

Letter to the Editor

Comment on the paper of Zdenek Vit, Daniela Gulkova, Ludek Kaluzá, Miroslav Zdražil: “Synergetic effects of Pt and Ru added to Mo/Al₂O₃ sulfide catalyst in simultaneous HDS of thiophene and hydrogenation of cyclohexene”

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The catalysis research team (Institute of Chemical Process Fundamentals, Prague) recently reported [1] their results on comparison of hydrodesulfurization (HDS) of thiophene and hydrogenation of cyclohexene (CHE). The data reported in this paper offer a possible answer to the question of whether identical sites are involved in CHE hydrogenation and thiophene HDS. This question is motivated by the fact that hydrogenation of the first C=C bond in thiophene is a possible rate-determining step in HDS because of the comparatively high energy barrier of this step due to the conjugation of the double bonds in the cycle.

Synergetic effects similar to those mentioned by Vit et al. [1] can be calculated from our data [2–4] for Co-, Ni-, Pd-, and Pt-added sulfided molybdena–alumina catalysts in CHE hydrogenation [2] and thiophene HDS [3,4]. In contrast, however, the correlation found on parallel activity changes of different catalysts in cyclohexane dehydrogenation and thiophene HDS activity [4,5] is not observed for CHE hydrogenation [1,2]. This raises the second question of whether there are active sites in CHE → cyclohexane conversion identical to those in CHE → benzene dehydrogenation—that is, how the similarities and differences in the catalyst behavior with respect to thiophene HDS and hydro-dehydrogenation of cyclic hydrocarbons can be explained.

Comparison of virtual rate constant (k') and activation energy (E) data in Tables 2 and 3 in [1] indicates that the higher rate constants for some of the catalysts are paired with higher activation energies. This is the case in, among others, CHE hydrogenation; the rate constant on NiMo/Al₂O₃ is higher than that on Pt/Al₂O₃, whereas the activation energy for this reaction is four times higher on NiMo/Al₂O₃ than on Pt/Al₂O₃. Equal

E values of this reaction for alumina-supported monometallic Pt and Ru are paired with a fourfold-higher rate constant on Pt compared with that on Ru. Similar examples can be seen for thiophene HDS, by, for example, comparing these data for NiMo/Al₂O₃ with the data for PtMo(S)/Al₂O₃. These observations raise the question of the compensation effect between Arrhenius constants, described by [6]

$$k_0 = \gamma^0 e^{hE} \quad \text{and} \quad \ln k_0 = hE + \gamma, \quad (1)$$

where $\gamma = \ln \gamma^0$, and expressing in general the correlation between the enthalpy and entropy of the rate-determining step of the catalytic process: formation or decomposition of the surface complex. However, the physical meaning of the constants γ^0 and h depends on what concept is accepted to explain the compensation effect. There are different concepts for this. Constable [6] explained the effect by exponential active site distribution on the heterogeneous catalyst surface. Balandin [7], following Constable's approach, applied the equation

$$ds = \phi(E) dE = \gamma^0 e^{hE} dE \quad (2)$$

for the energy distribution of catalytic sites by activation energy (i.e., by the energy of interaction between surface sites and reacting molecules) and derived from that the expression for k_0 in Eq. (1).

In Eq. (2), ds is the number of active sites (s = sum of sites, i.e., the catalytically active part of the surface) for a reaction in dE range of activation energy; γ^0 is the active sites number of maximal activity ($E = 0$), independent of activation energy; and h is the distribution parameter of active sites, indicating the number of sites at a given activation energy for a reaction.

Another concept, termed “isokinetic” and developed by Bond [8], explains the compensation effect from the intersection of Arrhenius plots of a reaction on different catalysts at the

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Table 1
 $\ln k_0$ values (k_0 in mol/(h kg_{cat}) units) in thiophene HDS and cyclohexene hydrogenation calculated from data in Tables 2 and 3 (Ref. [1])

Catalyst	HDS _{TH}	HYD _{CHE}
	$\ln k_0$	$\ln k_0$
Mo/Al ₂ O ₃	15.26	8.76
Pt/Al ₂ O ₃	8.16	6.14
Ru/Al ₂ O ₃	14.81	4.80
Pt–Mo(S)/Al ₂ O ₃	15.80	9.46
Ru–Mo(S)/Al ₂ O ₃	22.29	11.08, 23, 98 ^a
CoMo/Al ₂ O ₃	19.85	13.59
NiMo/Al ₂ O ₃	27.42	18.45

^a Calculated from $E = 41$ and 100 kJ/mol, respectively.

same temperature, with equal, “isokinetic” rates. The two approaches result in similar equations [9], as has been explained by Wootsch and Paál [10]. It is favorable to use Balandin’s approach here, because the approach of Vit et al. offers a possibility for comparing active sites for HDS with those of hydrogenation, with the latter being a step in HDS reactions.

It has been demonstrated that for numerous reactions, the compensation parameters are characteristic for a reaction type on different catalysts [11]. Their values can possibly help answer the questions raised with respect to the active sites of HDS and hydro-dehydrogenation. Table 1 gives the $\ln k_0$ values calculated from the rate constants and activation energies taken from Tables 2 and 3 in [1] for the two reactions. Fig. 1 presents the $\ln k_0$ versus E compensation plots for the different catalysts for HDS and HYD separately. Equation (1) is closely obeyed for CHE hydrogenation and somewhat weakly obeyed for thiophene HDS. The unusually low γ value of HDS in comparison with that of CHE hydrogenation contradicts the commensurable value of the rate constants for these two reactions. This raises the question of how closely the compensation plot represents the HDS-active sites for all of the catalysts involved. Fig. 2 shows a common compensation plot for the two reactions. This figure shows that, because of the much lower $\ln k_0$ values for HDS on the two monometallic catalysts, the correlation coefficient is somewhat lower for the common graph than for the separate ones. However, the correlation coefficient is higher for the common HDS-CHE graph than that for both of the separate ones: $R^2 = 0.9855$, representing the compensation plot of the five Mo-based catalysts. The γ value for these catalysts is also substantially higher: 1.393.

The equal site distribution for thiophene HDS and CHE hydrogenation allows us to suggest that the two reactions proceed on identical active sites on the Mo-based catalysts. This is in agreement with the conclusion of Kogan et al. [12] on the basis of the linear relationship between HDS and hydrogenation activity on sulfided, Co-promoted, and nonpromoted Mo/Al₂O₃ catalysts. The much lower HDS activity of monometallic samples supports the these authors’ conclusion as to the high number of sites with high S-mobility and HDS activity (which they term “rapid”) on sulfided molybdena compared with that on the monometallic samples.

The near-parallel placing (Fig. 2) of the $\ln k_0$ values for HDS on the two monometallic catalysts (“ h ” = 0.2375) suggests a site distribution nearly similar to that for CHE hydrogenation,

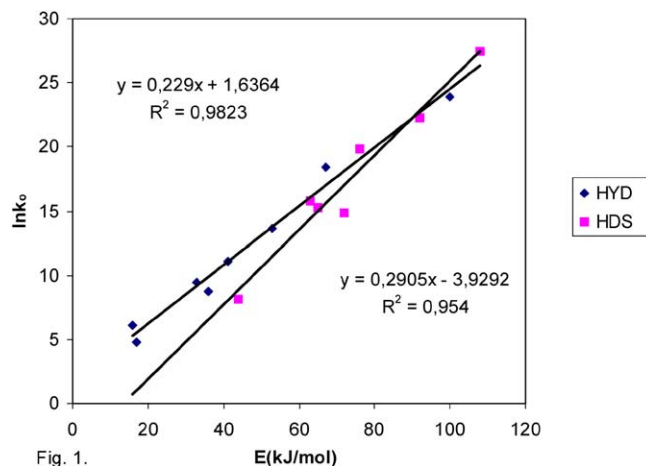


Fig. 1. Separate compensation plots for CHE hydrogenation and thiophene HDS for all catalysts in Ref. [1]. Constants: for HYD, $h = 0.229$, $\gamma = 1.6364$; for HDS, $h = 0.2905$, $\gamma = -3.9292$.

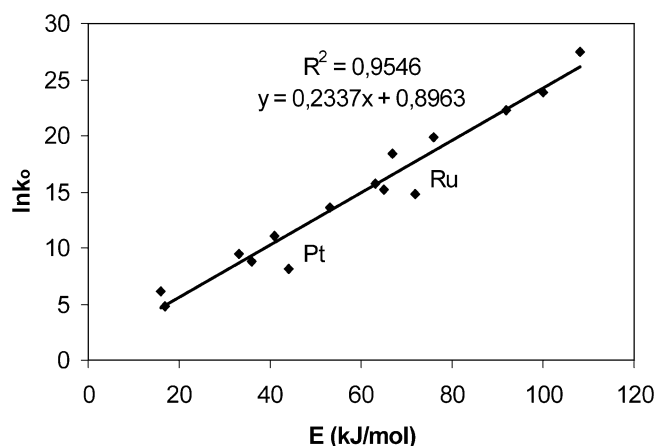


Fig. 2. Common compensation plot for CHE and HDS for all catalysts in Ref. [1]. Constants: $h = 0.2337$, $\gamma = 0.8963$.

whereas the much lower absolute value (“ γ ” = -2.29) indicates a much lower (~ 20 times) HDS site concentration at the respective energy levels than those for the MeMo(S)/Al₂O₃-type catalysts in [1]. This explains the substantially lower HDS activity of the two monometallic samples. The difference in site concentration of the two catalyst types determines the exceptionally low γ -value, calculated in the one-plot demonstration of HDS compensation effect in Fig. 1.

For comparison with data reported by Vit et al., Fig. 3 presents compensation plots for CHE hydrogenation, as calculated from data given previously [2], for five sulfided, alumina-supported catalysts and for dehydrogenation on nine sulfided, alumina-supported catalysts. (Note that kinetic parameters could not be extracted from CHE hydrogenation data for PdS-, PtS-, Pd-, and Pt-promoted MoO_x/Al₂O₃ because of the high degree of conversion, and for NiS and CoS because of the low degree of conversion.)

The virtual rate constants (k') were calculated by equation applied by Vit et al. [1],

$$k' = \frac{F_i}{W} \ln(1 - x_i)^{-1}, \quad (3)$$

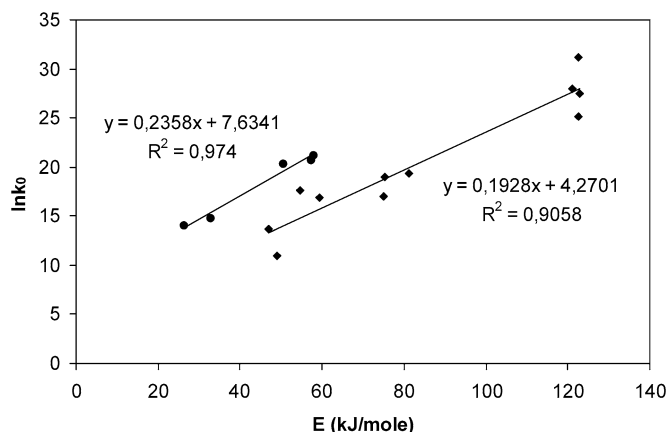


Fig. 3. Compensation plot for CHE hydrogenation on Al_2O_3 -supported $\text{MoO}_x(\text{S})$, $\text{CoMoO}_x(\text{S})$ -1 and 2, $\text{NiMoO}_x(\text{S})$ -1 and 2 [2]. Constants: $h = 0.2358$, $\gamma = 7.6341$. Compensation plot for cyclohexene \rightarrow benzene conversion on Al_2O_3 -supported $\text{MoO}_x(\text{S})$, $\text{Ni}(\text{S})$, $\text{Pd}(\text{S})$, $\text{CoMoO}_x(\text{S})$ -1 and 2, $\text{NiMoO}_x(\text{S})$ -1 and 2, $\text{PdMoO}_x(\text{S})$, $\text{PtMoO}_x(\text{S})$ catalysts [2]. Constants: $h = 0.1928$, $\gamma = 4.2701$.

where x_i is the degree of CHE conversion; F_i is the flow rate of CHE, equal to the flow rate of the H_2 carrier gas [13]; and W is the amount of catalyst.

Comparing the compensation plot in Fig. 2 with that for HYD in Fig. 3 shows practically equal distribution coefficients for HYD for the catalysts applied in [1] and [2], but with substantially higher γ values; the virtual rate constants are about 2 orders of magnitude higher than those obtained by Vit et al. This can be explained by the quite different experimental conditions as $\ln k_0$ and E values have been calculated from virtual

rate constants, k' , not independent of the reaction conditions. The high degrees of conversion were reached by much lower F/W than that applied in [2]. The hydrogen pressure in the pulse microcatalytic system was ~ 0.2 MPa, lower by one order of magnitude than that applied in the experiments of [1]. The high-pressure hydrogen presumably limited CHE adsorption to some extent.

Fig. 3 shows that the site distribution constant for CHE dehydrogenation is substantially lower than that for hydrogenation. This indicates different (at least partly so) active sites in these two reactions. On the basis of the principle of microscopic reversibility, this observation is in agreement with the statement of Qu and Prins [13] that hydrogenation of aromatics proceeds on sites different from those active in the hydrogenation of cycloalkenes.

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