Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Catalysis Today 130 (2008) 243–248
CATALYSIS TODAY
www.elsevier.com/locate/cattod

The HDS mechanism: Which “auxiliary” process takes place – sulfur isotopic exchange or replacement – and why is it important to know it?

Victor M. Kogan [*], George V. Isaguliants

The N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prospect, Moscow 119991, Russia

Abstract

In the light of general evaluation of the radioisotopic data obtained during the years of our research two possible ways of sulfur transfer from the catalyst into H_2S in the course of thiophene HDS have been reconsidered. These are (i) sulfur exchange between H_2S formed and the catalyst sulfur and (ii) extrusion of sulfide sulfur into the gas phase by the interaction of the catalyst SH group with H_2 with the further formation of H_2S. The data of our radioisotopic studies supports the second way, which proceeds within the “forcing out” mechanism. This mechanism assumes either of the two possible schemes of H_2S formation—(a) H_2 interaction with the catalyst bridge sulfur and (b) H_2 interaction with the SH group. The radioisotopic studies support the second possibility.

Keywords: Thiophene; SH groups; Radioisotopic study into the HDS mechanism; ^{35}S; H_2 dissociation; H_2S formation; Transition metal sulfides; Catalysis

1. Introduction

The mechanism of thiophene HDS was investigated in many publications ([1] and references within, [2–16]). Although various mechanisms of thiophene decomposition over sulfide catalysts have been proposed, the role of sulfide sulfur remains unclear. We studied thiophene HDS using both ^{35}S [18–23] and ^{3}H [17,21,23,24], which allowed us to suggest the “forcing out” mechanism [21,23]. According to it, the sulfur of thiophene “extrudes” the sulfide sulfur from the catalyst surface into the gas phase. The mechanism includes interaction of the gas phase H_2 with the SH group of the catalyst. The interaction explains a transfer of the radioactivity into the H_2S in the course of thiophene HDS over the catalyst labeled by ^{35}S (Scheme 1). However, an alternative mechanism could be supposed – radioactivity transfers from the sulfide catalyst into the H_2S molecule due to an isotopic exchange between the labeled catalyst *SH group and the H_2S formed (path **a**, Scheme 2). If it were the case, the change in molar radioactivity (MR) would not be related to the catalytic activity in the HDS. To obtain the answer to the question which of the mechanisms is realized is an aim of the article.

In recent computational studies [25–31] the interaction of the molecular hydrogen with the sulfide bridge sulfur is postulated. But according to the “forcing out” mechanism H_2 reacts with a catalyst SH group. So, another aim of the paper is to understand which of the alternative mechanisms is true. It is important for correct computing the key elementary steps of thiophene HDS, and, evaluating of the active sites functioning.

2. Experimental

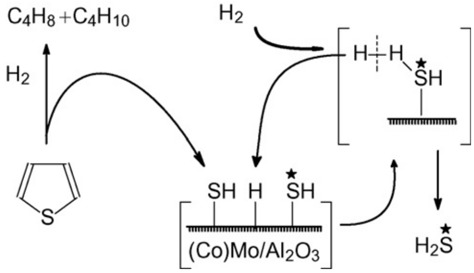
To prepare a sulfide catalyst labeled by ^{35}S the samples in oxide form were sulfidized in a 21 cm^3 autoclave by using elemental sulfur-(^{35}S) (H_2, 6 MPa, 360 °C, catalyst: sulfur ratio = 5:1 wt.). The catalyst samples labeled by ^{3}H were prepared by the sulfidation of the oxide form catalyst by non-radioactive sulfur in hydrogen-(^{3}H) atmosphere.

The sulfidized catalyst containing radioactive sulfur or tritium was loaded in a microreactor of an experimental pulse setup combined with a radiochromatograph. After the catalyst was treated in a He flow, the reactor was fed with hydrogen that also served as a carrier gas for a radiochromatograph and treated by a non-radioactive hydrogen flow to remove all

---

[*] Corresponding author.
E-mail address: vmk@ioc.ac.ru (V.M. Kogan).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.07.021



Scheme 1. A transfer of the radioactivity into the H_2S in the course of thiophene HDS over the catalyst labeled by ^{35}S according to the "forcing out" mechanism.

reversibly adsorbed hydrogen from the catalyst. The pulses of unlabeled thiophene or H_2S of a 1 μl and 0.2 cm^3 volume correspondingly were successively supplied to the catalyst. The signals from the TCD of the gas chromatograph (GC) and from a flow proportional counter of radioactivity, installed outlet of GC, were processed in the *on-line* regime.

Curves of H_2S MR as a function of the H_2S produced (cm^3) were calculated, equivalent to the dependence on the amount of reacted thiophene. H_2S MR values were normalized relatively to the value of the initial MR of sulfide sulfur on the catalyst (%). The dependencies obtained can be approximated by exponential equations of the following type:

$$\alpha = \sum A_i \exp(-\lambda_i x) \tag{1}$$

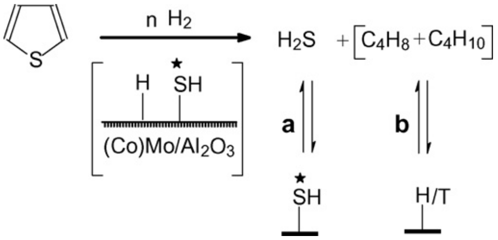
Each item of (1) describes the H_2S MR changes with an intensity determined by the value of the exponential power λ_i, this intensity being characteristic of active sites (AS) of the given type. Proceeding from Eq. (1), it is possible to estimate the amount of catalyst sulfur S_i (in mg) that can participate in H_2S formation (mobile part of sulfur) on the AS of the given type:

$$S_i = \frac{32}{22.4 \times 100} \int_0^\infty A_i \exp(-\lambda_i x)\,dx \tag{2}$$

Integration of (2) gives

$$S_i = \frac{32}{22.4 \times 100} \frac{A_i}{\lambda_i} \tag{3}$$

If more than one exponent describes the curve, i.e. if several types of active sites take part in the reaction, the total amount of mobile sulfur is estimated by the sum: $S_{mob} = \sum S_i$.



Scheme 2. Possible (**a**) $^{32}S \Leftrightarrow {}^{35}S$ and (**b**) H ⇔ T isotopic exchange reactions in the course of thiophene HDS.

3. Results

3.1. Thiophene HDS over catalyst-(^{35}S)

In the experiments of thiophene HDS on a catalyst sulfided by ^{35}S [17–20] radioactivity was detected only in the H_2S formed during the reaction but not in non-reacted thiophene, i.e. there was no exchange between sulfide sulfur and thiophene. Experiments in which the sulfidized catalyst was treated in a flow of hydrogen showed that no detectable amounts of H_2S were formed in the absence of thiophene. Thus, during HDS catalyst sulfur is replaced by sulfur from thiophene. Some of sulfur is "immobile", i.e. it cannot participate in the formation of H_2S during the HDS, and some can. The latter can be considered as "mobile". We have established correlations between catalyst activity in HDS and the amount of mobile sulfur and mobile sulfur reactivity (mobility). A share of mobile sulfur depends on catalyst composition, preparation and pretreatment conditions. Mobile sulfur is not uniform. It can consist of more and less mobile parts ("rapid" and "slow" sulfur). These two parts of mobile sulfur correspond to the two types of the sites that differ in the reactivity of the sulfur during the formation of H_2S and are named "rapid" and "slow". We attribute the "rapid" sites to Mo and the "slow" sites to Co or Ni [20,23].

3.2. Isotopic exchange between the catalyst-^{35}S and the gas phase H_2S

In the course of the experiment the curve of the MR of the H_2S depending on the amount of the H_2S passed over the catalyst labeled by ^{35}S was obtained. The curves obtained in the course of thiophene HDS and H_2S isotopic exchange (Fig. 1, curves 1 and 2) are close. This may be due to a possible competition between both processes if an essential amount of H_2S exists in the reaction zone. This is in a good agreement with a well-known observation that H_2S inhibits the main HDS reaction ([1] and references within, [32]).

3.3. Thiophene HDS over catalyst-^3H

To determine the source of hydrogen which takes part in H_2S formation we studied thiophene HDS on $CoMo/Al_2O_3$ containing irreversibly adsorbed hydrogen labeled by tritium [17,23]. An initial catalyst sample was sulfided in an atmosphere of radioactive hydrogen. To remove all reversibly adsorbed hydrogen ^3H from the catalyst, the sample was kept for 1 h at 360 °C in a flow of H_2 that was non-radioactive. Measurements of gas phase radioactivity showed that already during the first minutes of the H_2 treatment a significant amount of labeled hydrogen left the catalyst. However, some of the tritium remained on the catalyst and did not exchange with gas phase hydrogen, i.e. this tritium was irreversibly adsorbed on the catalyst during sulfidation.

In thiophene HDS experiments on the catalyst labeled by ^3H it was found that a tracer passes from the catalyst to the H_2S formed. At the same time, next to none radioactivity was found

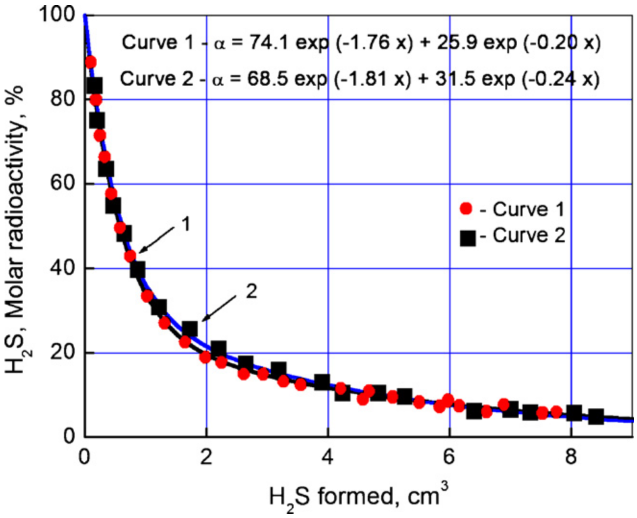


Fig. 1. Dependences of H_2S MR on the amount of H_2S formed in the course of (1) thiophene HDS over catalyst-^{35}S; and (2) isotopic exchange between catalyst-^{35}S and H_2S. .

in the hydrocarbons and unconverted thiophene. It follows that irreversibly adsorbed hydrogen participates in the HDS reaction but not in hydrogenation (HYD) or in hydrogen exchange reactions. The analysis of the dependence of the H_2S specific radioactivity on the amount of H_2S formed (Fig. 2) showed that irreversibly adsorbed hydrogen and sulfide sulfur of the CoMo catalyst behave similarly. Calculations proved that the total amounts of H_2S formed with irreversibly adsorbed hydrogen and H_2S formed with mobile sulfur are actually the same. In both experimental series the shares of H_2S formed on each type of active site were the same and the distributions of mobile sulfur and irreversibly adsorbed hydrogen on the catalyst were alike (Table 1). Hence, both sulfur and hydrogen transfer to H_2S from one and the same SH group.

This conclusion is supported by the results of measuring specific radioactivity (SR) of the catalyst sample and H_2S obtained by using liquid scintillation technique (Table 2). According to the radiometric analysis, the initial SR of the sulfided $CoMo/Al_2O_3$ catalyst treated in an unlabeled H_2 flow is 610 pulses/min mg. If we assume that all tritium chemisorbed on the catalyst is in the SH groups and linked exclusively to mobile sulfur, the SR of surface SH groups must be 21.8×10^3 pulses/min, related to 1 mg of mobile sulfur. This corresponds to the initial SR of H_2S formed in the reaction. So, the number of the irreversibly adsorbed hydrogen atoms is equal to the number of mobile sulfur atoms. This is another proof that irreversibly adsorbed hydrogen is in the SH groups that participate in the formation of H_2S and that in the course of thiophene HDS catalyst SH groups transfer to H_2S as a whole.

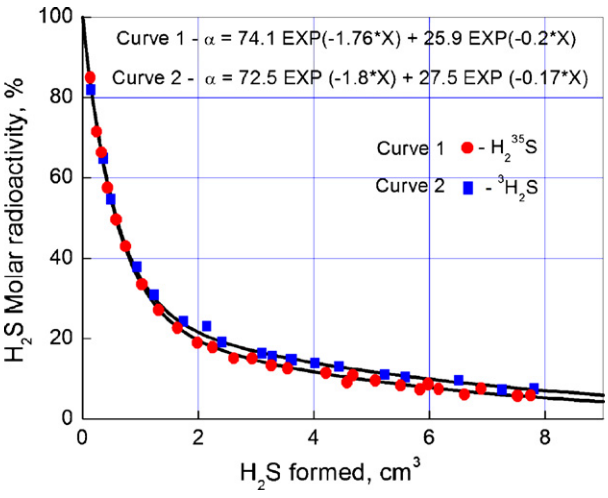


Fig. 2. Dependences of H_2S MR on the amount of H_2S formed in the course of thiophene HDS over sulfide catalyst (1) labeled by ^{35}S and (2) by ^{3}H.

Table 1

H_2S formation with the participation of mobile sulfur and irreversibly adsorbed hydrogen in the course of thiophene HDS on the sulfide catalyst samples labeled with ^{35}S and ^{3}H (360°, 100 mg catalyst loading, H_2 flow, thiophene pulse volume—1 μl)

	H_2S amount (cm^3)	
	^{35}S	^{3}H
Formed with participation of labeled atoms	2.45	2.89
Formed on "rapid" sites, belonged to Mo	0.60	0.58
Formed on "slow" sites, belonged to Co	1.85	2.31

3.4. *Thiophene HDS in hydrogen-^{3}H atmosphere over non-radioactive catalyst*

To evaluate the role of gas phase hydrogen in the HDS of thiophene we studied thiophene conversion in the atmosphere of H_2 labeled with tritium [21,23,24]. Radioactivity (^{3}H) was found in all the reaction products. Table 3 shows that the MR values of thiophene and hydrocarbons are proportional to the number of the H atoms in the above-mentioned molecules. The thiophene reduced molar radioactivity (RMR) defined as MR corresponding to 1 mol of hydrogen in a molecule is only 10% lower than that of the C_4-hydrocarbons. A relatively high value of the RMR of thiophene proves that hydrogen exchange takes place in thiophene before HDS. It follows that a fast isotopic exchange is under way between the gas phase and thiophene hydrogen.

Radioactivity was also discovered in H_2S but its RMR in the first pulses was about 120 times lower than that of the butenes and butane. Low H_2S radioactivity is caused by the changing rate of dissociation of molecules with different isotope contents—H_2 and T_2 (or HT; here and below ^{3}H is indicated as T), i.e. a kinetic isotopic effect (KIE). Since the dissociation

Table 2

Results of radiometric measurements of the catalyst labeled with ^{3}H and H_2S formed in the course of HDS on this catalyst

	SR (pulses/ min mg)	SR ($\times 10^{-3}$ pulses/ min mg S)
H_2S after sulfidation		21.2
H_2S from the catalyst[a]		21.0
Catalyst before HDS[b]	610	21.8
Catalyst after HDS	252	

[a] H_2S SR is detected at initial reaction time.

[b] H_2S MR is calculated based on 1 mg of mobile sulfur.

Table 3
MR of the products of thiophene HDS over non-radioactive CoMo/Al_2O_3 catalyst in a hydrogen-^3H flow (H_2 MR = 5.9 GBq/mol, 360 °C, 100 mg catalyst loading)

	C_4H_4S	C_4H_8	C_4H_{10}	H_2S
MR (GBq/mol)	9.33	19.53	25.25	0.04
RMR (GBq/mol)	4.67	4.88	5.05	0.04

RMR: reduced molar radioactivity.

of molecular hydrogen takes place before the HYD reactions, similar RMR values for H_2S and C_4-hydrocarbons could be expected. This is, however, not the case. It proves that the formation of H_2S is caused by the reaction of the catalyst SH groups with H_2. At the same time, HYD reactions proceed with the participation of preliminary dissociatively adsorbed hydrogen, and a KIE does not take place. As the SH group in the given experiment is non-radioactive, the RMR of the H_2S is determined by 0.5 of the MR of H_2. So, the value of the actual KIE is about 60.

The results of the above described experiments show that three types of hydrogen take part in the HDS over sulfidized (Co)Mo/Al_2O_3 catalysts: irreversibly adsorbed hydrogen from SH groups, reversibly and dissociatively adsorbed hydrogen and molecular hydrogen:

1. Irreversibly adsorbed hydrogen participates in the HDS reaction but not in hydrogenation or in hydrogen exchange reactions. Both surface sulfur and irreversibly adsorbed hydrogen transfer to H_2S from one and the same SH group. It means that in the course of thiophene HDS catalyst SH groups transfer to H_2S as a whole and that hydrogen from SH groups does not interact with a neighboring SH group. This hydrogen does not participate in isotopic exchange, or in the hydrogenation reaction or in C–S bond breaking.
2. Dissociatively and reversibly adsorbed hydrogen. This hydrogen is formed in the course of H_2 dissociation over metals with the formation of a type of hydride linked to Mo and easily participates in the reactions of hydrogenation and isotopic exchange. These reactions cannot be accompanied by the kinetic isotopic effect because hydrogen atoms were previously dissociated and a competition between protium and tritium does not take place.
3. Molecular hydrogen H_2. This hydrogen interacts with the SH group with the formation of H_2S and hydride hydrogen.

According to the suggested mechanism of thiophene HDS [21,23], a thiophene molecule is adsorbed on the catalyst surface characterized by a definite ratio between the number of vacancies and SH groups, corresponding to its balanced state. C–S bond breaking takes place at the expense of dissociatively adsorbed hydrogen that does not belong to any SH group. The break-up of a thiophene molecule results in the formation of a new SH group, and the ratio between the numbers of vacancies and SH groups changes in favour of the latter. Hence, the catalyst falls into a so-called "metastable" state which it can leave by forcing out any of the SH groups located on the catalyst surface as a result of its interaction with molecular hydrogen. H–H bond cleavage in the course of H_{2ads} interaction with an SH group is the limiting step of the reaction.

4. Discussion

4.1. On the mechanism of sulfide sulfur transfer from the catalysts to the gas phase

If a sulfur transfer from the catalyst-(^{35}S) into the gas phase H_2S by the isotopic exchange is claimed the H_2S formed in thiophene HDS would next interact with the catalyst sulfur according to Scheme 2**a**. This "auxiliary" process could proceed as a competitive reaction alongside with the main reaction of thiophene HDS. To be the cause of the observed radioactivity in the H_2S formed the isotopic exchange by ^{35}S must proceed much faster than the main reaction. Otherwise, the adsorption of the H_2S would inhibit the main thiophene HDS, which is not observed under the given experimental conditions. Taking this into account and using the experimental data, we have considered three possible mechanisms of such exchange (here ^{35}S is indicated as S*).

A catalyst SH group obtains reversibly adsorbed hydrogen and exchanges it with a gas phase H_2S molecule:

$$\text{Me-T} + \text{Me-S}*\text{H} + \text{H}_2\text{S} \Leftrightarrow \text{T-S}*\text{H} + \text{Me-H} + \text{Me-SH} \tag{4}$$

Two neighboring catalyst SH groups participate in an isotopic exchange reaction:

$$2\text{Me-S}*\text{T} + \text{H}_2\text{S} \Leftrightarrow \text{T}_2\text{S}* + \text{Me-SH} + \text{Me-S}*\text{H} \tag{5}$$

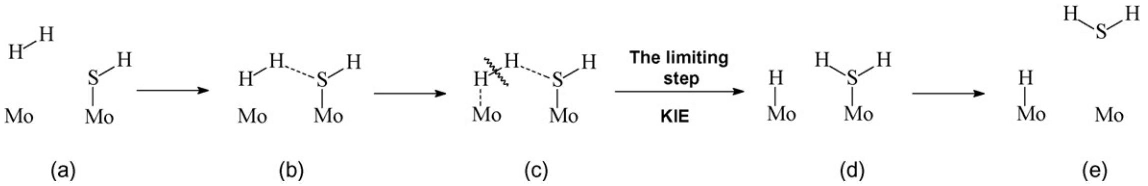
The exchange reaction is

$$\text{Me-S}*\text{T} + \text{H}_2\text{S} \Leftrightarrow \text{T-S}*\text{H} + \text{Me-SH} \tag{6}$$

where reaction (6) proceeds through the formation of the intermediate complex:

If one of the mechanisms took place the ^3H_2S MR in the experiments described in Section 3.4 would be equal to one (T_2S—Eq. (5)) or half of the MR of the gas phase hydrogen (TSH—Eqs. (4) and (6)). However, according to the experimental data (Table 3) the H_2S MR is 120 times lower than the MR of the gas phase hydrogen. Besides, as it was reported in [29], the H_2S adsorption and dissociation are almost non-activated processes, whereas the H_2S departure needs as much energy as the destruction and desorption of a sulfurorganic compound. Hence, the process of sulfur exchange between the catalysts and the H_2S cannot be much faster that the main process of thiophene HDS.

Thus, the radioactivity of H_2S formed in the course of thiophene HDS on a sulfide catalyst labeled by ^{35}S is not caused by the isotopic exchange of a H_2S with the catalyst ^{35}SH groups but proceeds due to forcing out the ^{35}SH group in the form of H_2S into the gas phase.



Scheme 3. Probable mechanism of H_2 interaction with SH group on sulfide Mo catalyst. (a) Pre-coordination of the H_2; (b) H_2 coordination by H atom on the S atom of the SH-group; (c) coordination of the H_2 by the second atom on the Mo and breaking of the H–H bond; (d) formation of the Mo hydride and adsorbed H_2S; (e) desorption of the H_2S and new site formation.

4.2. *Selecting the mechanism of interaction of the H_2 and the catalyst sulfur from the two*

According to the ‘‘forcing out’’ mechanism the limiting step of thiophene HDS is the interaction of the catalyst SH group with the gas phase hydrogen:

$$SH_{(ads)} + H_{2(g)} \rightarrow H_2S_{(g)} + H_{(ads)} \tag{7}$$

The observed KIE (Section 3.4) is in favour of the fact that the most energy consuming process here is the rupture of the H–H bond. In series of their computational studies Payen and coworkers [25–31] came to the same conclusion. However, there is a difference between the key steps of the ‘‘forcing out’’ mechanism and the mechanism proposed by Payen et al. According to [25–31], gas phase H_2 interacts with bridge sulfur:

$$S_{(ads)} + H_{2(g)} \rightarrow SH_{(ads)} + H_{(ads)} \tag{8}$$

Meanwhile, if reaction (8) took place on the catalyst labeled by ^3H (Section 3.3) the H_2S that left the catalyst would be non-radioactive because first, gas flow hydrogen is non-radioactive and $SH_{(ads)}$ formed is non-radioactive either and second, further reaction of the H_2S formation:

$$SH_{(ads)} + H_{(ads)} \rightarrow H_2S_{(g)} \tag{9}$$

proceeds with the participation of non-radioactive reversibly adsorbed $H_{(ads)}$. It is non-radioactive because the process of $^3H \Leftrightarrow {}^1H$ isotopic exchange between the catalyst surface and the gas flow is very fast and after a few minutes of the catalyst-^3H treatment under an H_2 flow all radioactive hydrogen is replaced by the non-radioactive.

Actually the SR of the H_2S formed at the beginning of thiophene HDS is equal to the SR of the H_2S formed in the course of sulfidation of the catalyst in the $^3H_2$ atmosphere (Table 2). It is because the dissociatively adsorbed hydrogen-^3H reacts with sulfide sulfur during sulfidation:

$$S_{(ads)} + {}^3H_{(ads)} \rightarrow {}^3HS_{(ads)} \tag{10}$$

and the ^3HS group further participates in the H_2S formation as a whole. Hence, under reaction conditions the gas phase H_2 interacts with the SH group according to (7).

The value of the KIE ≈ 60 (Section 3.4) also witnesses in favour of Eq. (7). Indeed, according to [33], the contribution of the stretching vibrations to the value of the KIE of H/T cannot be higher than 16 but the contribution of the deformation vibrations can raise this value up to 50–75.

Because there cannot be deformation vibrations in biatomic H_2 molecule, we believe they can appear in the intermediate $H–H\cdots S–H$ where H_2 coordinates on the SH group by one of the H atoms but not by the molecule centroid (Scheme 3). The second H atom can be coordinate on the neighboring Mo atom. Such intermediate configuration will lead to H_2 dissociation and the formation of H_2S and reversibly adsorbed hydride hydrogen that participates in HYD reactions.

Acknowledgement

One of the authors thank the Russian Foundation for Basic Research for their support of the part of the research by the grant 05-03-39006_a.

References

[1] H. Topsøe, 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, Heidelberg, New York, 1996, p. 310.
[2] P.Z. Owens, C.H. Amberg, Can. J. Chem. 40 (1962) 947.
[3] P. Desikan, C.H. Amberg, Can. J. Chem. 42 (1964) 843.
[4] G.V. Smith, C.C. Hincley, F. Behbahany, J. Catal. 30 (1973) 218.
[5] R.J. Mikovsky, A.J. Silvestri, H. Heinemann, J. Catal. 34 (1974) 324.
[6] M.R. Blake, M. Eyre, R.B. Moyes, P.B. Wells, Stud. Surf. Sci. Catal. 7 (1981) 591.
[7] J.T. Roberts, C.M. Friend, J. Am. Chem. Soc. 108 (1986) 7204.
[8] K.F. McCarty, G.L. Schrader, J. Catal. 103 (1987) 261.
[9] C. Thomas, L. Vivier, J.L. Lemberton, S. Kasztelan, G. Pérot, J. Catal. 167 (1997) 1.
[10] A. Ishihara, H. Godo, R. Kamamori, W. Qian, T. Kabe, Appl. Catal. A: Gen. 182 (1999) 345.
[11] E.W. Qian, Y. Hachiya, K. Hirabayashi, A. Ishihara, T. Kabe, K. Hayasaka, S. Hatanaka, H. Okazaki, Appl. Catal. A: Gen. 244 (2003) 283.
[12] F. Dumeignil, H. Amano, D. Wang, E.W. Qian, A. Ishihara, T. Kabe, Appl. Catal. A: Gen. 249 (2003) 255.
[13] A. Ishihara, J. Lee, F. Dumeignil, R. Higashi, A. Wang, E.W. Qian, T. Kabe, J. Catal. 217 (2003) 59.
[14] A.N. Startsev, E.V. Artamonov, Y.I. Yermakov, Appl. Catal. 45 (2) (1988) 183.
[15] A. Wang, Y. Wang, T. Kabe, Y. Chen, A. Ishihara, W. Qian, P. Yao, J. Catal. 210 (2002) 319.
[16] A.N. Startsev, Catal. Rev. Sci. Eng. 37 (1995) 353.
[17] G.V. Isagulyants, A.A. Greish, V.M. Kogan, in: M.J. Phillips, M. Ternan (Eds.), Proc. 9th Intern. Congr. Catal., Ottawa, Canada, 1988, vol. l, p. 35.
[18] V.M. Kogan, A.A. Greish, G.V. Isagulyants, Catal. Lett. 6 (1990) 157.
[19] V.M. Kogan, N.T. Dung, V.I. Yakerson, Bull. Soc. Chim. Belg. 104 (1995) 303.
[20] V.M. Kogan, N.N. Rozhdestvenskaya, I.K. Korshevets, Appl. Catal. A: Gen. 234 (2002) 207.

[21] V.M. Kogan, Appl. Catal. A: Gen. 237 (2003) 161.

[22] V.M. Kogan, R.G. Gaziev, S.W. Lee, N.N. Rozhdestvenskaya, Appl. Catal. A: Gen. 251 (2003) 187.

[23] V.M. Kogan, Transition metal sulfides. Chemistry and catalysis, in: T. Weber, R. Prins, R. van Santen, NATO ASI Series, Kluwer Academic Publishers, 3. High Technology, vol. 60, 1998, pp. 35–271.

[24] G.V. Isagulyants, A.A. Greish, V.M. Kogan, Kinet. Katal. 28 (1987) 638 (in Russian).

[25] S. Cristol, J.-F. Paul, E. Payen, D. Bougeard, J. Hafner, F. Hutschka, Stud. Surf. Sci. Catal. 127 (1999) 327.

[26] A. Travert, H. Nakamura, R.A. van Santen, S. Cristol, J.F.E. Payen, J. Am. Chem. Soc. 124 (2002) 7084.

[27] S. Cristol, J.-F. Paul, E. Payen, D. Bougeard, S. Clémendot, F. Hutschka, J. Phys. Chem. B 104 (2000) 11220.

[28] S. Cristol, J.-F. Paul, E. Payen, D. Bougeard, S. Clémendot, F. Hutschka, J. Phys. Chem. B 106 (2002) 5659.

[29] J.-F. Paul, E. Payen, J. Phys. Chem. B 107 (2003) 4057.

[30] F. Dumeignil, J.-F. Paul, E. Veilly, E.W. Qian, A. Ishihara, E. Payen, T. Kabe, Appl. Catal. A: Gen. 289 (2005) 51.

[31] S. Cristol, J.-F. Paul, Ch. Schovsbo, E. Veilly, E. Payen, J. Catal. 239 (2006) 145.

[32] B. Delmon, Bull. Soc. Chim. Belg. 104 (1995) 173.

[33] L. Melander, W.H. Saunders, Reaction Rates of Isotopic Molecules, John Wiley & Sons Inc., New York, 1980.