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Catalyst's sulfur displacement by thiophene, as monitored by exchange of ^{35}S radiotracer

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The isotopic exchange has been studied between catalyst radiosulfur and H_2S, formed in thiophene hydrodesulfurization (HDS) (named S-displace) on alumina supported molybdena, on $CoMoO_x$, $PdMoO_x$, $PtMoO_x$ and on silica–alumina supported $NiWO_x$. S-displace was compared with radiosulfur exchange data between catalyst radiosulfur and gas phase H_2S (S^{exc}) determined previously. The extent of S^{exc} was higher than that of the S-displace for Mo, CoMo in and NiW, whereas the extent of S-displace from PdMoO and PtMoO was significantly higher, than that of S^{exc}. Thiophene HDS product distribution data are discussed in terms of increased C=C hydrogenation and C–C hydrogenolysis activity, explained by increasing H_2S production with longer circulation time of the thiophene/H_2 mixture, The $C_1/C_3<1$ ratios among C_4-hydrogenolysis products indicate some coke formation. The decrease of thiophene HDS activity is presumably a consequence of increasing site-blocking with the formation of more H_2S and coke with longer duration of thiophene treatment.

KEY WORDS: sulfur exchange; thiophene hydrodesulfurization; coke formation; MoO_x; $CoMoO_x$; $PdMoO_x$; $PtMoO_x$; $NiWO_x$.

1. Introduction

Literature data indicate a parallelism between catalyst hydrodesulfurization (HDS) activities and the amounts of exchangeable sulfur in sulfided catalysts [1–5]. Sulfur exchange between non-labeled sulfur (^{32}S, denoted through S) and the labeled one (^{35}S, denoted through *S) is monitored by the decrease of gas phase radioactivity of $H_2{}^*S$ (i.e.[^{35}S] H_2S) during its interaction with a sample sulfided by "S" or by its increase in the reverse process (see e.g. Ref. [3]). Sulfur uptake and exchange studies are carried out also with *S-labeled organic compounds, using mostly thiophene [6, 7] and dibenzothiophene (see e.g. Ref. [8]). Sulfur exchange data between catalyst sulfur and $H_2{}^*S$, formed in HDS of the *S labeled organic compounds were determined by these methods. The absence of any direct exchange between catalyst sulfur and sulfur in thiophene or dibenzothiophene was confirmed. This was valid for the case of interaction of *S containing catalyst with the organic compound [7] as well as for contacting *S-labeled thiophene [6] or *S-dibenzothiophene [2, 8] with non-radioactive catalyst.

It was found however that the nature of the sulfiding agent could essentially affect the HDS activity [9], as treatment of the catalyst with H_2S/H_2 resulted in a deeper sulfidation than treating it with thiophene [6, 10]. High pressure *S uptake and sulfur exchange studies indicated however nearly identical results with those obtained with $H_2{}^*S$ and * S-labeled dibenzothiophene [11].

Sulfur uptake and exchange data determined by catalyst ↔ thioorganic compound interaction represent processes initiated by sites, active in HDS, whereas the sites which do not participate in that reaction are involved only via surface migration of sulfur.

It was of interest to make a direct comparison of sulfur exchange:

$$^*S_{cat} + H_2S \leftrightarrow S_{cat} + H_2{}^*S \qquad (1)$$

with the S-exchange between $^*S_{cat}$ in catalysts, labeled beforehand with radiosulfur by circulation of H^*S/H_2, and that of H_2S produced by HDS of thiophene, circulated over those catalysts. The question to be decided by this was: to what extent is the fraction of *S in the catalyst replaceable by H_2S produced on sites, active in HDS? There are substantial differences between the productivities of the different sites. This is seen from the results of kinetic studies [12] indicating that the reduction of sulfur overlayers on Mo(100) in pure H_2 is much different from that in the presence of: thiophene. The existence of the so called "rapid" and "slow" sites – well known from the radiotracer studies performed by the Moscow research group [4–7, 13] – supports also the differences in the productivities of sites. Consequently the answer to the question, raised above is determined on the one hand, by the site productivity correlation between HDS sites and sites, active in irreversible H_2S uptake. On the other hand, the difference between the extent of $^*S_{cat}$-exchange depends on the correlation between the number of sites active in HDS and those, active in irreversible uptake of H_2S.

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A further motivation of the study was the observed effect of thiophene treatment on HDS selectivity [14]: the hydrocarbon product distribution, namely the values of

$$\eta = \frac{\Sigma B^{=}}{B + C_{1-3}} \tag{2}$$

indicating the ratio of the amounts of butanes ($\Sigma B^{=}$) to the sum of products of hydrogenation (B) and of C–C hydrogenolysis (C_{1-3}) determined in thiophene HDS on sulfided catalyst samples decreased with increasing thiophene circulation time over them. At long run (~20–80′) thiophene treatment the η-values approached those observed in conversion on the reduced samples. The HDS conversion rates on Mo, CoMo and NiW approached also the values determined for the reduced samples. The thiophene HDS activity of sulfided PdMo and PtMo samples decreased also substantially with increasing circulation time of thiophene.

These observations raised the question: whether the nearly identical behavior of samples treated with thiophene on the long run and reduced samples would be a result of catalysts' desulfurization, as a consequence of higher sulfur displacement by sulfur produced in HDS reaction, in comparison with the extent of sulfur exchange by process (1)? How far does resist catalyst sulfur to long run treatment with thiophene?

To answer these questions sulfur exchange data, determined for the same catalysts [3, 15] were compared with those of sulfur diplacement (i.e. of catalyst *S exchange with thiophene HDS produced S).

2. Experimental

The experiments were carried out on alumina supported molybdena (denoted Mo), on molybdena–alumina containing Co, Pd or Pt (CoMo, PdMo and PtMo respectively) and with amorphous silica–alumina supported tungsten-oxide, promoted with nickel (NiW). Preparation procedure, and characteristic data for Mo, CoMo, NiW and PdMo, PtMo have been reported earlier [3, 15–17]. The Mo content of the catalysts was $\sim 5 \times 10^{20}$ atoms/g. The W, Co, Ni, Pd and Pt content in the catalysts was ~4.3, 3.6, 1.6, 1.5 and 0.93×10^{20} atoms/g respectively, as determined by prompt-gamma activation analysis [18].

The gas recirculation system for studying H_2S uptake and measuring gas phase radioactivity was described previously [15, 19]. Details of the radioactivity measurements are given elsewhere [15]. The catalyst samples (50 mg each) in the reactor vessel of 83 cm^3 volume, were exposed after evacuation to $H_2{}^*S/H_2$ mixtures at about 53 kPa of total pressure,~ 4 kPa H_2S partial pressure, at 673 K. The mixtures were circulated through the catalyst for 60 min until a constant gas phase radioactivity was reached. The total sulfur uptake (S_T) was calculated from the loss of initial radioactivity (I_o) of the $H_2{}^*$ S/H_2 mixtures:

$$S_T = Y_1 = m_{so}(1 - I_1/I_o) \tag{3}$$

where m_{so} is the number of H_2S molecules in the initial mixture and I_1 is the gas phase radioactivity at the end of the run. The errors for Y-values in this run were ± 10%, as reported in for Mo, NiW, PdMo, PtMo [3] and for CoMo [15]. The samples after sulfidation were subjected to evacuation treatment in vacuo for 2 h to remove the reversibly adsorbed S species.

The sulfidation procedure, m_{so} and Y_1 data were reported in [3, 15]. At the end of the vacuum treatment a thiophene/H_2 mixture (of 4 ~ kPa thiophene and of 53.3 kPa total pressure) was circulated over the catalysts for determination of the actual sulfur exchange between gas phase H_2S and catalyst's *S. Samples from the mixture were taken with a loop of ~ 1 cm^3 for radioactivity measurements until a constant gas count rate (I_{sc}) was reached. Then the respective product distribution data including the degree of thiophene conversion were determined with a 5 m long GC column of 18% squalane on chromosorb P, and the respective number of H_2S molecules (m_{sc}) were calculated The uncertainty in the determination of the mean degree of conversion was ±0.0143%, as determined from parallel measurements with eight sulfided CoMo samples.

The amounts of gas phase H_2S molecules (viz the sum $H_2S + H_2{}^*S$) exchanged with H_2S at the end of the thiophene treatment (Y_{sc}) were calculated [3] by:

$$Y_{sc} = m_{so}(I_{sc}/I_o) \tag{4}$$

At equilibrium, the number of moles of $H_2{}^*S$ in the gas phase (*Y) is [3] the difference between the extent of exchange of catalysts sulfur species (X_{sc}), and that adsorbed reversibly on the catalyst, $^*Y_{ad}$:

$$^*Y_{sc} = X_{sc} - {}^*Y_{ad} \tag{5}$$

The total amount $(S + {}^*S)$ of displaceable by (i.e. exchangeable with) "m_{sc}" H_2S molecules produced in thiophene HDS catalyst's sulfur (X_d) to be calculated by expression:

$$X_d = m_{sc}Y_{sc}/(m_{sc} - Y_{ad} - Y_{sc}) \tag{6}$$

as demonstrated in Ref. 3 for the total exchangeable sulfur (X_T), where Y_{ad} denotes the amount of reversibly adsorbed H_2S (S^{ads}), reported previously for these catalysts [3,15], and denoted there as Y_2.

Comparison of the X_d-values with the X_T-s, determined for these catalysts in previous studies [3, 15] indicates for the different catalysts the difference between the displacement of catalyst sulfur by H_2S, formed in thiophene HDS and that by gas phase H_2S.

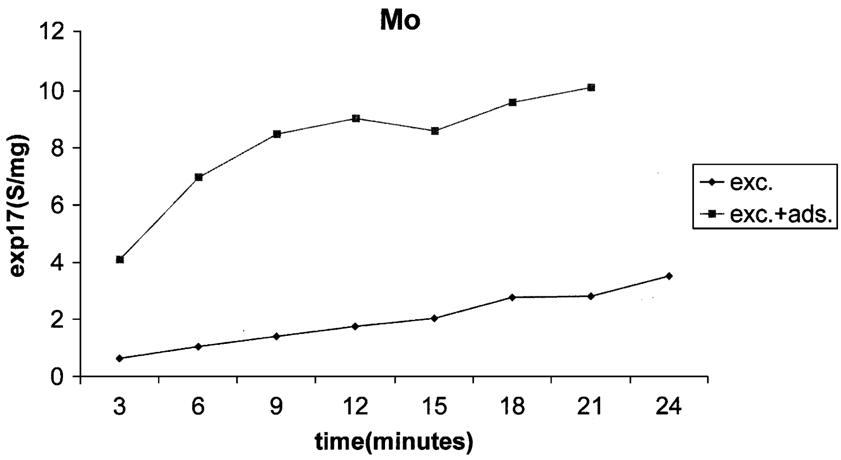

Figure 1. Amounts of exchanged $*S_{cat}$ and those of $*S_{ads}$ + $*S_{exc}$.

3. Results and discussion

Table 1 contains the m_{sc}-values – the amounts of H_2S formed in thiophene HDS up to the constant gas phase radioactivity was reached. The periods for approaching constant I_{sc} were in the range of 20–80 min for the different catalysts, and the respective conversion degrees were in the interval of 0.45–0.85. The time periods are dependent presumably on the differences in the HDS rates over the different catalysts [13], since special sulfur-exchange experiments indicated no significant differences with respect to their S^{exc} and S^{exc} + adsorption rates, determined by the method, described in [15]. The constant S^{exc} and $(S^{exc} + S^{ads})$ values were approached after ~ 20–30 min. This is illustrated with the exc vs. time and (exc + ads) vs. time graphs for Mo on figure 1.

Table 1 summarizes also the Y_{sc} values calculated by equation (3). To calculate X_d-s, the Y_{ad} values, determined previously [3, 15] for these catalysts were used and corrected to the actual H_2S pressure as done in [3] $(^{c}Y_{ad})$.

No other substances besides H_2S and H_2 were present by $^{c}Y_{ad}$ determination. It should be considered also the hindrance of $H_2{*}S$ adsorption by reversible molecular adsorption of thiophene. Two approximations seemed best [20]:

(i) one-point attachement to the surface by through the sulfur atom. Then both the H_2S and thiophene molecules require one vacancy;

(ii) a multi-point attachement of the cycle of the thiophene molecule to the surface, possibly by π-bonding, occupying three sites. The corrected Y_{ad} values were calculated for case i:

$$^{cl}Y_{ad} = ^{c0} Y_{ad}[m_{sc}/(m_{sc} + m_t)] \qquad (7a)$$

and for case ii:

$$^{c3}Y_{ad} = ^{c0} Y_{ad}[m_{sc}/(m_{sc} + 3m_t)] \qquad (7b)$$

respectively, $(^{c}Y_{ad}$ is Y_{ad} corrected for the actual H_2S pressure, as done in the absence of other substances [3]; it is denoted here $^{c0}Y_{ad}$, as valid if assuming the reversible thiophene adsorption $\ll$ H_2S adsorption).

Table 2 contains the $^{cl}X_d$ and $^{c3}X_d$ values, calculated by equations (7a) and (7b) wit h$^{Cl}Y_{ad}$ and $^{C3}Y_{ad}$ respectively. The $^{c0}X_d$ values are given, calculated with $^{0}Y_{ad}$ i.e. for the case of no reversible adsorption of thiophene. For comparison we added the X_T values determined for these catalysts previously [3, 15] from $H_2S \leftrightarrow S_{cat}$ exchange experiments.

Data in table 2 indicate that the X_d values differ significantly from the X_T data, Consequently the sites of irreversible H_2S adsorption should not be considered as fully identical with the sites, active in thiophene HDS: both their number and activity in H_2S uptake can be different (different in part, presumably). For Mo, CoMo and NiW both the $^{cl}X_d$ and $^{c3}X_d$ are significantly lower, than the respective X_T values, i.e. the sulfur in these

Table 1
Thiophene conversion and sulfur exchange on sulfided catalysts $T = 673$ K

Catalyst	$m_{sc}10^{17}$ mol./mg	m_t10^{17} mol./mg	$Y_{sc}10^{17}$ S atoms/mg	$Y_{ad}10^{17}$ S atoms/mg	$^{c}Y_{ad}10^{17}$ S atoms/mg	$^{cl}Y_{a}10^{17}$ S atoms/mg	$^{c3}Y_{ad}10^{17}$ S atoms/mg
Mo	9.20	11.49	1.25	4.17	3.46	1.69	0.77
CoMo	8.86	11.34	1.26	3.70	2.08	0.91	0.43
NiW	16.68	5.06	0.57	4.71	4.10	3.14	2.15
PdMo	12.78	7.22	2.06	5.10	4.12	2.62	1.53
PtMo	16.94	4.56	1.14	5.25	4.62	3.65	2.56

Table 2

Calculated data of the amounts (in 10^{17} S atoms/mg) of sulfur displaced and the respective ratios of displaceable catalyst sulfur $T = 673$ K

Catalyst	$^{c0}X_d$	$^{c1}X_d$	$^{c3}X_d$	$^{a}X_T$	$^{c1}g_d$	$^{c3}g_d$	$^{a}g_T$
Mo	2.58	1.86	1.60	3.36	0.38	0.32	0.68
CoMo	2.02	1.66	1.56	2.14	0.23	0.22	0.30
NiW	0.81	0.74	0.6 8	1.05	0.10	0.09	0.14
PdMo	3.98	3.26	2.86	1.58	0.34	0.30	0.16
PtMo	1.73	1.58	1.46	1.07	0.27	0.25	0.18

[a] X_T and g_T are the arithmetic mean of $X_{T3} + X_{T4}$ and of $g_3 + g_4$ respectively

catalysts is more easily removed by surface S-species produced in H_2S chemisorption – than by those, produced in thiophene HDS. The opposite effect was observed in the case of the samples, containing Pd and Pt. This seems to be in agreement with the high mobility of sulfur on supported Pd, Pt and PdPt documented thoroughly by Kabe et al. [20, 21]. The high H_2S release from PdMo in comparison with that from PtMo is presumably a consequence of the higher sulfur content in surface PdS_x in comparison with PtS_y, as indicated by XPS [17]. Another reason can be the presence of sulfur in elemental form under sulfidation conditions similar to those applied here, as indicated by XRD and electron microscopy [17]. Elemental sulfur is highly exchangeable even at low temperature (393 K) as observed recently [22].

In table 2 are collected also the calculated values of the mobile sulfur fractions:

$$g_d = X_d / S_{cat} \tag{8}$$

where S_{cat} is the amount of irreversible S-uptake, determined before [3, 15]. $g_d < g_T$ for Mo, CoMo and NiW, whereas for PtMo and PdMo $g_d > g_T$ i.e. in case of these catalysts the fraction of displaced sulfur is higher than that determined in exchange with H_2S. The g_d data indicate that a high fraction of catalyst sulfur (~ 10–70%) is not removable when treated with thiophene.

To answer the question, raised in the Introduction on the nearly identical product distribution in thiophene HDS over reduced samples (not sulfided with gas phase H_2S) and sulfided ones, treated with thiophene, the amounts of not displaceable, stable sulfur (S_{st}) treated with thiophene on the long run, can be calculated by the expression:

$$S_{st} = S_{cat} - X_d \tag{9}$$

Table 3 compares these S_{st}-s with $^{irr}q_t$ – the amounts of sulfur, bonded to the reduced samples, that were exposed to a single thiophene pulse. For $^{irr}q_t$-s were accepted the differences between irreversible sulfur uptakes from H_2S pulses by samples unexposed ($^{irr}q_1$) and exposed ($^{irr}q_2$) previously to one thiophene pulse:

$$^{irr}q_t = {}^{irr}q_1 - {}^{irr}q_2 \tag{10}$$

The $^{irr}q_i$ and thiophene HDS values were reported for Mo, CoMo, PdMo and PtMo [23]. The $^{irr}q_2$ was not available for NiW; $^{irr}g_t$ for this catalyst was calculated from the amount of H_2S, produced in thiophene HDS [16], accepting that the ratio of H_2S uptake was equal with that from gas phase H_2S [16]. The $^{irr}q_t$ data are collected also in table 3. It is worth mentioning that the ratio of irreversible sulfur uptake by Mo, CoMo and PtMo from the gas phase H_2S differed from the ratio of sulfur uptake from H_2S arising via thiophene HDS. This indicates again that H_2S chemisorption sites – presumably a part of them – should be considered as being different from the HDS sites. These differences – like those between X_d and X_T – are caused presumably by

Table 3

Irreversible sulfur uptakes in 10^{16} S/mg $T = 673$ K

Catalyst	$^{a}S_{cat}$ 10^{16} S/mg	S_{st} 10^{16} S/mg	$^{b\ irr}q_1$		$^{irr}q_t$	
			10^{16} S/mg	$\%H_2$ S[c]	10^{16} S/mg	$\%H_2$ S[d]
Mo	50.2	23.0	5.8	60.2	1.3	47.5
CoMo	70.2	50.7	7.0	73.1	0.1	2.4
NiW	40.4	32.3	2.9	23.5	0.3	23.5
PdMo	96.8	57.0	5.2	54,0	1.4	54.0
PtMo	57.9	40.6	5.1	52.7	1.9	21.8

[a] irreversible uptake reported in [3, 16]

[b] $^{irr}q_1$: from [16, 23] $^{irr}q_t$: calculated by [10] from data in [22], for NiW from HDS conversion in [16], assuming uptake % of H_2S equal with that from the first H_2S pulse.

[c] q_1 in percents of a H_2S pulse.

[d] q_t in percents of HDS conversion, for NiW from HDS conversion in [16] assuming uptake % of H_2S equal with that from the first H_2S pulse.

Table 4
Distribution of C_4 hydrocarbons formed in thiophene HDS[a:] the butenes/butane ratio $T = 673$ K

Pretreatment[b] Proc. no.	Catalyst				
	Mo	CoMo	NiW	PdMo	PtMo
1	6.8	10.6	12.2	1.9	1.5
4(2′)	11.2	14.2	17.3	13.9	4.9
4(20′)	4.3	1.9	8.8	1.7	0.4
4(∼ 80′)	–	1.2	6.2	1.0	0.3

[a]From data in [14],
[b] Proc 1: reduced, Proc 4(x'): sulfided , treated in thiophene/H_2 for x min.

the differences both in the activity and in the concentration of active sites. The equal percentage of H_2S uptakes by PdMo indicates by no means a general identity of HDS and H_2S chemisorption sites: possibly this equality is a consequence of compensation of the sites' concentration with their activities.

Data in table 3 indicate that a substantial fraction of S_{cat} resisted to the long run thiophene treatment. The irreversible sulfur content of the reduced samples due to the conversion of the first thiophene pulse is $<6\%$, i.e. substantially lower, than the S_{st} values. Consequently the similarities observed [14] between reduced samples and those treated with thiophene in a long run with respect to their product selectivities (η-values) can not be explained by elimination of sulfur from them during thiophene treatment. It is clear (table 4) that the ratio butenes/butane among the HDS products, formed on reduced samples, increased at sulfidation (see those ratios at 2′ circulation). On the other hand, it decreased with increasing circulation time, and on sulfided samples treated with thiophene/H_2 for 20 and 80′ its value was lower than in case of the reduced ones. This also contradicts the assumption that the initial state of the reduced samples would be restored upon thiophene treatment. This observation can be explained by the interrelationship of the concentration of $H^{\delta+}$, $H^{\delta-}$ and $SH^{\delta-}$ surface species formed in dissociation of H_2 and H_2S:

$$H_2 \leftrightarrow H^{\delta+} + H^{\delta-} \tag{11}$$

$$H_2S \leftrightarrow H_2^{\delta+} + SH^{\delta-} \tag{12}$$

The presence of H_2S, blocking a part of sites decreases the concentrations of $H^{\delta+}$ and $H^{\delta-}$ species, being equal in the absence of H_2S, but it results in a higher $H^{\delta+}$ concentration [(see equation (12)] in comparison to that of the $H^{\delta-}$ species. This explains, why H_2S favors hydrogenation compared to C–S breakage, and – with increasing circulation time and in presence of H_2S – increased butane selectivities in comparison with butenes at decreasing thiophene HDS conversion [24].

The decreasing butene:butane ratio is concomitant also with the increase of C_4-hydrogenolysis (formation of C_1–C_3 products) with increasing thiophene circulation time [14], because the C–C and C–H bond strengths are higher at the C=C bond in $B^{=}2$ – being present among HDS products in higher amounts than $B^{=}1$ – in those bond strengths in butane [25]. The increased hydrogenation and hydrogenolysis selectivity explains the decreasing values of η with increasing circulation time.

Table 5 presents a survey of C_1–C_3 hydrocarbon distribution among HDS products for obtaining more information on possible changes in the status of the sulfided catalysts upon thiophene treatment. It is seen from data in this table that the C_1:C_3 ratio is lower

Table 5
Amounts of C_1–C_3 hydrocarbon products formed in thiophene HDS (in 10^{16} mols/mg) $T = 673$ K

Catalyst	Pretreatment	C_1	C_2	C_3	$C_3 - C_1$	C_3:C_1
Mo	Reduced	0.82	0.17	0.12	−0.71	0.14
	Circulation2′	0.47	0.23	0.69	0.23	1.48
	Circulation 20′	3.36	1.42	4.78	1.34	0.40
CoMo	Reduced	1.19	0.85	0.36	−0.82	0.31
	Circulation2′	1.27	0.12	0.11	−1.16	0.09
	Circulation20′	1.16	2.36	3.48	2.33	3.0
	Circulation92′	4.16	7.51	7.69	3.53	1.85
NiW	Reduced	0.004	0.002	0.008	0.004	2.0
	Circulation2′	0.330	0.28	0.566	0.236	1.72
	Circulation20′	2.80	3.06	10.87	8.04	3.88
	Circulation90′	7.28	8.27	22.80	15.5	3.13
PdMo	Reduced	0.831	0.056	0.102	−0.726	0.122
	Circulation2′	0.690	0.563	0.826	0.136	1.20
	Circulation20′	1.96	0.658	11.58	9.62	7.07
	Circulation80′	3.54	11.40	18.96	15.42	5.36
PtMo	Reduced	0.242	0.048	0.024	−0.208	0.10
	Circulation2′	0.346	0.506	0.478	0.132	1.38
	Circulation20′	1.046	0.879	7.30	6.25	6.98
	Circulation83′	3.54	6.89	14.76	11.22	4.17

significantly among HDS products, formed after circulating thiophene/hydrogen for 20 and 80 min than in case of the reaction on reduced samples. Moreover, this ratio is <1 in case of all catalysts after 20 and 80 min circulation time, similarly to a previous observation with NiMo catalysts [19]. Considering the primary stoichiometry of the hydrogenolysis of C_4-hydrocarbons ($C_4 \rightarrow C_3 + C_1$) the amount of C_1 should not be lower than that of C_3. (The reverse [$C_3/C_1 < 1$] is possible, as a result of further C_3- and C_2-conversion to methane.) The value $C_1/C_3 < 1$ indicates a carbon deficit among hydrocarbons, presumably due to coke formation on the catalysts under these conditions, possibly by the so-called "carbon route", i.e. by migration of carbon atoms, formed in the reaction of deep fragmentation of C–C and C–H bonds on the surface, followed by formation of carbonaceous islands [26]. It should be noted that literature data [26–30] exclude the possibility of direct, one step $C_1 \rightarrow C_2$ conversion at these conditions. It proceeds either in a lower, <523 K temperature region [27, 28] and/or via carbonaceous surface intermediates [26, 29, 30]. The C_2-yield in these cases is lower than that of methane by one order of magnitude. The amounts of primary carbon losses at C_4-hydrogenolysis were calculated as the difference of the amounts: $\Sigma C_3 - C_1$. The carbon deficit calculated by this way indicates the minimal amounts of coke formation by fragmentation of C_4-hydrocarbons, as carbon, formed via fragmentation of C_2- and C_3-hydrocarbons, is not considered by this calculation. These (minimum) amounts of produced carbon (see last column in table 4) increased with increasing circulation time. Calculations indicated the highest carbon losses on NiW and PdMo catalysts: the C/(Ni + W) and C/(Pd + Mo) ratios were 0.26 and 0.27 at 80' circulation times respectively.

These data indicate the presence of a substantial amount of coke on the catalysts. This explains – besides the blocking increasing parts of surface sites by the presence of increasing amounts of H_2S – why the activities of the samples treated by thiophene were near to, or lower than those of the fresh, reduced catalysts.

4. Conclusions

Isotopic exchange data between catalyst radiosulfur and gas phase H_2S differ from data of exchange with H_2S produced in thiophene HDS. This indicates that sites of H_2S chemisorption differ presumably in part from HDS sites. Sulfur exchange data indicate that only a part of catalyst sulfur is displaced from the catalyst during a long treatment (20–80 min) with thiophene/H_2. Presumably the increasing H_2S formation enhances the hydrogenation of butenes and hydrogenolysis of C_4-hydrocarbons, formed in thiophene HDS. Product distribution of C_1–C_3 hydrocarbons indicates increasing coke formation with longer treatment of the catalysts by thiophene.

References

[1] D.A. Scarpiello, A.A. Montagna and J. Freel, J. Catal. 96 (1985) 276.

[2] T. Kabe, W. Qian, W. Vang and A. Ishihara, Catal. Today 29 (1996) 197.

[3] F.E. Massoth, T. Koltai and P. Tétényi, J. Catal. 203 (2001) 33.

[4] V.M. Kogan, N.N. Roshdestvenskaya and I.K. Korsevets, Appl. Catal. Gen. 234 (2002) 207.

[5] V.M. Kogan, Appl. Catal. Gen. 237 (2002) 207.

[6] G.V. Isagulyants, A.A. Greish and V.M. Kogan, in: *Proc. of the 9th Int. Congr. Catalysis*, M.J. Philips and M. Ternan eds. 1(Canadian Inst of Chem, Ottawa, 1988) pp. 35.

[7] V.M. Kogan, A.A. Greish and G.V. Isagulyants, Catal. Lett. 6 (1990) 157.

[8] W. Qian, Q. Zhang, Y. Okoshi, A. Ishihara and T. Kabe, J. Chem. Soc. Farad. Trans. 93 (1997) 1821.

[9] G.V. Isagulyants, A.A. Greish and V.M. Kogan, Kinetics Catal. Engl. Tr. 28 (1987) 220.

[10] V.M. Kogan and N.M. Parfenova, in: *1st Eur. Symp. Hydrotreating and hydrocracking of Oil fractions*, eds. G.F. Froment, B. Delmon and P. Grange (Elsevier Science, 1997). p. 449.

[11] T. Kabe, W. Qian, K. Tanihata, A. Ishihara and M. Goda, J. Chem. Soc. Farad. Trans. 93 (1997) 3709.

[12] A.J. Gellman, M.E. Bussell and G.A. Somorjai, J. Catal. 107 (1987) 103.

[13] V.M. Kogan, N.M. Parfenova, R.G. Gaziev, N.N. Rozhdestvenskaya and I.K. Korshevets, Kinet. Catal. 44 (2003) 583. (English Translation).

[14] P. Tétényi and T. Koltai, React. Kinet. Catal. Lett. 82 (2004) 371.

[15] T. Koltai, F.E. Massoth and P. Tétényi, React. Kinet. Cat. Lett. 71 (2000) 85.

[16] T.I. Korányi, M. Dobrovolszky, T. Koltai, Z. Paál, K. Matusek and P. Tétényi, Fuel Proc. Tech. 61 (1999) 55.

[17] Z. Paál, T. Koltai, K. Matusek, J.M. Manoli, C. Potvin, M. Muhler, U. Wild and P. Tétényi, Phys. Chem. Chem. Phys. 3 (2001) 1535.

[18] Zs. Kasztovszky, Zs. Révay, G. Molnár, A. Wootsch and Z. Paál, Catal. Commun. 3 (2002) 553.

[19] T. Koltai, E.E. Massoth and P. Tétényi, in: *2nd Eur. Symp. Hydrotreating and hydrocracking of Oil fractions*, eds. G.F. Froment, B. Delmon and P. Grange (Elsevier Sci., 1999) p.137.

[20] H. Topsoe, B.S. Clausen and F.E. Massoth, in: *Hydrotreating Catalysis, Science and Technology* and references therein (Springer VI, Berlin, 1995).

[21] T. Kabe, W. Quian, Y. Hirai, L. Li and A. Ishihara, J. Catal. 19 (2000) 191.

[22] S.Yamada, D. Wang, S.Li, M. Nishikawa, W. Quian, A. Ishihara and T. Kabe, Chem. Commun. (2003) 842.

[23] M. Dobrovolszky, K. Matusek, Z. Paál and P. Tétényi, J. Chem. Soc. Farad. Trans. 86 (1993) 3137.

[24] J. Leglise, L. Finot, J.N.M. van Gestel and J.C. Duchet, in: *2nd Eur. Symp. Hydrotreating and Hydrocracking of Oil Fractions*, and references therein, eds. G.F. Froment, B. Delmon and P. Grange (Elsevier Sci. 1999) p. 51.

[25] M. Szwarc, Chem. Rev. 47 (1950) 75.

[26] A. Sárkány, H. Lieske, T. Szilágyi and L. Tóth, in: *Proc. 8th Int. Congr. Catal. Berlin (Vl. Chem.)*, vol. 3 (1984) p. 623.

[27] M. Belgued, A. Amariglio, P. Pareja and H. Amariglio, J. Catal. 159 (1996) 441.

[28] Z. Hlavathy, Z. Paál and P. Tétényi, J. Catal. 166 (1997) 118.

[29] T. Koerts, H.J. Deelen and R.A. van Santen, J. Catal. 138 (1992) 101.

[30] L. Guczi, K.V. Sharma and L. Borkó, Catal. Lett. 39 (1996) 43.