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Sulfur exchange capacity and thiophene hydrodesulfurization activity of sulfided molybdena-alumina catalysts promoted by nickel

Pál Tétényi, Tamás Ollár*, Tibor Szarvas

Institute of Isotopes, Hungarian Academy of Sciences, P.O. Box 77, H-1525, Budapest, Hungary

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ABSTRACT

The capacity of sulfur exchange (i.e. S$_{TE}$—the total number of exchangeable sulfur atoms) has been determined at 673 K in a circulation system with H$_2$S (partial pressure ~2.5 and 25 kPa) for five sulfided catalyst samples: molybdena-alumina (Mo12), NiO/Al$_2$O$_3$ (Ni12) and three Ni-promoted molybdena-alumina with different Ni:Mo ratios [NiMo(0.X)]. A linear correlation has been found between the S$_{TE}$ values and thiophene hydrodesulfurization activity of the catalyst samples, containing Mo. The S$_{TE}$ values have been determined also in exchange between catalyst sulfur and thiophene, for three samples: Mo12, Ni12, and NiMo(0.35) for comparison of the S-exchange affinity of S in thiophene with that in H$_2$S. The isotope exchange capacity of sulfur bound to the catalyst (^{35}S$_{cat}$) with sulfur in H$_2$S was substantially higher than that with sulfur in thiophene, but the sequence of the S$_{TE}$ values was similar for the three samples, i.e., NiMo(0.35) > Mo12 > Ni12.

1. Introduction

Catalytic hydrodesulfurization is a widely applied process in hydrotreatment and hydrocracking of oil fractions [1–3]. A number of review papers indicate the wide spread of research studies in this field. It should be mentioned the survey [4] describing the present state in hydrodesulfurization of polyaromatic sulfur compounds, a review, focusing on the poisoning effect of sulfur compounds and on conditions of desulfurization processes for "preserving the octane rating of the fraction" [5]. Metal-promoted sulfided MoO$_x$ (and WO$_x$) are the most frequently applied catalysts in the hydrodesulfurization (HDS) processes, the oxides being sulfided prior to use. A part of most recent studies is focused to Ni- and Co- promoted Mo- or NiW-sulfides on alumina [6–8] or silica–alumina and a number of other supports, e.g. ZrO, TiO$_2$, zeolites and mixed oxides [9,10] Studies are oriented also to the structure surface layers on transition metal-sulfides [11] and on phosphides [12].

In a recent paper [13] we presented data on sulfur uptakes by five supported catalyst samples prepared by similar method with the same alumina support: a non-promoted molybdena-alumina containing 12 mass% of MoO$_3$ (denoted as Mo12), alumina supported Ni of ~6 mass% of NiO (denoted there Ni12) and three nickel-promoted molybdena-alumina samples with Ni:Mo atomic ratios of 0.15, 0.35 and 0.6 [NiMo(0.15), NiMo(0.35) and NiMo(0.6), respectively]. The amounts of sulfur uptake by the different samples were determined by radioactive sulfur (^{35}S) as tracer and by X-ray photoelectron spectroscopy (XPS). The maximum amount of irreversible sulfur uptake was observed on NiMo(0.35). In agreement with this, the surface S/(n_{Ni} + n_{Mo}) ratio determined by XPS had its maximum value also with this sample.

Comparison of the amounts of irreversible sulfur uptake (S$_{cat}$) with thiophene HDS activity [expressed as the number of converted molecules for a definite time on a definite mass of the catalyst (mol/s mg^{-1} units denoted as m_{TH})] indicated some tendency ($R^2 = 0.8792$) to linear correlation [14]. This was different from an earlier observation in experiments performed in this laboratory [15] with six alumina supported (Mo, CoMo, NiMo PtMo, PdMo and NiW-1) samples and with a silica–alumina supported one (NiW-2). However, a definite correlation was observed there between the total number of exchangeable (mobile) sulfur atoms and the thiophene HDS activity of those catalysts. Definite, positive correlation between sulfur exchange capacity and catalytic hydrodesulfurization activity has also been observed in some previous studies [16–19]. Nevertheless, data in some other reports, e.g. those of Startsev et al. [20] contradict to the existence of a correlation between sulfur exchange capacity and HDS activity of the catalysts.

These results motivated to determine the radiosulfur (^{35}S[S] denoted *S) exchange capacities (S$_{TE}$) of the five alumina supported samples [13] and to compare these data with the thiophene HDS rates (m_{TH} 10^{17} mol/s mg$_{cat}$) values determined previously in [14] on these samples. It was of interest also to compare the radiosulfur exchange capacity of the samples *S$_{cat}$ in nonradioactive H$_2$S (H$_2$S ↔ *S$_{cat}$) with that in thiophene (C$_4$H$_4$S ↔ *S$_{cat}$). It should be

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* Corresponding author.
E-mail address: ollar@iki.kfki.hu (T. Ollár).

* Units for amounts of S and S-containing compounds in 10^{17}atoms/mg or 10^{17}molecules/mg, respectively

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Nomenclature

S_{total}	the amount of total sulfur uptake, measured by gas phase radioactivity.
${}^{G}S_{cat}$	the amount of irreversible sulfur uptake measured by gas phase radioactivity.
${}^{G}S_{rev}$	the amount of reversible sulfur uptake, calculated by: ${}^{G}S_{rev} = S_{total} - S_{rev}$
${}^{s}S_{cat}$	the amount of irreversible sulfur uptake measured by the catalyst radioactivity.
S_{exc}	the amount of sulfur exchange measured by gas phase radioactivity change at circulation of H_2S containing mixture over sulfided catalyst.
S_{TE}	the total amount of exchangeable sulfur atoms in the catalyst calculated from S_{exc}.
${}^{TH}S_{TE}$	the total amount of sulfur atoms in the catalyst interacting with sulfur in (via exchange with sulfur in H_2S formed in thiophene HDS followed by addition to butadiene or/and by direct exchange). Determined at circulation of thiophene/H_2 mixture over sulfided catalyst, labeled with ${}^{*}S$ calculated from the distribution of radioactivity between H_2S and thiophene.
${}^{H_2S}S_{TE}$	the total amount of sulfur atoms in the catalyst, exchangeable with sulfur in H_2S formed from thiophene Determined at circulation of thiophene containing mixture over sulfided catalyst labeled with ${}^{*}S$ calculated from the radioactivity of H_2S produced over sulfided catalyst.
H_2S_{add}	the actual amount of H_2S-addition to C_4H_6 hydrocarbons.
$H_2S_{T.add}$	the total amount of H_2S-addition to C_4H_6 hydrocarbons.
g	the S_{TE}/S_{cat} ratio
m_{so}	the total initial amount of H_2S in the H_2S/H_2 mixture in the circulation experiments
${}^{H_2S}m_{so}$	the total amount of H_2S formed in circulation of the thiophene/H_2 mixture.
m_{TH}	the amount of converted thiophene (in pulse system).
ε, E, Q_{XY}	the activation energy, the energy barrier and the XY bond strength values in kJ mol^{-1}

noted that literature data indicated the absence of any direct sulfur exchange between the sulfur content of the catalyst and thiophene [21,22] or dibenzothiophene [23].

However, special measurements in our laboratory indicated [24] that thiophene formation by interaction of butadiene with H_2S [25] proceeds also via interaction of butadiene/H_2 mixture with sulfur, bound irreversibly both to Mo12 and NiMo(0.35). It follows from this and from the high thiophene hydrodesulfurization rates on these samples [14] that the “sulfur exchange in thiophene” possibly proceeds on the sulfided catalyst sample the following way:

$$C_4H_4S + H_2 \rightarrow (C_4H_6S)$$
$$\leftrightarrow C_4H_4 + H_2S + {}^{*}S_{cat} \leftrightarrow H_2{}^{*}S + C_4H_4 + S_{cat} \leftrightarrow C_4H_4{}^{*}S + H_2 \quad (I)$$

The appearance of ^{35}S labeled thiophene would indicate that this process really proceeds, and its extent could be calculated from the hydrogen sulfide/thiophene radioactivity ratio.

The studies cited here raise the following questions:

- Is there any correlation between sulfur exchange capacity and thiophene hydrodesulfurization activity of the catalysts?
- What correlation exists between the extent of $H_2S \leftrightarrow {}^{*}S_{cat}$ and that of $C_4H_4S \leftrightarrow {}^{*}S_{cat}$?
- Are the extents of these two exchange processes equal? Is their ratio different for various catalysts?
- To what extent do the amounts of exchange depend on the amount of sulfur, bound irreversibly to the catalyst, i.e. what is the S_{TE}/S_{cat} ratio for the different catalysts?
- What is the $H_2{}^{*}S$:$C_4H_4{}^{*}S$ radioactivity ratio among the products of exchange, indicating the ratio between sulfur exchange and H_2S-addition to C_4 hydrocarbons?

The purpose of the present study was to answer these questions.

2. Determination and calculation of sulfur exchange capacity

The method of sulfur exchange determination between H_2S and catalyst sulfur:

$$ {}^{*}S_{cat} + H_2S \leftrightarrow S_{cat} + H_2{}^{*}S \qquad \text{(II)}$$

was developed, described and applied in our laboratory in cooperation with Massoth [15] for molybdena-alumina (MoO_x) and a number of metal-promoted MoO_x samples. By this method the catalyst sample in oxide form is sulfided in the reactor vessel with $H_2{}^{*}S$ of I_o initial radioactivity by circulating a mixture of $H_2{}^{*}S/H_2$ of different ratio at ~53 kPa total pressure and 673 K (Scheme *a*). The sample after evacuation of the system should be exposed to circulating nonradioactive H_2S/H_2 gas mixture containing at the start m_{so} moles of H_2S (in 10^{17} mol/mg$_{cat}$units). The circulation is continued until the increasing gas phase radioactivity reaches a standard value (denoted as I_α). The amount of sulfur exchange (denoted ${}^{a}S_{exc,}$ in the same unites as m_{so}) is calculated then by the expression:

$$ {}^{a}S_{exc} = m_{so}\frac{I_\alpha}{I_\beta} \qquad (1)$$

in the same units than m_{so}. In Scheme *b*, another sample of the same oxide is sulfided with nonradioactive H_2S and treated subsequently with a mixture of $H_2{}^{*}S/H_2$ of I_o radioactivity. The actual exchange values in this process (${}^{b}S_{exc}$) are calculated by the equation:

$$ {}^{b}S_{exc} = m_{so}\frac{(I - I_\beta)}{I_O} \qquad (2)$$

where I_β is the gas phase radioactivity at the end of the run. It has been shown in detail in our former study [15] that for calculation of the total exchangeable sulfur {${}^{a}S_{TE}$ and ${}^{b}S_{TE}$, respectively) the actual amounts of reversible sulfur uptakes (${}^{G}S_{rev}$) and the S_{exc} should also be considered, as some exchanged and reversibly adsorbed sulfur reside on the surface, consequently the radioactivities of these amounts do not appear in the values of I_α and I_β. Thus, the respective equations for calculation of the total sulfur exchange amounts in Schemes *a* and *b* are as follows:

$$ {}^{a}S_{TE} = \frac{m_{so}{}^{a}S_{exc}}{(mso - {}^{G}S_{rev} - {}^{a}S_{exc})} \qquad (3)$$

$$ {}^{b}S_{TE} = m_{so}\frac{({}^{b}S_{exc} - {}^{G}S_{rev})}{(m_{so} - {}^{b}S_{exc})} \qquad (4)$$

At equal $H_2{}^{*}S/H_2$ and H_2S/H_2 ratio (and $S_{cat} = {}^{*}S_{cat}$) the total sulfur exchange between gas phase $H_2{}^{*}S \leftrightarrow S_{cat}$ should be equal to $H_2S \leftrightarrow {}^{*}S_{cat}$, Consequently, the method of sulfur uptake and exchange determination is to be proved by the equality of the S_{TE}

values, determined at equal H_2S/H_2 ratio of gas mixtures i.e. equal m_{so} in processes *a* and *b*, viz:

$$^{a}S_{TE} \approx {}^{b}S_{TE} \tag{5}$$

This equation has been found valid for three different alumina supported (MoO_x, Co- and Pt-promoted MoO_x) samples [15].

Determination and calculation of sulfur exchange between thiophene and catalyst sulfur is a more complex task. Circulation of gas phase H_2/thiophene mixture over $^*S$ labeled catalysts results in the formation of $H_2{}^*S$. The appearance of $C_4H_4{}^*S$ cannot be excluded, either, due to the reaction between $H_2{}^*S$ and butadiene [21–25] and due to the interaction between $^*S_{cat}$ and butadiene [24]. For calculation of the total sulfur exchange ($^{TH}S_{TE}$) values in conversion at circulation of a H_2/thiophene mixture, the reversible adsorption of thiophene (TH_{rev}), the ratio of hydrogen sulfide and thiophene among the sulfur containing products of thiophene conversion [i.e.: ($\mu_{H_2S} = I_{H_2S}/(I_{H_2S} + I_{TH})$ and ($\mu_{TH} = I_{TH}/(I_{H_2S} + I_{TH})$ respectively)] should also be considered, as that shown by Eq. (6):

$$^{TH}S_{TE} = \frac{m_{so}S_{exc}}{(m_{so} - \mu_{H_2S}S_{rev} - \mu_{TH}TH_{rev} - S_{exc})} \tag{6}$$

The selective sulfur exchange of H_2S formed in thiophene HDS ($^{H_2S}S_{TE}$) should be calculated by Eq. (7):

$$^{H_2S}S_{TE} = \frac{^{H_2S}m_{so}S_{exc}}{(^{H_2S}m_{so} - S_{exc} - S_{rev})} \tag{7}$$

where $^{H_2S}m_{so}$ is the amount of H_2S formed in thiophene HDS

The appearance of radioactive sulfur in thiophene would indicate that some thiophene sulfur ↔ $^*S_{cat}$ exchange also takes place, possibly via $^*S_{cat}(H_2{}^*S) + C_4H_6$ interaction (H_2S addition) besides the sulfur exchange. The amount of this conversion (denoted H_2S_{add}) has been calculated from the $H_2{}^*S/C_4H_8{}^*S$ radioactivity ratio (I_{TH}/I_{H_2S}) among the thiophene conversion products:

$$H_2S_{add} = S_{exc}\frac{I_{TH}}{I_{H_2S}} \tag{8}$$

and then

$$H_2S_{T.add} = \frac{m_{so}H_2S_{add}}{(m_{so} - \mu_{TH}TH_{rev} - S_{exc})} \tag{9}$$

where the sum of $^{H_2S}S_{TE} + H_2S_{T.add}$ approaches the value of S_{TE}.

It should be noted, however, that H_2S_{add} and $H_2S_{T.add}$ express the appearance of ^{35}S in thiophene upon the interaction of thiophene with sulfur labeled catalysts. This does not mean that hydrogen sulfide addition is accepted as the only way of ^{35}S labeled thiophene formation.

3. Experimental

MoO_3/Al_2O_3 of 12 mass% of MoO_3 (Mo12) samples were prepared by impregnation of a Pural γ-Al_2O_3 (210 m^2/g) with an aqueous solution of ammonium heptamolybdate. The Ni/Al_2O_3 catalyst (denoted Ni6, elsewhere Ni12) was prepared by impregnation of the alumina, with an aqueous solution of nickel nitrate calculated for ~6 mass % of NiO on the catalyst.

The wet samples were dried and calcined for 5 h at 723 K. The three Ni-promoted molybdena-alumina samples (0.75, 1.75 and 3 mass % calculated for Ni) were prepared by impregnation of the dried, (not calcined) Mo12 sample with aqueous nickel nitrate solution, dried and calcined for 5 h at 773 K temperature. The three samples are denoted as NiMo(0.15), NiMo(0.35) and NiMo(0.6) respectively in agreement with their calculated Ni:Mo atomic ratio, their general sign would be NiMo(0.X). Mo and Ni content of the samples are presented in Table 1, as determined by the Prompt Gamma Activation Analysis (PGAA) method.

The sulfur exchange capacity of the catalysts has been determined on the samples immediately after their treatment in vacuum, following sulfur uptake determination [13]. The Mo- and Ni-catalysts have been prepared by impregnation of γ-Al_2O_3 with an aqueous solution of ammonium heptamolybdate or of nickel nitrate followed by drying and calcination or reduction with hydrogen respectively. The Ni promoted Mo-samples were prepared by impregnation of the dried Mo-sample with aqueous nickel nitrate solution. The detailed preparation method of the catalysts, their Mo- and (or) Ni-content and some of their characteristic data determined before [13,14] are presented here in Table 1.

The purity of the chemicals, applied in experiments: thiophene (Merck&Co of purity, >98%), hydrogen sulfide (Messer Hungarogas LT, purity of 99%), $H_2{}^{35}S$ (radiochemical purity of 98.5% synthesized here in the laboratory of Institute of Isotopes Ltd. Co.) and hydrogen (Messer Hungarogas LT, purity of 99.5%) was checked by chromatography. The gas recirculation system for studying H_2S uptake and exchange was described previously [15,16,26,27]. The catalyst samples (calcined, $\sim 5 \times 10^{-3}$ g each) were sulfided by H_2S/H_2 or $H_2{}^*S/H_2$ mixture of about 53 kPa total pressure and ~2.4–26.7 kPa H_2S partial pressure (p_{H_2S}) in a circulation apparatus of 111.3 cm^3 with a reactor vessel of 26.5 cm^3 volume. The amounts of total and reversible sulfur uptakes of the samples ($^{G}S_{total}$ and $^{G}S_{rev}$ respectively) have been determined from the radioactivity changes in the gas phase, as described before [13,15,16]. The amounts of irreversible sulfur uptake have been calculated as $S_{cat} = {}^{G}S_{total} - {}^{G}S_{rev}$. The S_{cat} values, determined by direct radioactivity measurements of the $^*S$-labeled samples, indicated [13] a good agreement with those calculated from the gas phase radioactivity values. The samples after sulfidation were subjected to evacuation, after that they only contained irreversibly bound sulfur [15]. Some $^*S$-labeled samples have been treated for 60 min in H_2 of 53 kPa pressure for checking the stability of their sulfur (sulfide) phase. No gas phase radioactivity has been observed then; this indicated that the irreversibly bound sulfur was not removable by hydrogen at these conditions, different from the observations at a much higher (0.5 MPa) pressure of hydrogen [28].

Table 1
Characteristic data of the catalysts.

Catalyst[a]	n_{Ni} (10^{17} atoms/mg)		n_{Mo} (10^{17} atoms/mg)		Surface area (m^2/mg)[d]	m_{TH} (10^{17} mol/s.mg)[e]
	calc[b]	PGAA[c]	calc[b]	PGAA[c]		
Mo12	–	–	5.03	6.7	155	2.63
NiMo(0.15)	0.77	0.96	5.03	5.75	172	3.76
NiMo(0.35)	1.80	2.25[d]	5.03	6.43[f]	179	5.89
NiMo 0.6)	3.08	3.93	5.03	6.51	182	4.51
Ni 6	6.15	6.40	–	–	164	0.19

[a] All catalysts supported on Al_2O_3 of S.A. 212 m^2/g.
[b] Calculated.
[c] Determined by PGAA.
[d] Ref. [13].
[e] Ref. [14].
[f] Estimated from similar correlations between calculated Ni and Mo data determined by PGAA.

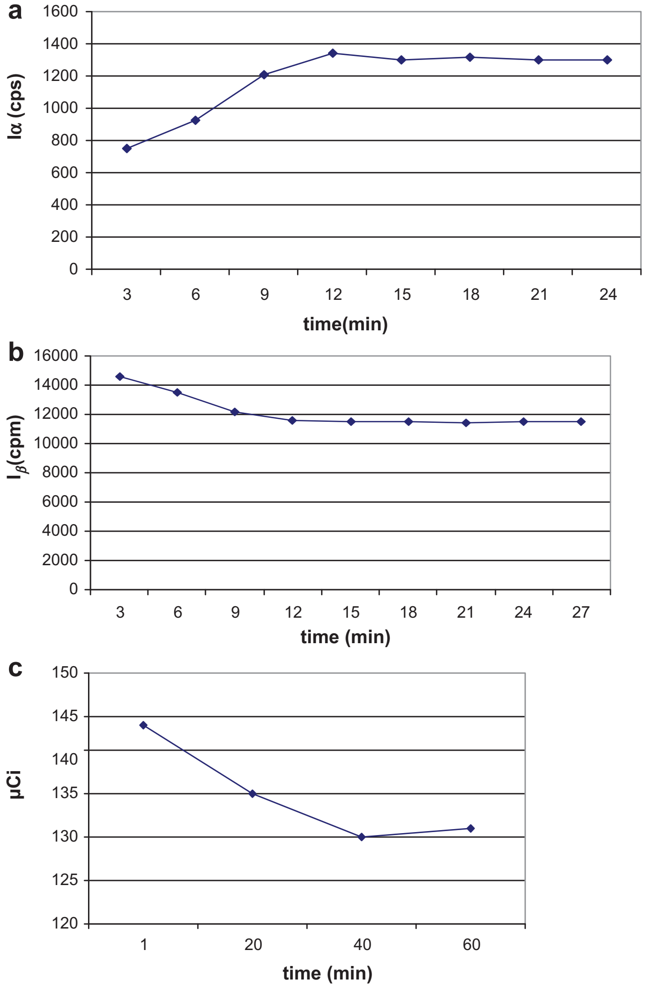

Fig. 1. Demonstration of radiosulfur exchange at 673 K ($S_{cat} \leftrightarrow H_2S$) vs. time by gas phase radioactivity. Catalyst: NiMo(0.35) (a) $^*S_{cat} \leftrightarrow H_2S$, as followed by increase of direct gas phase radioactivity; (b) $S_{cat} \leftrightarrow H_2{}^*S$, as followed by decrease of direct gas phase radioactivity measurements; (c) $S_{cat} \leftrightarrow H_2{}^*S$ as followed by the gas phase radioactivity values measured by liquid scintillation.

The sulfur exchange experiments were performed immediately after evacuation of the system with the sulfided samples at 673 K, the sulfidation temperature. The samples sulfided with $H_2{}^*S$ and vacuum treated were exposed to circulating H_2S/H_2 mixture of different (0.047:0.953–1:1) H_2S:H_2 ratio (proc. *a*). The samples sulfided with non-labeled H_2S were exposed to $^*S$-labeled hydrogen sulfide in a mixture in which the $H_2{}^*S/H_2$ ratio was equal to that applied for sulfidation of these samples with H_2S (proc. *b*).

Details of gas phase radioactivity determination are given elsewhere [26]. Gas mixture samples were taken for radioactivity measurements in 15 min intervals using a 1 cm^3 volume loop. The gas phase radioactivity changes due to the radiosulfur exchange process were followed under this treatment with a flow-through doped CaF_2 scintillation detector [29]. Gas phase radioactivity values have been checked by liquid scintillation measurements, as described before [13,27].

Data of sulfur uptakes by NiMo(0.35) are presented on Fig. 1a and, as examples of the gas phase radioactivity changes measured in 3 min intervals. The constant radioactivity, in processes *a* (I_α) and *b* (I_β) was reached for ~20 min, like to all catalysts in the case of exchange experiments. It is seen from the example of liquid scintillation measurements with the same catalyst (Fig. 1c) that somewhat longer time is required to reach the exchange equilibrium. The exchange experiments were continued therefore for 60 min in all H_2S experiments.

For determination of the sulfur exchange data in the interaction $S_{TH} \leftrightarrow {}^*S_{cat}$, a mixture of non-radioactive thiophene (~2.4 kPa, the maximum partial pressure to deal with gas phase thiophene under the given experimental conditions) and hydrogen (~51.6 kPa) was circulated at 673 K over the sulfided catalyst samples (5×10^{-2} g each) immediately after evacuation.

H_2S and thiophene sulfur exchange were compared on Ni12, Mo12 and NiMo(0.35) samples presulfided with $H_2{}^*S/H_2$ mixtures of ~53 kPa total pressure, of 2.4 and of 26.7 kPa partial pressure of $H_2{}^*S$. NiMo(0.35) was selected for this series of experiments because of the maximum irreversible sulfur uptake capacity [13] and thiophene HDS activity [14] of this sample among the NiMo(0.X) samples of different chemical composition. For comparison of the S-exchange between catalyst sulfur and H_2S with the exchange of sulfur in thiophene, it has been determined in these experiments that the thiophene conversion rates, the hydrocarbon and H_2S content of the products and the distribution of radioactive sulfur among H_2S and thiophene.

The thiophene conversion products have been determined by gas chromatography; Chrompac CP 9001 capillary column, their radioactivity was measured in LSC—liquid scintillation counting (PerkinElmer TR 2800). To this, the combusted products were absorbed in 1.5 cm^3 0.1 N NaOH and solubilized in a special liquid scintillation cocktail Clinisosol™ (Inst. of Isotopes Comp. LT). Distribution of sulfur radioactivity among H_2S and thiophene has been determined by liquid scintillation after 60, 120 and in some

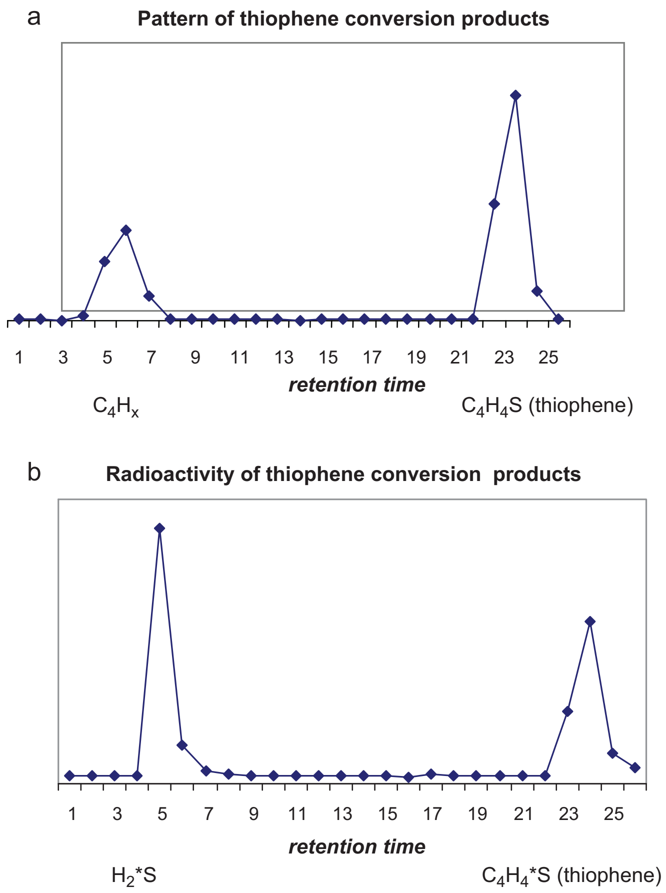

Fig. 2. HDS product distribution at conversion of thiophene on sulfided NiMo(0.35) (a) C_4-hydrocarbons:thiophene correlation (b) Distribution of radioactivity among thiophene and H_2S at conversion of thiophene on catalyst sulfided with $H_2{}^*S$.

cases after 180 min. Fig. 2a and b are presented as examples for the thiophene HDS product distribution and their radioactivity.

4. Results and discussion

The suitability of the circulation method detailed before [15] for determination of sulfur exchange in H_2S, it has been proved by the validity of Eq. (7). The S_{rev}, S_{cat} and S_{TE} values are presented in Table 2. They were determined at different H_2S/H_2 ratio for NiMo(0.35), with the respective calculated ratio of S_{TE}/S_{cat} (denoted g). Comparison of data obtained for two different NiMo(0.35) samples at experiments with the mixture of the same (1:1) H_2S/H_2 ratio indicated that the maximal error of the mean values is observed for the $^{b}S_{TE}$-s ~ 10%. The $^{a}S_{TE}$ values [calculated by Eq. (5)] are nearly equal with the $^{b}S_{TE}$-s [calculated by Eq. (6)] at exchange of any $p_{H_2S} : p_{H_2}$ ratio in the range of 0.1:0.9–1:1. This indicates besides the validity of Eq. (7), that the adsorption and exchange equilibrium on this catalyst has been reached under conditions applied for these experiments. The S_{exc} and S_{TE} values were the highest in the case of exchange in the gas mixture of $p_{H_2S}/(p_{H_2S} + p_{H_2}) = 0.5$, (i.e. $H_2S/H_2 = 1$). No definite tendency—like that for the S_{TE} and S_{cat} values, can be observed, as the g-values are practically equal (~0.9) at $p_{H_2S}/(p_{H_2S} + p_{H_2}) \approx 0.5$ and 0.05, respectively.

In Table 3 are presented the values of S_{exc} and $^{a}S_{TE}$, determined and calculated by Eqs. (1) and (3) from the $H_2S \leftrightarrow {}^{*}S_{cat}$ sulfur exchange experiments performed on the five catalysts with H_2S/H_2 gas mixture of p_{H_2S}~27 kPa and for three of them also at p_{H_2S}~2.5 kPa, for comparison. The Table contains also the sulfur uptake and exchange data for samples (denoted Mo-2 and NiMo-2) of the same chemical composition as those of the Mo12 and NiMo(0.6) respectively, determined and presented before [15].

It can be seen that the sulfur uptakes and the S_{exc} and S_{TE} values at p_{H_2S}~2.5 kPa are lower than those at p_{H_2S}~27 kPa for all samples. The g-value for Mo12 is higher at low p_{H_2S} in agreement with that for Mo-2. That was explained in Ref. [15] by the different structures of surface MoS_x, formed at different partial pressure of H_2S.

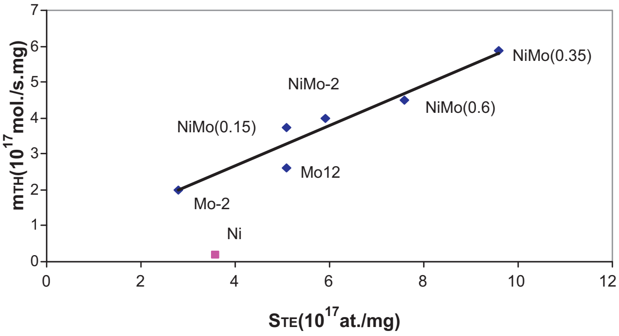

Fig. 3. Correlation between total exchange of sulfur in H_2S and thiophene HDS-activity of the different catalysts (cited from [8] and [9]). ♦ (or ♦): samples of Mo-content, ■ (or ■): alumina supported Ni {the S_{TE} values determined at $p_{H_2S} = 27$ kPa for the catalysts (see Table 2).

The S_{exc} and S_{TE} values are significantly different for the different catalysts. Fig. 3 presents the m_{TH} vs. S_{TE} graph, indicating a better correlation ($R^2 = 0.9192$) between H_2S sulfur exchange capacity and thiophene conversion activity of these samples in comparison with results observed before [13] between S_{cat}. The correlation between thiophene HDS activity and total sulfur exchange observed before for the different catalysts [15] is in agreement with observations [28,29] indicating a definite correlation between sulfur exchange, named there the amount of "labile sulfur". This correlation between HDS and S-exchange has been observed [30] also for HDS of dibenzothiophene on a Mo/Al_2O_3 catalyst (of 16 wt%Mo). The determined activation energy values for this reaction (84–92 kJ mol^{-1}) are near to that determined in our laboratory for thiophene HDS [14] on Mo12: 84 kJ mol^{-1}.

The correlation between the total sulfur exchange capacity and thiophene HDS activity confirms the conclusion drawn [15] about

Table 2
Sulfur uptake and exchange[a] with irreversibly bonded S on NiMo(0.35) at different partial pressure[b] of H_2S at 673 K.

p_{H_2S}	m_{so}	$^{G}S_{total}$	$^{G}S_{rev}$	$^{G}S_{cat}$[c]	$^{a}S_{exc}$[d]	$^{b}S_{exc}$[d]	$^{a}S_{TE}$[d]	$^{b}S_{TE}$[d]	^{a}g	^{b}g
26.7	109.2	22.9	11.7	11.2	7.9	20.1	9.70	10.30	0.88	0.93
26.7	109.2	23.3	13.7	9.6	7.7	20.3	9.58	8.19	1.00	0.85
16.0	65.4	16.1	9.1	7.0	4.7	13.3	6.00	5.38	0.86	0.76
5.3	21.7	13.2	7.9	5.5	2.0	9.8	3.68	3.55	0.65	0.65
2.5	10.5	5.8	2.2	3.6	2.0	4.1	3.32	3.42	0,92	0.95

[a] In 10^{17} mol/mg.
[b] p_{H_2S} in kPa $p_{H_2} + p_{H_2S} = 53.31$ kPa.
[c] The maximal error of the mean value is: 8%.
[d] The maximal error of the mean value is: 10%.

Table 3
Sulfur uptake from H_2S and exchange[a] with catalyst sulfur for the different catalysts; T:673 K.

Catalyst	$^{G}S_{total}$		$^{G}S_{rev}$		$^{G}S_{cat}$		$^{a}S_{exc}$		$^{a}S_{TE}$		g	
	I[b]	II[c]	I[b]	II[c]	I[b]	II[c]	I[b]	II[b]	I[b]	II[c]	I[b]	II[c]
Mo12[d]	7.4	10.1	2.1	3.1	5.3	7.0	2.7	4.7	5.0	5.1	0.94	0.72
NiMo(0.15)[d]	–	23.5	–	17.4	–	6.1	–	4.1	–	5.1	–	0.84
NiMo(0.35)[d]	5.8	23.1	2.2	12.7	3.6	10.4	1.9	7.8	3.3	9.6	0.92	0.92
NiMo(0.6)[d]	–	23.5	–	15.2	–	8.3	–	6.5	–	7.6	–	0.91
Ni12[d]	2.9	10.9	1.5	6.1	1.4	4.8	1.5	3.3	2.1	3.6	1.50	0.75
NiMo-2[e,f]	–	24.0	–	9.9	–	14.1	–	3.4	–	6.0	–	0.43
Mo-2[e,f]	8.8	12.1	4.2	7.2	4.6	5.1	2.5	2.6	3.2	2.8	0.69	0.55

[a] In 10^{17} mol/mg.
[b] Determined at p_{H_2S}~2.5 kPa.
[c] p_{H_2S}~27 kPa.
[d] Determined before $^{G}S_{total}$, $^{G}S_{rev}$ and $^{G}S_{cat}$ at p_{H_2S}~27 kPa for these samples {see Table 1 in [13]}.
[e] S_{total}, S_{rev}, S_{cat}, S_{exc} and S_{TE} data, determined before {see Y_1, Y_2, S^{cat}, S_{irr}, S_{exc} and S_{TE} respectively, in Table 2, Ref. [15]}.
[f] Mo-2 and NiMo-2:molybdena-alumina, and Ni-promoted molybdena-alumina samples of chemical content, similar to those of Mo-12 and NiMo(0.6) in this study, respectively.

the decisive role of the number of exchangeable sulfur atoms in the HDS activity of the sulfided Mo-based catalysts, explained there by the number of vacancies on edge sites of the Mo slabs. The higher (by ~40%) value of m_{TH} on NiMo(0.15) in comparison with that on Mo12 [14] at equal S_{TE} and lower S_{cat} values, is connected possibly with the somewhat higher ratio of the exchangeable sulfur on NiMo(0.15), as indicated by the higher g-value (Table 3). This sample occupies a specific place among the NiMo catalysts. The lower HDS activity, higher activation energy and lower S_{TE} value for this sample in comparison with the remaining two NiMo samples [14] is caused presumably by the low deposition degree of Ni on MoO_x [31] and the presence of two distinct surface phases [32]. This restricts the promoter effect of Ni: to produce S-uncovered Lewis acid sites extracting outermost S-atoms and to impede the free access to the sites [33].

The high ratio of exchangeable sulfur (g = 0.7–0.9) indicates a higher dispersion (higher S_{edge}/S_{top} ratio) of these samples, than that determined before [15] for Mo-2 and NiMo-2. This is supported by the much lower g-values for Mo-2 and NiMo-2 in comparison with those obtained for Mo12 and NiMo(0.6) respectively. Sulfur uptake and exchange data for Mo-2 (101 m^2/g S.A.) and NiMo-2 (117 m^2/g S.A) presented earlier [15], differ substantially from the S_{cat}- and S_{TE}-values presented in Table 3 for the samples of the same molybdenum content and Ni:Mo ratio in Mo12 (155 m^2/g S.A.) and Ni:Mo(0.6) of 182 m^2/g of S.A. respectively. The difference in the samples surface areas is connected presumably, with the different alumina supports in this pair of significantly different specific surfaces: 180 and 210 m^2. Nevertheless, these samples fit to the m_{TH} vs. S_{TE} correlation presented by the graph in Fig. 3.

The maximal sulfur exchange capacity, i.e. the maximal amount of exchangeable sulfur atoms (S_{TE}) on NiMo(0.35) is explained by the maximal number of Ni atoms an the surface on this samples in comparison with the other NiMo(0.X) samples. This follows from data in Ref. [14]. The maximal activity in dehydrogenation cyclohexane → benzene + $3H_2$ was observed on this sample at 573 K temperature. This indicated a maximal surface concentration on this catalyst as this reaction occurs only on a number of metal catalysts—including Ni—in the temperature range 548–673 K. The higher surface concentration of Ni-atoms on NiMo(0.35) overcompensates the lower activation energy values of this reaction on the NiMo(0.6) sample., as indicated by the 80% higher conversion rate of cyclohexane on this sample. The thiophene HDS conversion rate on NiMo(0.35) is also higher with ~30% than that on the sample of 0/35 Ni:Mo ratio. These data are in agreement and support the conclusion made by Aray et al. [33]: about the nature of NiMoS edge sites "...the promoter Ni are the most accessible atoms to the exterior of the edges". This is important both for the sulfided samples and for the partly reduced ones as the ratio of atomic nickel is only about 10% in the latter [13] Consequently the repulsive effect of oxygen in non-reduced NiO should be eluded by the reactant for interaction with Ni.

Monometallic Ni behaves differently from the Mo containing samples. $S_{TE}/S_{cat} > 1$ for the Ni12 sample, determined with the mixture of 0.05:0.95 H_2S/H_2 ratio. This indicates a higher number of exchanging sulfur atoms, than the number of sulfur species, bound irreversibly to nickel. This sample does not fit also to the linear correlation between S_{TE} and m_{TH}, presented in Fig. 3. This possibly indicates a different mechanism of thiophene HDS on monometallic Ni in comparison with that on Mo containing samples. Data presented in Table 4 on the molecular composition of hydrocarbon products of thiophene HDS support this assumption on the characteristic difference between monometallic Ni and the Mo-containing samples in the mechanism of thiophene HDS on these catalysts. A significant difference in $C_{<4}$ selectivity values is observed between monometallic Ni and the NiMo catalysts. It is worth mentioning that the $Bu_2^=/Bu_1^=$ ratio, an indicator characterizing the correlation of two different HDS routes [34–37] is in the range of ~2 for all Mo-containing samples, whereas the respective value is ~5 in case of Ni12. The difference between Ni12 and the other samples is especially high with respect to the distribution of all thiophene HDS products (see the last column of Table 3).

Table 4
Molecular composition (%) of hydrocarbons produced in thiophene HDS. T: 673 K; circulation time: 5 min.

Catalyst	Bu	$Bu_1^=$	$Bu_2^=$	$Bu_2^=/Bu_1^=$	$\sum C_{<4}$
Mo12	8.4	29.7	55.9	1.88	6.0
NiMo(0.15)	3.9	32.2	61.1	2.03	2.8
NiMo(0.35)	3.3	29.1	63.1	2.17	4.5
NiMo(0.6)	7.7	31.1	57.8	1.84	3.4
Ni12	29.4	8.8	47.7	5.42	14.0

The thiophene conversion data determined for radiosulfur labeled NiMo(0.35), Mo12 and Ni12 samples at high contact time in the circulation system are presented in Table 5. The HDS conversion activity of the three samples has the same sequence [NiMo(0.35) > Mo12 > Ni12] as observed in the case of a pulse system [14]. It is obvious that the HDS conversion activity of samples sulfided with the H_2S/H_2 ratio of 4.5/95.5 is significantly higher than that of the same samples if they were sulfided with the mixture of 1:1 ratio. This is in agreement with the well-known observation: H_2S inhibits the main HDS reaction [1]. The higher amounts of vacancies on samples sulfided with the mixture of lower H_2S/H_2 ratio results in a higher effectiveness of active sites, in a higher ratio of "fast sites", as stated by Kogan and Isaguliants [38].

Table 5 contains also the corresponding data on distribution of radioactive sulfur between thiophene and H_2S. The appearance of thiophene with significant ratio of products radioactivity indicates the interaction between catalyst sulfur and C_4-hydrocarbons, products of thiophene HDS. For all samples $I_{H_2S} > I_{TH}$, the value of their ratio depends, however, on the contact time. The different catalytic behavior is expressed also in the radioactivity distribution between HDS products: I_{TH}/I_{H_2S} ratios are in the range of 0.05–0.27 for NiMo(0.35) and Mo12, whereas this ratio falls into in a much higher range (0.2–0.6) in the case of Ni12, i.e. the differences between the radioactivity of H_2S and thiophene are substantially lower on this catalyst.

The presence of radioactive thiophene among products of thiophene conversion on radiosulfur labeled catalyst is—totally or in part—the result of butadiene + H_2S interaction. This is thermodynamically possible: at these conditions $K_p \sim 28$ and the concentration of thiophene at equilibrium would be ~82–85% as calculated from literature data [39]. Our special experiments also indicated [24] that this reaction occurs on all the three samples, but the conversion rates are different. However, a direct sulfur exchange between catalyst sulfur and thiophene cannot be excluded, as it has been mentioned before; further studies are required directed to solve this problem.

The relatively higher I_{TH}/I_{H_2S} ratio on Ni12 is presumably the consequence of the significantly lower thiophene HDS conversion in comparison with that on Mo12 and NiMo(0.35). Results of a recent study indicate [37] that the active sites are similar for hydrogenation (i.e. via tetrahydrothiophene) and desulfurization (via C_4-hydrocarbons) routes of HDS. Consequently the higher I_{TH}/I_{H_2S} ratios for Ni12 expresses the higher difference in the ratio in "specific" catalytic activities of these sites in the two processes—$C_4H_4{}^*S$-production and HDS—on this catalyst in comparison with Mo12 and NiMo(0.35).

The radiosulfur exchange data of sulfur in thiophene have been collected in Table 6. The ${}^{TH}S_{TE}$ values were calculated by Eq. (6) applying S_{exc}, μ_{H_2S} and μ_{TH} data determined at 60 min conversion of thiophene. The S_{rev} data were determined from H_2S

Table 5
Thiophene conversion and radioactivity distribution of products.

Catalyst	Sulfided in $H_2{}^*S/H_2$ (mol%)	Thiophene circulation time (min)	Converted thiophene (%)	μ_{H_2S} $[I_{H_2S}/I_{H_2S}+I_{TH}]$	μ_{TH} $[I_{TH}/I_{H_2S}+I_{TH}]$
Mo12	4.5/95.5	30	83.8	0.899	0.101
Mo12	4.5/95.5	60	89.1	0.839	0.161
Mo12	4.5/95.5	120	93.1	0.874	0.126
Mo12	50/50	60	70.8	0.784	0.216
Mo12	50/50	120	71.3	0.879	0.122
Mo12	50/50	180	81.6	0.951	0.049
NiMo(0.35)	4.5/95.5	30	86.9	0.790	0.210
NiMo(0.35)	4.5/95.5	60	91.2	0.910	0.090
NiMo(0.35)	4.5/95.5	120	95.8	0.944	0.056
NiMo(0.35)	50/50	60	81.9	0.898	0.102
NiMo(0.35)	50/50	120	89.5	0.938	0.062
NiMo(0.35)	50/50	180	96.7	0.947	0.047
Ni12	4.5/95.5	30	50.0	0.647	0.353
Ni12	4.5/95.5	60	64.9	0.621	0.379
Ni12	4.5/95.5	120	75.5	0.620	0.380
Ni12	50/50	60	32.0	0.832	0.168
Ni12	50/50	120	45.0	0.862	0.135
Ni12	50/50	180	50.5	0.790	0.210

Table 6
Sulfur (H_2S) uptake by and sulfur exchange of thiophene[a] with presulfided catalysts; T:673 K.

Catalyst	S_{rev}		S_{exc}		${}^{TH}S_{TE}$		${}^{H_2S}S_{TE}$		H_2S_{add}		$H_2S_{T.add}$	
Presulf. %H_2S	4.5	50	4.5	50	4.5	50	4.5	50	4.5	50	4.5	50
Mo12	2.1	1.8	1.2	1.3	1.7	1.8	1.59	1.34	0.19	0.32	0.22	0.37
NiMo(0.35)	3.6	3.2	1.4	2.1	2.7	4.4	1.98	3.64	0.16	0.24	0.19	0.31
Ni 12	2.0	1.5	1.4	1.6	2.0	2.2	1.38	0.75	0.85	0.32	0.95	0.38

[a] In 10^{17} S atoms/mg units and 10^{17} TH or H_2S mol/mg units respectively.

uptake and are presented in the table, TH_{rev} values (the reversible adsorption of thiophene) were determined [24] by adsorption of ^{35}S-labeled thiophene [7.6×10^{16} and 6.7×10^{16} mol/mg for Mo12 and NiMo(0.35), respectively]. The TH_{rev} value for Ni12 was estimated to be 5.2×10^{16} mol/mg from the S_{rev} measured for Ni12 and by considering the ratios S_{rev}/TH_{rev} for NiMo(0.35) and Mo12 (Table 7).

In Table 6 are presented also the ${}^{H_2S}S_{TE}$ values (i.e. the total exchange values of sulfur in H_2S formed in HDS of thiophene) calculated by Eq. (7). These are 1.7×10^{17} and 1.8×10^{17} mol/mg for Mo12 presulfided with mixtures of 4.5 and 50% H_2S respectively. The fact that the sums ${}^{H_2S}S_{TE} + H_2S_{add}$ are equal to 1.81×10^{17} and 1.71×10^{17} mol/mg i.e. to the respective ${}^{TH}S_{TE}$ values in Table 6, indicates the reliability of these calculations. The higher difference between the sum ${}^{H_2S}S_{TE} + H_2S_{add}$ and the ${}^{TH}S_{TE}$ values in the case of Ni-containing samples—especially in case of Ni—is presumably the consequence of the higher $\Sigma C_{<4}$ (and lower ΣC_4) ratio among the products (see data in Table 4).

The comparison of the thiophene sulfur exchange data with those for H_2S in Table 2 indicates that the degrees of sulfur exchange—expressed in the S_{TE} values—are definitely higher in the case of sulfur exchange in H_2S, i.e. $S_{TE} > {}^{H_2S}S_{TE}$. The sequence of sulfur exchange activity is however the same for S in thiophene than that of S in H_2S, for the three samples: NiMo(0.35) > Mo12 > Ni12.

Table 7
Adsorption potentials ($Q_{X\text{-cat}} + Q_{Y\text{-cat}}$) of the catalysts and activation barrier values (E_{XY}) for H and CS bond dissociation (units in kJ).

Catalyst	$Q_{H\text{-cat}} + Q_{S\text{-cat}}$	$Q_{C\text{-cat}} + Q_{S\text{-cat}}$	${}^{a}E_{SH}$	${}^{b}E_{SC}$
Mo12	–	185	–	112
NiMo(0.15)	334	165	6	132
NiMo(0.35)	376	229	−76	65
NiMo(0.6)	365	222	−25	72
Ni 12	214	194	106	103

[a] Accepting for Q_{SH} 340 kJ [41].
[b] Accepting for Q_{CS} 297 kJ [42].

The higher S_{exc} and S_{TE} of sulfur in H_2S could be explained by Balandin's approach [40] on the basis of the energy barrier values of the two exchange processes. If the exchange $H_2S \leftrightarrow H_2{}^*S$ would require the dissociation of S–H bonds then the energy barrier of this process on the catalyst (${}^{cat}E_{SH}$) would be

$$ {}^{Cat}E_{SH} = Q_{SH} - [Q_{H\text{-cat}} + Q_{S\text{-cat}}] \tag{10} $$

The exchange of sulfur in thiophene: $C_4H_4S \leftrightarrow H_2{}^*S$ both the direct (if it proceeds at all) and the stepwise way would require the C–S bond dissociation with the energy barrier to be calculated by the expression:

$$ {}^{cat}E_{SC} = Q_{SC} - [Q_{C\text{-cat}} + Q_{S\text{-cat}}] \tag{11} $$

The bond strength values Q_{SH} and Q_{SC} are 340 [41] and 297 kJ [42], respectively, whereas the $Q_{C\text{-cat}}$, $Q_{S\text{-cat}}$ and $Q_{H\text{-cat}}$ denote the bond strengths of the respective atoms with the catalyst. These values have been determined [43] for our alumina supported NiMo(0.X) and Ni12 samples by Balandin's kinetic method. The ${}^{cat}E_{SH}$ and ${}^{cat}E_{SC}$ values calculated by Eqs. (10) and (11) are presented in Table 6, and indicate that the energy barrier of S-exchange in thiophene would be definitely higher than that in H_2S, whereas the sequences of the adsorption potentials.

($Q_{H\text{-cat}} + Q_{S\text{-cat}}$) and ($Q_{C\text{-cat}} + Q_{S\text{-cat}}$) are identical for the NiMo samples. This explains the higher S exchange between ${}^*S_{cat}$ and S in H_2S, in comparison with that of S in thiophene. The maximum adsorption potentials for NiMo(0.35) explains the maximum activity of this sample in sulfur exchange and thiophene hydrodesulfurization. This is in agreement also with the much lower activation energy of thiophene HDS on NiMo(0.35), in comparison with that on Ni12 and Mo12 [14].

The Moscow Group in the N.D. Zelinsky Institute based on studies of thiophene HDS in atmosphere of H_2 labeled with tritium (^3H) and evaluation of the radioactivities in all reaction products [21,22] came to the conclusion [38], that thiophene HDS and exchange in H_2S proceeds by the same mechanism, and the rate limiting step of this process is:

$$H^*S\text{–cat} + H_2 \rightarrow H^{\cdots}\text{cat} + H_2{}^*S\text{–cat} \qquad \text{(III)}$$

i.e. the interaction between surface-bonded $^*SH$ and gas phase, or physisorbed H_2. Consequently the dissociation of S–H bond(s) plays no role in the sulfur exchange of thiophene. This is in agreement with data in Table 7, as the S–H bond dissociation on the Mo containing samples is an exothermic process, consequently, by the bond strength approach this step could not be a rate determining one. From other side, both the thiophene hydrodesulfurization, resulting—via recyclization—in formation of $^*S$-labeled thiophene and the direct exchange of sulfur in thiophene ($C_4H_4S \leftrightarrow H_2{}^*S$)—if it proceeds at all—would require the S–C bond dissociation of a high energy barrier.

It should be noted that the lower activation energy of sulfur exchange—named their S-liberation—in comparison with that of dibenzothiophene HDS on the same Mo/Al_2O_3 [30] catalyst indicates a definite difference between the two processes. It follows from this that there would be of interest to determine the activation energy values of $^*S_{cat}$ exchange with S in H_2S that of $^*S_{cat} \rightarrow$ for comparison those with the values in exchange of $^*S_{cat}$ with sulfur in thiophene.

5. Conclusions

The amount of total sulfur uptake and exchange is a function of the partial pressure of gas phase H_2S. Both the reversible H_2S-uptakes and the irreversible ones decrease with decreasing H_2S partial pressure; the latter becomes nearly constant at low partial pressure. Sulfur exchange data indicate that a high ratio (70–90%) of irreversibly bound sulfur is exchangeable with sulfur in gas phase H_2S; it follows from that a high dispersion (S_{edge}/S_{top} ratio) of the samples. A definite linear correlation was found between the total H_2S sulfur exchange capacity of the Mo-containing catalysts and their thiophene hydrodesulfurization activity. The maximal amount of exchangeable S-atoms, and the maximal HDS activity of nickel promoted molybdena of 0.35:0.65 Ni:Mo ratio is explained—in agreement with Aray's conclusion—by the maximal number of surface Ni-atoms accessing the reacting molecules on that sample.

Comparison of sulfur exchange by hydrogen sulfide formed in thiophene HDS ($^{H_2S}S_{TE}$) with S_{cat} ($H_2S \leftrightarrow {}^*S_{cat}$) and that by thiophene ($^{TH}S_{TE}$ in $C_4H_4S \leftrightarrow {}^*S_{cat}$) indicates that the total sulfur exchange (S_{TE}) in $H_2S \leftrightarrow {}^*S_{cat}$ is different from that occurring at conversion of thiophene on catalysts containing $^*S_{cat}$. At $p_{H_2S} = 27$ kPa H_2S $^{H_2S}S_{TE} > {}^{TH}S_{TE}$; this is observed also at $p_{H_2S} = 2.4$ kPa with the exception of monometallic Ni. The S_{TE}/S_{cat} values are different for the different samples. This value is the highest on NiMo(0.35) both for $^{H_2S}S_{TE}$ and $^{TH}S_{TE}$.

The radioactivity data indicate that some H_2S addition to C_4-hydrocarbons, products of thiophene conversion occurs on all samples, besides sulfur exchange between $^*S_{cat}$ and H_2S in case of thiophene conversion. The ratio of the two processes was different for the different samples; the H_2S addition was, however, substantially lower than that of the S-exchange.

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References

[1] H. Topsoe, B.S. Clausen, F.E. Massoth, Hydrotreating catalysis, science and technology, in: J.R. Anderson, M. Boudart (Eds.), Catalysis—Science and Technology, vol. 11, Springer Verlag, Berlin/New York, 1996.
[2] S. Eijsbouts, Stud. Surf. Sci. Catal. 121 (1999) 21–36.
[3] M. Egorova, R. Prins, J. Catal. 225 (2004) 417–427.
[4] D.D. Whitehurt, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 345–472.
[5] S. Brunet, D. Mey, G. Perot, C. Bouchy, F. Diehl, Appl. Catal. A 278 (2005) 143–172.
[6] V.M. Kogan, Kinet. Catal. 46 (2005) 77–87.
[7] Z. Vit, D. Gulkova, L. Kaluza, M. Zdrazil, J. Catal. 232 (2005) 447–455.
[8] M. Egorova, R. Prins, J. Catal. 241 (2006) 162–172.
[9] G.M. Dhar, B.N. Sirivas, M.S. Rhana, M. Kumar, S.K. Maity, Catal. Today 86 (2003) 45–60.
[10] M. Breysse, P. Afanasiev, C. Geantot, M. Vrinat, Catal. Today 85 (2003) 5–16.
[11] R.R. Chianelli, M.H. Siadati, M.P. Rosa, G. Berhault, J.P. Wilcoxon, R. Bearden, B.L. Abrams, Catal. Rev. Sci. Eng. 48 (2006) 1–41.
[12] W. Rechetilowsky, Chem. Ing. Tech. 79 (2007) 729–740.
[13] P. Tétényi, T. Ollár, Z. Schay, P. Schnörch, T. Szarvas, Appl. Radiat. Isot. 66 (2008) 1190–1195.
[14] P. Tétényi, P. Schnörch, O. Tellinger, React. Kinet. Catal. Lett. 97 (2009) 141–150.
[15] F.E. Massoth, T. Koltai, P. Tétényi, J. Catal. 203 (2001) 33–40.
[16] T. Koltai, F.E. Massoth, P. Tétényi, React. Kinet. Catal. Lett. 71 (2000) 85–92.
[17] P. Tétényi, V. Galsán, React. Kinet. Catal. Lett. 74 (2001) 251–257.
[18] V.M. Kogan, A.A. Greish, G.V. Isagulyants, Catal. Lett. 6 (1990) 157–162.
[19] W. Quian, A. Ishihara, G. Wang, M. Godo, T. Tsuzuki, T. Kabe, J. Catal. 170 (1997) 286–294.
[20] A.N. Startsev, E.V. Artamonov, Yu.I. Yermakov, Appl. Catal. 45 (1988) 183–190.
[21] G.V. Isagulyants, A.A. Greish, V.M. Kogan, in: M.J. Philips, Ternan (Eds.), Proc. 9th Int. Congress on Catalysis, vol. 1, The Chem. Inst. of Canada, Ottava, Ontario, Canada, 1988, pp. 35–41.
[22] V.M. Kogan, in: T. Weber, R. Prins, R. van Santen (Eds.), Transition Metal Sulfides Chemistry and Catalysis 3, High Technology NATO ASI Series, Kluwer, Dordrecht, 1998, pp. 235–272.
[23] C.G. Gachet, E. Dhainaut, L. de Morgues, J.P. Claudy, P. Fouilloux, Bull. Soc. Chim. Belg. 90 (1981) 1279–1285.
[24] T. Ollár, T. Szarvas, P. Tétényi, unpublished results.
[25] G.V. Isaguliants, A.A. Greish, M.A. Riaschenceva, H.M. Minachev, E.P. Belanova, L.I. Kovalenko, Izv. Acad. Nauk SSSR Ser. Chim. 27 (1978) 2289–2293.
[26] T.I. Korányi, M. Dobrovolszky, T. Koltai, K. Matusek, P. Tétényi, Fuel Proc. Technol. 61 (1999) 55–71.
[27] M. Dobrovolszky, K. Matusek, Z. Paál, P. Tétényi, J. Chem. Soc. Faraday Trans. 89 (1993) 3137–3142.
[28] A. Ishihara, J. Jpn. Petrol. Inst. 51 (2008) 73–82.
[29] F. Dumeignil, J.F. Paul, E.W. Qian, A. Ishihara, E. Payen, T. Kabe, Res. Chem. Intermed. 29 (2003) 589–607.
[30] S.T. Hong, D.R. Park, S.J. Yoo, J.-D. Kim, H.S. Park, Res. Chem. Intermed. 32 (2006) 857–870.
[31] B. Delmon, Bull. Soc. Chim. Belg. 104 (1995) 173–187.
[32] M.J. Ledoux, S. Hantzer, J. Guille, Bull. Soc. Chim. Belg. 96 (1987) 855–862.
[33] Y. Aray, J. Rodriguez, A.B. Vidal, S. Coll, J. Mol. Catal. A: Chem. 271 (2007) 105–116.
[34] V. Moravek, M. Kraus, Collect. Czech. Chem. Commun. 50 (1985) 2159–2169.
[35] K.C. Campbell, M.L. Mirza, S.J. Thomson, G. Webb, J. Chem. Soc. Faraday Trans. 80 (1984) 1689–1704.
[36] V.M. Kogan, N.N. Rozhdestvenskaya, I.K. Korshevets, Appl. Catal. A: Gen. 234 (2002) 207–219.
[37] H. Wang, E. Iglesia, J. Catal. 273 (2010) 245–256.
[38] V.M. Kogan, G.V. Isaguliants, Catal. Today 130 (2008) 243–248.
[39] Yu.A. Afanasieva, M.A. Ryasentseva, Kh.M. Minachev, I.I. Levitski, Russ. Chem. Bull. 19 (1970) 1892–1896.
[40] A.A. Balandin, Adv. Catal. 19 (1969) 1–210.
[41] J.W.C. Johns, D.A. Ramsay, Can. J. Phys. 39 (1961) 210–219.
[42] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.
[43] P. Tétényi, O. Tellinger, React. Kinet. Mech. Catal. 99 (2010) 99–109.