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Synergism and Antagonism in Thiophene Hydrogenolysis Mediated by Bimetallic Sulfide Catalysts—the Interacting Bond Method

Nikolai N. Bulgakov and Anatolii N. Startsev*

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 235 5756

Thermodynamic calculations in terms of the method of interacting bonds (MIB) have been attempted so as to study the enthalpy of H_2S formation in the reaction of H_2 with S atoms adsorbed on M^I (where M^I is a first-row transition metal), entering into the composition of sulfide bimetallic species $\{M^I–M^{II}S_2\}$ (M^{II} = Mo, W).

Recently, a new mechanism of thiophene hydrogenolysis based on the bimetallic active centre of hydrodesulfuration (HDS) catalysts has been suggested.[1–3] Activation of the thiophene molecule takes place on Ni (Co) atoms,[4] located in a square-planar arrangement of sulfur atoms, while H_2 activation occurs on the terminal S atoms in the edge plane of a MoS_2 (WS_2) single slab. Synergism in the catalytic system results from the synchronous interaction between the reacting thiophene and hydrogen molecules in the coordination sphere of the sulfide bimetallic species (SBMS), the active component of HDS catalysts.[2,3]

On adding the first-transition row metal to WS_2 (bulk and supported on SiO_2) a two-peak dependence of catalyst activity is observed in thiophene hydrogenolysis, with activity maxima on Cr and Ni (Co). A non-additive decrease of activity (antagonism) is found on introducing Ti, V, Mn and Cu.[5] High resolution electron microscopy data have shown[6] that the active component of the silica-supported bimetallic sulfide (M^I–WS_2) catalysts is crystallized in a structure which is typical for HDS catalysts and for highly dispersed MoS_2. According to X-ray photoelectron spectroscopy data[5] the decrease of electron density on M^I atoms into the SBMS composition in comparison with the binary sulfides of these metals confirms the similar square-planar arrangement of M^I in bimetallic catalysts. These arguments allow one to suggest the preservation of the SBMS structure in all the above cases. A similar two-peak dependence was first obtained in refs. 7 and 8, and further extends to many other catalytic systems, including the sulfide ones.[9]

In the present paper we attempt to explain the effects of synergism and antagonism in thiophene hydrogenolysis over bimetallic sulfide catalysts in terms of the method of interacting bonds (MIB). In the MIB method the enthalpy of atomization H_{at} of the multiatomic system is represented by the sum of contributions from separate bicentral bonds, the strength of which is characterized by parameter E (bond energy) and interaction between bonds is expressed in parameter Δ; H_{at} is expressed by eqn. (1),

$$H_{at} = \sum_i E_i \nu_i (2 - \nu_i) - \sum_{i>k} \sum \nu_i \nu_k \Delta_{ik} \qquad (1)$$

where the bond coefficients ν_i are variation parameters determined from the maximum of H_{at}.

It was supposed that the active component was of SBMS structure, in which an ion of transition metal M^I is localized in the centre of a square made of S atoms situated in the plane (IOĪO) of MoS_2 (WS_2). Previously, the MIB was used to analyse the SBMS structure[10] and to study the heats of adsorption of sulfur-containing molecules on SBMS of different composition.[11] The method was also employed in ref. 10 to explain the synergism from the standpoint of anion vacancy participation in a catalytic cycle, but no correlation with activity was found.

The reaction of thiophene hydrogenolysis is considered to proceed in two steps, each containing several elementary stages, (i) and (ii)

Table 1 The dependence of certain parameters[a] (kcal mol^{-1}) on the nature of the M^I metal in SBMS of $\{M^I–WS_2\}$ composition.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E_{M^I–S}$	420.3	418.4	359.0	343.1	359.0	355.6	361.5	294.1	302.9
$E_{M^I–W}$	391.6	405.4	370.7	337.2	376.6	379.9	379.9	352.7	291.4
Δ_{M^I}	64.4	71.1	54.8	39.3	57.5	59.0	59.0	46.4	18.0
$-\Delta H_1$	63.6	78.7	96.7	77.8	102.1	107.9	103.3	134.7	65.7
δ_{Co}	44.4	29.3	11.3	30.1	5.9	0	4.6	26.8	42.3
δ_{Ni}	39.7	24.6	6.6	24.5	1.2	4.6	0	30.4	37.6

[a] M^I–S and M^I–W bond energies (E); ΔM^I bond coefficients; ΔH_1 reaction enthalpies; and enthalpy reaction deviations (δ_{Co}, δ_{Ni}) from the optimal value accepted for Co and Ni, respectively.

$$S_{ads} + H_{2(g)} \rightarrow [\,] + H_2S_{(g)} \quad \text{(i)}$$

$$[\,] + C_4H_4S_{(g)} + 2H_{2(g)} \rightarrow S_{ads} + C_4H_{8(g)} \quad \text{(ii)}$$

where [ ] is a vacant coordination site. Based on Temkin's rule[12] governing the close enthalpies of both the stages for the most active catalysts, it was shown in ref. 10 that thiophene adsorption occurs over Ni (or Co) atoms located in a square-planar arrangement of S atoms and situated close enough to Mo (W) atoms (~2.4 Å), the latter leading to the formation of direct metal–metal bonds between the different atoms.

On substitution of Ni (Co) atoms in SBMS by the atoms of metals of the first transition row Ti, V, ... Cu, Zn the enthalpy ΔH_1 of the first stage of thiophene hydrogenolysis was calculated, using the parameters defined in refs. 10 and 11, and those for the considered systems M^I–S were determined in the present paper from the heats of formation of the corresponding sulfides (see Table 1).

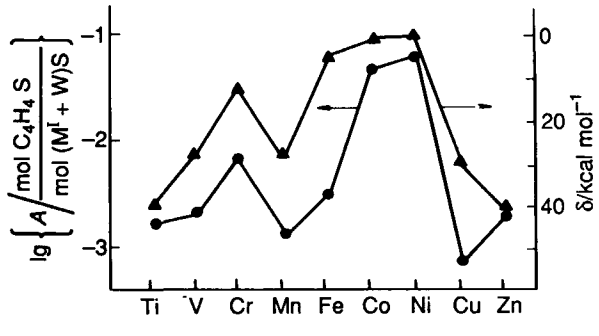

Fig. 1 Dependence of activity (A) of catalysts $\{M^I–WS_2\}/SiO_2$ in thiophene hydrogenolysis[5] and deviations (δ) of reaction enthalpies ΔH_1 from the optimal value accepted for Ni and Co based on the nature of the metal M^I in SBMS composition

Let us suppose that ΔH_1 determines to a large extent the change in activity of the $\{M^I–M^{II}S_2\}$ system in the row considered. From the experimental data it follows that the optimum value of ΔH_1 for catalysis is achieved in the case of Ni (Co). Therefore, the values of ΔH_1 deviation calculated for other metals entering into the SBMS composition can serve as a measure of the activity deviation of the given catalytic system from the most active one. In Fig. 1 these deviations are correlated with the experimental activities obtained in ref. 5 for the $\{M^I–WS_2\}$ row. A similar picture is obtained for the row $\{M^I–MoS_2\}$. From Table 1 and Fig. 1 it follows that a decrease in activity can result both from a very strong bond M^I–S (Ti, V, Mn, Zn) and a very weak one (Cu–S).

A good correlation confirms the assumption about the decisive role of the bond strength of adsorbed sulfur on the M^I atom in SBMS, the source of activated H_2 remaining unchanged (MoS_2, WS_2). In addition, the correlation presented confirms the correct choice of structure for the active centre of HDS catalysts and the mechanism of this reaction.

It should be noted that the double-peak correlation of activity with the position of the transition metal was found in ref. 13 (but in ref. 13 the first maximum activity was found with V and the first minimum with Cr; this work demonstrates another correlation), in which another hypothesis on the nature of active sites and another calculation method were used.

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