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On the Concerted Mechanism of Thiophene Hydrogenolysis by Bimetallic Sulphide HDS Catalysts in terms of the Interacting Bonds Method

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The enthalpy of adsorption of thiophene, tetrahydrothiophene and H_2S on the Ni(Co) atoms of the sulphide bimetallic species (SBMS) of hydrodesulphurisation catalysts has been estimated in terms of the Interacting Bonds Method (IBM).

Recently a new mechanism of C—S bond hydrogenolysis mediated by bimetallic sulphide catalysts has been put forward.[1–3] According to this hypothesis thiophene hydrogenolysis is considered to be a process proceeding in the coordination sphere of the sulphide bimetallic species (SBMS): the active component of hydrodesulphurisation (HDS) catalysts. Adsorption of thiophene is proposed to occur on the Ni(Co) atoms, which are in a square-planar environment of S atoms, and H_2 activation occurs with participation of the Mo(W) atoms. This hypothesis has been experimentally proved by selenophene adsorption studied by EXAFS.[4] A similar conclusion was obtained in ref. 5.

On consideration of this mechanism of thiophene hydrogenolysis two questions arise: (*i*) Why is thiophene adsorbed, but H_2S desorbed on the active centre? (*ii*) Why are none of the possible intermediates [*e.g.* tetrahydrothiophene (THT)]

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observed in the reaction products?[6] The answers are presented in this communication, obtained by calculation of the enthalpy adsorption of thiophene, THT and H_2S on the active centre by the interacting bonds method (IBM).

IBM has been described in ref. 7 and used[8] to estimate the enthalpies of S atom addition – removal on sulphide catalysts. In terms of IBM the multiatomic system is described by a set of bicentral bonds where interaction between these bonds is taken into consideration. The enthalpy of atomization H_{at} is expressed by eqn. (1), where the semiempirical parameters E_i (bond energy) and Δ_{ik} (bond interaction) are determined from the experimental enthalpies of formation of the appropriate compounds. The bond coefficients ν_i are variation parameters determined from the energy minimum condition, *i.e.* from the maximum of H_{at}, because it has been assumed for simplicity that E_i and $\Delta_{ik} > 0$, and therefore $H_{at} > 0$.

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

In order to calculate the heat of adsorption of H_2S, thiophene and THT the parameters determined in ref. 8 were used (all values in kJ mol^{-1}):

$E_{Ni-S} = 361.1$; $E_{Co-S} = 355.6$; $E_{Mo-S} = 458.6$;
$E_{W-S} = 518.0$; $E_{Ni-Mo} = 321.7$; $E_{Co-W} = 379.1$;
$E_{Ni-W} = 379.5$; $E_{Co-Mo} = 321.3$;
$\Delta_{Ni} = 59.0$; $\Delta_{Co} = 59.0$; $\Delta_{Mo} = 90.4$; $\Delta_{W} = 117.6$; $\Delta_{S} = 188.3$.

The other parameters were calculated in our study: $E_{H-S} = 444.3$; $E_{H-C} = 569.0$; $EE_{C-C}^{thiophene} = 619.2$ (calculated from $\Delta_f H$ of benzene); $E_{C-C}^{THT} = 405.0$ (from cyclopentane); $E_{C-S}^{thiophene} = 405.0$; $E_{C-S}^{THT} = 288.7$ kJ mol^{-1}. In all cases the adsorption on Ni(Co) atoms is considered as part of SBMS in a square-planar environment of S atoms (so-called γ-centres[8]).

The heats of adsorption calculated for H_2S, thiophene and THT are shown in Table 1. The small values of $\Delta_{ads}H$ confirm the essential reversibility of H_2S adsorption in the reaction conditions and the possibility of adsorbed H_2S being supplanted by thiophene. The high $\Delta_{ads}H$ for THT reflects the practical irreversibility of the latter. This fact accounts for the absence of partially or completely hydrogenated types of thiophene in the reaction products.[1,3,6] This also means that the only way to complete the catalytic cycle is the rupture of the C—S bond with desorption of the reaction products (butenes, butane, H_2S) in the gas phase.

Table 1 Heats of adsorption of S-containing molecules on SBMS of different compositions

SBMS composition	$\Delta_{ads}H$/kJ mol^{-1}		
	H_2S	Thiophene	THT
Co/MoS_2	48.1	88.7	146.9
Ni/MoS_2	51.0	92.5	151.0
Co/WS_2	50.0	90.8	149.8
Ni/WS_2	52.7	94.6	154.0

Thus the calculation by IBM of heats of adsorption of thiophene, THT and H_2S on Ni(Co) atoms in a square-planar environment of S atoms of SBMS demonstrates the possibility of thiophene hydrogenolysis proceeding *via* a concerted mechanism.

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