WS_2 and Cu decreases its activity, while Ni decreases the activity of ReS_2 (Fig. 1). Similarly, addition of Cu to W/SiO_2 and Ni to Re/SiO_2 leads to a non-additive decrease in activity (Fig. 2). A non-additive increase in activity has been observed upon addition

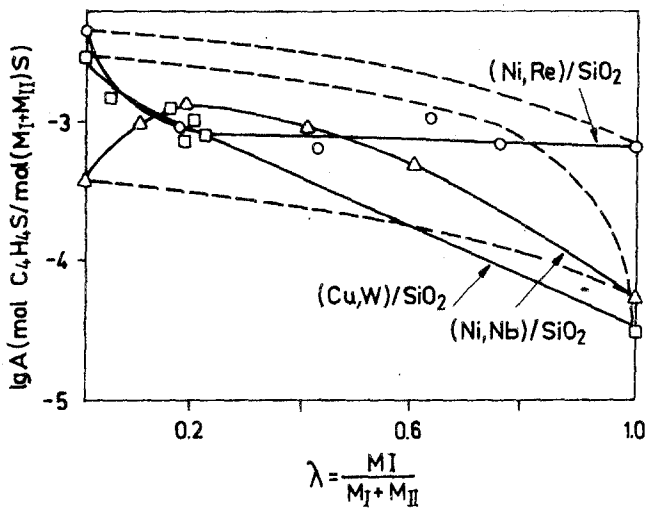

Fig. 2. Activity of SiO_2-supported bimetallic sulfide catalysts vs. catalyst composition

Table 1

XPS data on the state of M_I in bimetallic sulfide catalysts

Catalyst	BE (eV) of electrons in the levels				Refs.
	C 1s	Ni $2p_{3/2}$	Co $2p_{3/2}$	Cu $2p_{3/2}$	
NiS		852.9			13,14
Ni/WS_2		854.0			13
Ni/WS_2	284.8	854.7			this work
Ni/ReS_2	284.8	853.9			this work
Co_9S_8	284.6		778.4		15
Co/MoS_2	284.3		779.0		15
Co/WS_2	284.8		780.1		this work
Cu_2S	284.8			931.8	this work
Cu/WS_2	284.8			933.2	this work

of Ni to Nb/SiO_2 [17], a maximum synergistic effect being observed in the region $\lambda = \frac{Ni}{Ni+Nb} = 0.35$ (Fig. 2).

The data obtained can be interpreted in terms of the SBMS formation both on the surface of bulky WS_2 and ReS_2 and on SiO_2. Changes in activity of the M_I/WS_2 and $(M_I,W)/SiO_2$ systems (Fig. 1) can be explained by the "electron effect" [18], i.e., when the key role in the activation of the S-containing molecule is played by its interaction with the M_I ion. For the $Ni-NbS_2$ system, NbS_2 is known to be active in hydrogenation reactions only at sufficiently high temperatures [19]. One can, therefore, suppose that a low value of synergism (in comparison with $Ni-WS_2$ and $Ni-MoS_2$) is due to a more difficult activation of dihydrogen. Antagonism in the Ni/ReS_2 system seems to result from a change in the reaction mechanism. In fact, Re catalysts possess higher activity than Ni, Mo and W samples; however, in contrast to these latter, the products of thiophene hydrogenolysis always contain tetrahydrothiophene (THT) in large amounts. The addition of Ni resulted in a decrease in content of THT in the reaction products and its complete disappearance at $\lambda > 0.5$.

The principles of changes of the properties of sulfide catalysts with a presumable SBMS structure are in good agreement with the literature data; however, for a deep insight into the mechanism of their catalytic action, further in situ investigations of the adsorption of reacting molecules and theoretical calculations of their activation in the coordination sphere of the SBMS are needed.

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