Catalysis Today 149 (2010) 224–231

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

On the dynamic model of promoted molybdenum sulfide catalysts

V.M. Kogan [a,*], P.A. Nikulshin [b]

[a] N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47, Leninsky Prospect, Moscow 119991, Russia
[b] Samara State Technical University, 244, Molodogvardiyskaya St., Samara 443100, Russia

ARTICLE INFO

Article history:
Available online 22 April 2009

Keywords:
Transition metal sulfides
Catalysis
CoMoS catalysts
Thiophene
Hydrodesulfurization
Reaction mechanism

ABSTRACT

On the basis of the fundamental concepts of catalysis by transition metal sulfides (TMSs) a new dynamic model of the promoted Mo-sulfide catalysts functioning under HDS conditions has been developed. According to the model under hydrogen atmosphere sulfidation degree of the edges of different layers of the slab can vary and surface sulfur can migrate from one layer to a neighboring layer so that average sulfidation state of the slab remains constant under given reaction conditions. The model describes oscillations by sulfur and promoter atoms between the adjacent layers of the slab on the atomic scale level. The driving force of such processes is the heterolytic dissociation of the gas phase hydrogen and formation of hydride hydrogen linked to a promoter atom. This hydride hydrogen triggers an electron transfer from a promoter to Mo with the formation of the vacancy. This model correlates with radioisotopic data and an earlier suggested “forcing out” mechanism and gives some new interpretations of the important statements of the electron theory of promotion and the “rim-edge” model.

1. Introduction

Creating high-performance catalysts for ultra clean fuel production makes it necessary to study thoroughly the structure and operation of the TMS catalyst and understand the roles of its structural components in the course of catalytic transformations. Nowadays the basic principles of creating and regularities of operating of the TMS catalysts are formulated. This comprehension was achieved in many respects thanks to the contributions of Topsøe and co-workers [1–5], who suggested a model of CoMoS phase and Chianelli et al. who explained the electronic mechanism of promoting Mo and W sulfides by Co and Ni [6,7] and suggested the “rim-edge” model of location and operating of the hydrogenation (HYD) and desulfurization (DS) of active sites [8–10]. The application of scanning tunnel microscopy (STM) technique for investigation of TMSs [11–16] allowed researchers to visualize some of the key-important images and supported these conceptions.

In the majority of the models [17–25] a catalyst is considered as a stable structure whose active sites are invariable no matter if they participate in the reaction or not. Yet, according to Delmon [26], all kinds of the active sites in hydrotreating catalysts result from some sort of dynamic process. He emphasized that all the active sites are really formed under catalytic conditions. In view of this statement a study of active site dynamics is needed to forecast catalytic properties of the TMSs. In this paper basing on the insights and conceptions of the catalysis by TMS we suggest a dynamic atomic scale model of behavior of the active sites in the presence of hydrogen and consider earlier received data in the light of this model.

2. Active sites of TMS catalysts

Though many experimental data have been gathered and many theories about the mechanism of sulfur organic compounds on a sulfide catalyst surface have been proposed, a number of important questions have not been answered so far. The structure and functioning of sulfide catalyst active sites, the role of the support and the promoter in the reaction and the hydrogen activation mechanism are not fully understood.

It is well-known that molybdenum disulfide has a layer structure where flatness of the Mo^{4+} cations is placed between two layers of the S^{2-} anions. In the crystallite of layer structure every Mo atom is surrounded by 6 sulfur atoms in trigonal–pyramidal coordination where every S atom is bonded with three Mo atoms [27–33]. Two single layers S–Mo–S of hexagonal MoS_2 crystallite are shown on Fig. 1. The layers are oriented in such a way that Mo-edges (where Mo atoms are terminal ones) of one layer are placed under or bellow S-edges (limited by final sulfur) of a neighboring layer. The basal panes are fully completed by sulfur atoms and seem catalytically inactive.

On the Mo-edge every Mo atom coordinates four S atoms and on the S-edge every S atom coordinates two Mo atoms. Under reaction conditions both Mo and S-edges are unstable [17–24,34]:

---

[*] Corresponding author. Tel.: +7 499 1358910; fax: +7 499 1355328.
E-mail address: vmk@ioc.ac.ru (V.M. Kogan).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.03.023

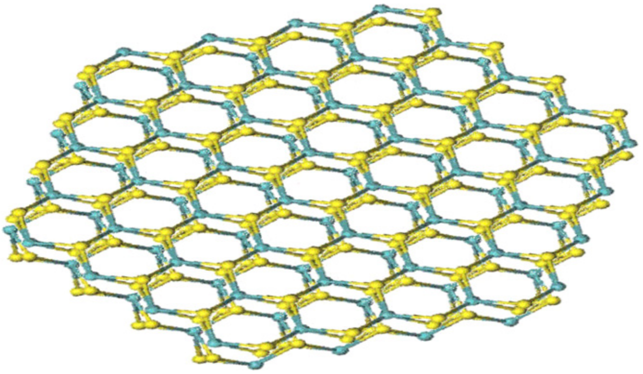


Fig. 1. Hexagonal MoS_2 crystallite exposing Mo- and S-edges. Adapted from [32].

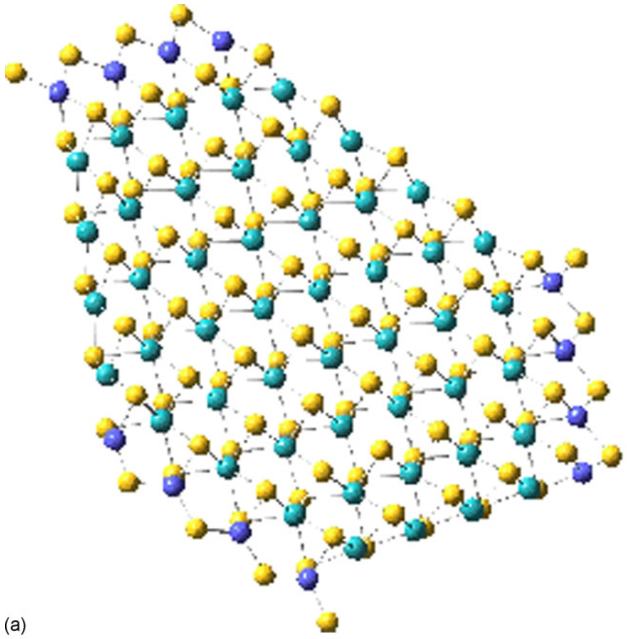
hydrogen can react with sulfur of the S-edges resulting in the vacancies formation. The H_2S can dissociatively adsorb on the coordinative-unsaturated Mo atoms of the Mo-edges. It is seen on Fig. 1 that molybdenum exists of the surface either in 4-fold of in 6-fold coordination. Sulfur atoms removal from the S-edge is accompanied by the reduction of Mo^{6+} of this S-edge to Mo^{4+} whereas sulfur addition to the Mo-edge in the bridge position leads to the oxidation of Mo^{4+} to Mo^{6+}. Recently using STM for the first time, vacancy images on the monolayer MoS_2 supported by a gold carrier were obtained [13]. The STM data also proved the existence of the surface SH groups [13,14]. In promoted molybdenum sulfides the atoms of a promoter (Co or Ni) are located on the S- or Mo-edges of the slab depending on their sulfidation state and ability to accept the atoms of a promoter (Fig. 2):

According to the “rim-edge” model [8–10], the HYD and DS sites are identical in their structure but the HYD are located on the rims, whereas the DS sites are situated both on the rims and the edges of the MoS_2 crystallites (Fig. 3). The sites placed on the spatial angles of the crystallites are attributed as HYD sites. Varying the ratio of the diameter of the crystallite to its height one can change a proportion of these sites and selectivity of the catalyst in HYD and DS reactions. The “rim-edge” model is widely discussed in [7,26,27,32–46] but it does not allow us to specify the composition of the active sites and to explain the reasons for different locations of the DS and HYD sites.

Basing on radioisotopic testing of sulfide catalysts, it was shown that sulfide sulfur of the catalyst is not uniform and differs by its ability to participate in H_2S formation in the course of thiophene HDS [47–49]. Some part of the catalyst sulfur is immobile, i.e. it cannot participate, and some is able to transfer to hydrogen sulfide during the HDS reaction and, thus, can be considered as mobile. The data [47,50] proved that mobile sulfur belongs to surface SH groups. After mobile sulfur (or SH groups) is eliminated from the catalyst surface in the form of H_2S, the active site is formed. Mobile sulfur, in its turn, consists of more or less mobile fractions (“rapid” and “slow” sulfur – more and less active SH groups). In [47,50] the correlations between catalyst activity in HDS and the amount of mobile sulfur and mobile sulfur reactivity (mobility) were established. Sulfur can leave catalyst surface into gas phase only if another S-containing molecule is adsorbed on the catalyst, i.e. as a result of its “extrusion” [47]. Basing on the radioisotopic examinations of the promoted and non-promoted catalysts [48,50] the “rapid” sites were attributed to the Mo sulfide promoted by Co or Ni and the “slow” sites to the non-promoted Mo sulfide.

3. Dynamic model of the TMS catalysts

In [50] it was found that the ratio of covered by sulfur and not covered (reduced) surface of the active phase in non-promoted MoS_2 crystallite is close to 1:1, which corresponds to computational data [51]. For CoMoS catalysts this ratio is 1.4:1. It means that in promoted catalysts the sulfidation degree of the surface of the active phase is 70%. That is why we selected a combination of two edges of the neighboring layers of the promoted MoS_2 slab depicted in [52]: S-edge in 50% sulfidation state and the Mo-edge in fully sulfidized state (Fig. 4) so that average sulfidation state of two edges would be about 70–75% which is close to reality. Initially the atoms of promoter (Co) were located on the Mo-edge.



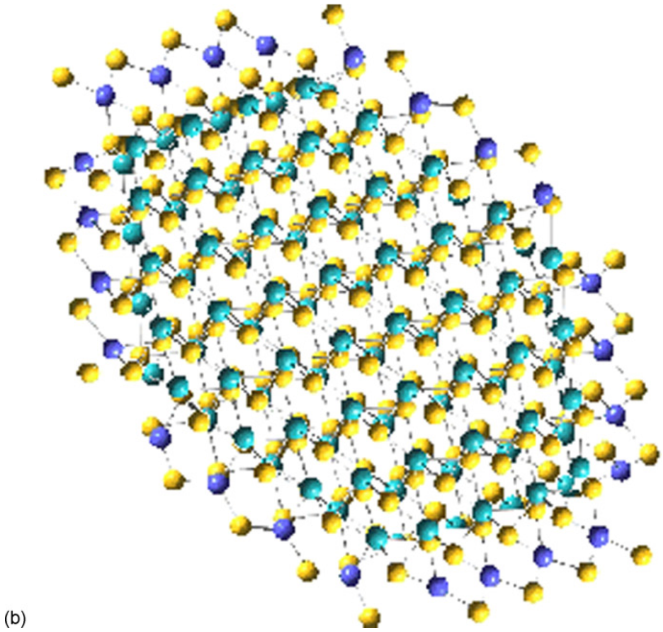


Fig. 2. (a) One-layer slab of the MoS_2 promoted by Co. Here and bellow: S, yellow circle, Mo, light blue circle, Co, dark blue circle. (b) Two-layer slab of the MoS_2 promoted by Co.

3.1. *The active sites of the TMS catalysts in H_2 atmosphere without thiophene adsorption*

Recently on the basis of the radioisotopic data of measuring H/T kinetic isotopic effect in the course of thiophene HDS in the (^{3}H)-labelled molecular hydrogen atmosphere [47] we suggested that

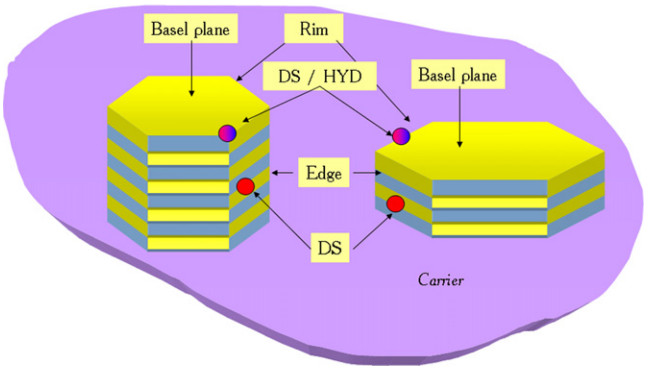


Fig. 3. The "rim-edge" model. Adapted from [8]. Two CoMoS slabs with the same amount of Mo and different promotion degree—smaller for left slab and higher for right slab differ in their diameter and height.

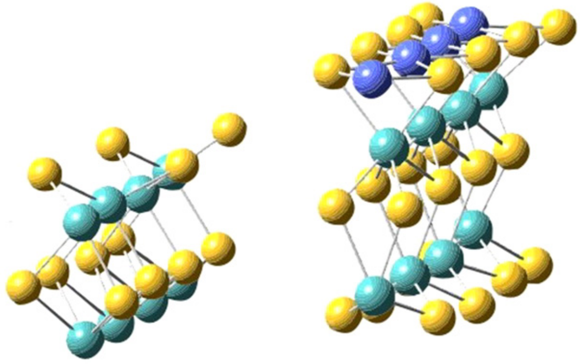


Fig. 4. Left: S-edge unpromoted (50% sulfidized); right: Mo-edge fully promoted (100% sulfidized). Adapted from [52].

the gas phase H_2 coordinates on the SH group by one of the H atoms but not by the molecule centroid [53]. The second H atom coordinates on the neighboring Mo atom. Such intermediate configuration leads to the heterolytic dissociation of the H_2 and formation of the H_2S and hydride hydrogen linked to molybdenum (Scheme 1).

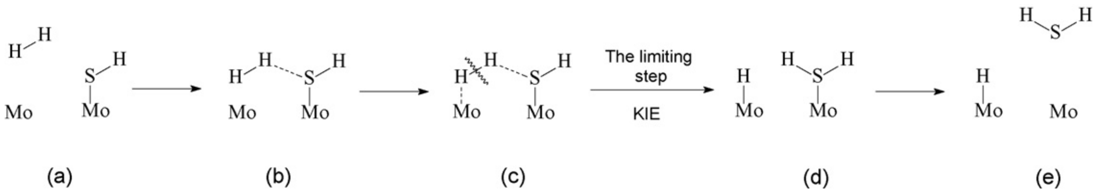
Similarly, for promoted CoMoS catalyst we believe that the first step of the reaction is an interaction of molecular hydrogen with bridge sulfur of the promoted Mo-edge of the catalyst followed by heterolytic dissociation of the H_2 with the formation of the SH group and hydride hydrogen linked to Co (Scheme 2, steps a–c).

According to Harris' and Chianelli's concept of promoting effect [6,7,54] the Co donates electron to the anti-bonding orbital of the Mo and *eo ipso* weakens one of the Mo–S bonds making it easier to form a vacancy (Fig. 5). However, this concept does not explain what a cause of this process is. We believe that hydride hydrogen triggers electron transfer from Co to Mo (Scheme 2, step d). As soon as a Mo atom captures an electron, one of the Mo–S bonds weakens and ruptures (Scheme 2, step e). Simultaneously, hydride hydrogen obtains positive charge and leaves Co atom for bridge sulfur with weakening and rupture of Mo–S bond and the formation of the H_2S (Scheme 2, steps e–f) and its desorption (Scheme 2, step g). Because the neighboring S-edge is not fully sulfidized, it easily captures this hydrogen sulfide until its full sulfidation (Fig. 6). An intermediate structure formed on the Mo-edge contains weakly bonded Co atoms. In this state the Co atoms are affected by the repulsion from the Mo atoms of the Mo-edge and the attraction by the S atoms of the neighboring S-edge (Fig. 7). As a result, Co–S bonds brake and Co atoms move from the Mo-edge to the fully sulfidized S-edge (Fig. 8, step 1). After the elimination of hydrogen from the S-edge (possibly into the gas phase, or onto a carrier, or onto neighboring edges) and rebuilding of the Mo-edge (step 2) the S-edge promoted by Co atoms, interacts with gas phase hydrogen (step 3). At this stage the Mo-edge is partly reduced (sulfidation state is about 50%), whereas the S-edge is fully sulfidized. The interaction of molecular hydrogen with the S-edge proceeds similarly to the interaction of the H_2 with the Mo-edge (Scheme 2) through the heterolytic dissociation of the H_2 molecules on sulfur atoms of the S-edge and the formation of hydride hydrogen on Co atoms. Energetic expediency of a similar process for NiMoS catalyst was recently proved by Weber and van Veen by quantum chemical computations [55]. After electron transfer hydride hydrogen changes its electric charge and moves to the SH group forming H_2S on the S-edge. Then this H_2S moves to the Mo-edge for its complete sulfidation (Fig. 9 steps 1–2):

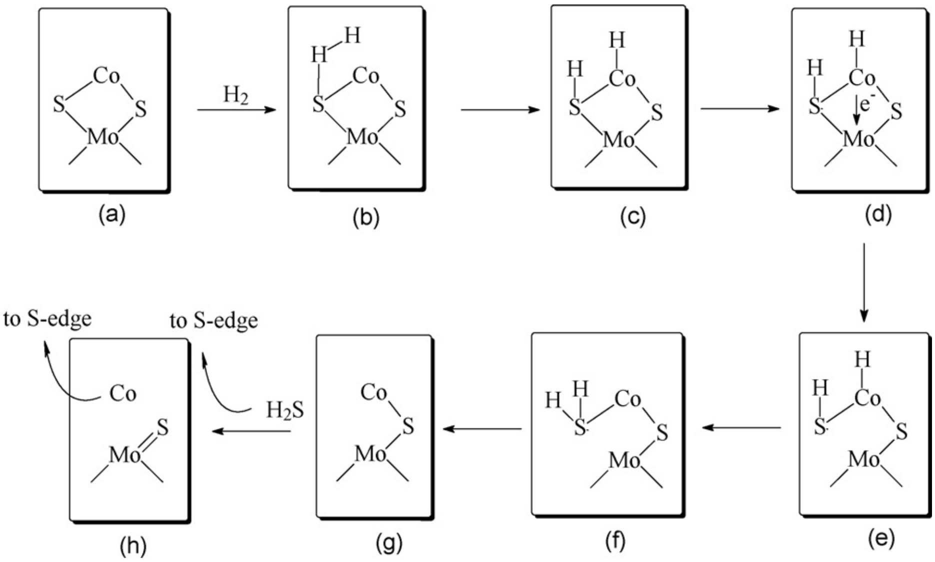
Similarly to the mechanism elimination of the Co atoms from the Mo-edge depicted on Fig. 8, the Co atoms of the S-edge are affected by attraction by sulfur atoms of the Mo-edge and simultaneous repulsion from the Mo atoms of the S-edge. These lead to transfer of the Co atoms to the fully sulfidized Mo-edge (steps 3–4, Fig. 9). After hydrogen removal from the Mo-edge (step 5, Fig. 9) the system of two edges of adjacent layers of promoted MoS_2 becomes to the initial sulfidation state of the Mo- and S-edges shown on Fig. 4. Thus, the "life cycle" of the TMS catalyst in hydrogen atmosphere without adsorbing S-containing compound is over (Fig. 10). This cycle illustrates the mechanism of oscillation by sulfur and cobalt between adjacent layers in multilayered promoted MoS_2 slab when adsorption of S-containing compound does not take place on the vacancies of the slab. The intensity of the oscillations affects the reactivity of the active sites located on the edges of the slab because the oscillations determine the rate of the vacancies formation. Because such oscillations cannot occur on one layered CoMoS crystallites and may take place only on the multilayered slabs it explains the fact that CoMoS phase of Type II is more active than the CoMoS phase of Type I [56 and references within].

3.2. Effect of thiophene adsorption on the functioning of the active sites of the TMS catalysts

When the adsorption of S-containing compound (thiophene, for instance) takes place, some steps of the cycle differ from the described above. It becomes clear if compare two schemes of the transformation of single CoMoS cluster with and without



Scheme 1. 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.



Scheme 2. The mechanism of H_2 interaction with bridge sulfur of the promoted Mo-edge and following transformations of the edge. Heterolytic dissociation of the H_2 on the Mo-edge between the Co and S atoms, transfer of electron density from the Co to the Mo atom and formation of the H_2S molecules on the Mo-edge and their migration onto the S-edge.

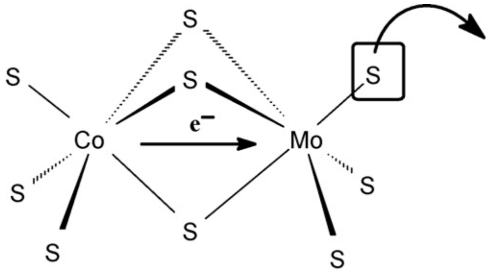


Fig. 5. The synergetic effect of Co or Ni on MoS_2-based catalyst HDS activity. Adapted from [6].

thiophene adsorption (Fig. 11). The upper scheme (11a) shows the process of the formation of a new vacancy as a result of Co elimination. The bottom scheme (11b) shows that when thiophene adsorbs the mutual repulsion between Co and Mo disappears as a consequence of compensating the positive charge of Mo by the electron density from the sulfur of thiophene. As a result, Co remains on the cluster and further conversions of thiophene proceed in accordance with the "forcing out" mechanism [47–50].

It is very likely that a more reactive "rapid" site is located on a single CoMoS cluster (Fig. 11a,b (3)) and a less reactive "slow" site on an unpromoted Mo-sulfide cluster (Fig. 11b, (4)). Unpromoted Mo-sulfide clusters are responsible for HYD reactions, whereas Co promoted Mo-sulfide sites are responsible for hydrogenolysis of the C–S bond, or for desulfurization [57]. When thiophene adsorbs on the vacancy of the "rapid" site, the proton linked to Co moves to the SH group of the "slow" site on the adjacent layer. As a result, an H_2S and a new vacancy on the adjacent layer are formed. Under hydrogen atmosphere "slow" (unpromoted) and "rapid" (promoted) sites located on the adjacent edges of a promoted CoMoS slab are constantly turning into each other during the so-called oscillation process. According to the "rime-edge" model, the HYD sites are preferably placed on the rims of the slab which can be easily explained by the suggested mechanism. If we assume that HYD sites consist of unpromoted Mo-sulfide clusters ((4), Fig. 11a) and DS sites – of promoted CoMoS clusters ((3), Fig. 11a), which corresponds to "slow" (S) and "rapid" (R) sites respectively, it means that to capture the Co atoms from the neighboring edge by the Mo sites is twice less probable for the sites on the rim than for the sites on the edge of the CoMoS slab because this site can capture atoms of a promoter both from "upper" and "lower" layers. As for the site on the rim of the slab, it can capture only the promoter atoms from one—namely "lower" side (Fig. 12). That is why Co-promoted "rapid" sites responsible for DS are mainly formed on the edges of the slabs and unpromoted Mo "slow" sites—on the rims.

On the basis of a wide range of the isotopic examinations of TMS catalysts "rapid" sites were attributed to the CoMo or NiMo sites whereas "slow" sites to Co(Ni)-sulfides [48,50,57]. This conclusion was made in the course of the analysis of the dependencies of mobile sulfur amount (a) and active sites productivities (b) on the Co/(Co + Mo) atomic ratio, obtained in the course of thiophene HDS over $CoMo/Al_2O$ catalysts of various

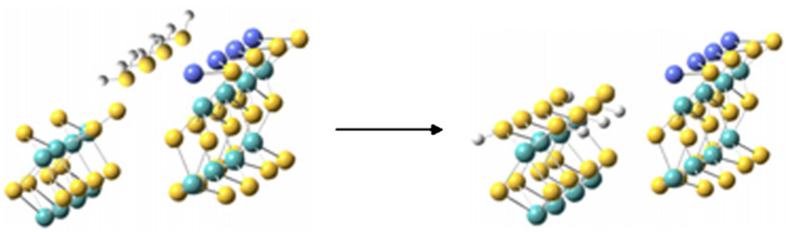


Fig. 6. Migration of the H_2S molecules from the Mo-edge onto the S-edge and rebuilding of the S-edge. Here and bellow—white circle: hydrogen.

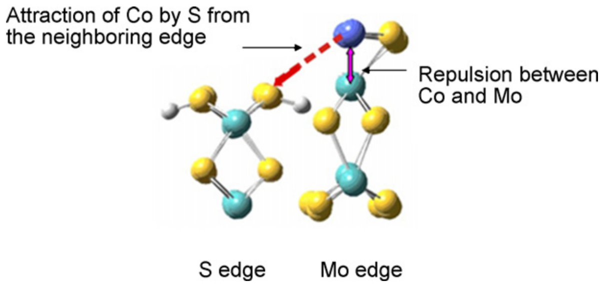


Fig. 7. Interaction between the Co atoms of the Mo-edge and the S-atoms of the S-edge and repulsion between the Co and Mo atoms of the Mo-edge.

composition. Increasing the amount of the promoter in the active phase caused a decrease in the amount of "rapid" sulfur and an increase in "slow" sulfur. This was true for all the samples under study with 4–12% Mo loading (Fig. 13a). Simultaneously increasing Co amount caused a higher productivity of the active sites (Fig. 13b). The decrease in the amount of "rapid" sulfur was explained in [50] by blocking of some "rapid" sites by Co-sulfide particles. Now we reconsider the reasons for the decrease in the light of the new mechanism discussed above. Indeed, if in [48,50,57] we attributed the "slow" sites to Co-sulfide particles, now we believe that the "slow" sites are non-promoted Mo sites (Fig. 11a, position 4). We checked all the experimental data from

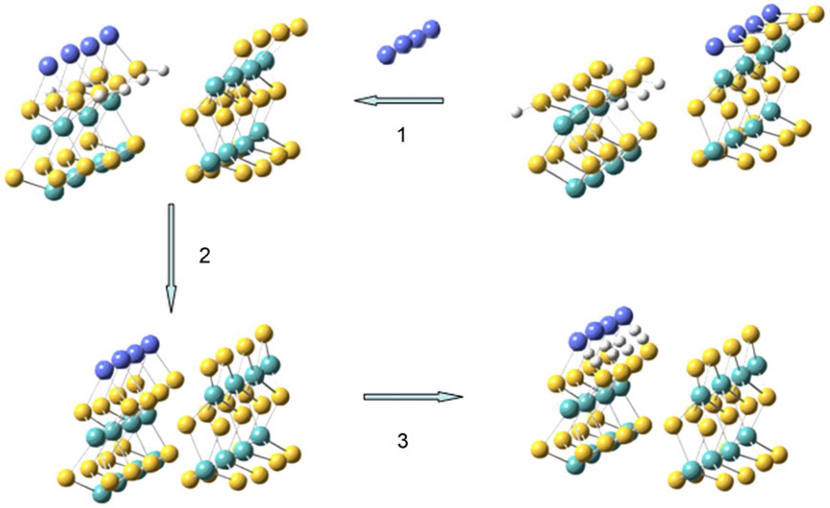


Fig. 8. Migration of the Co atoms from the Mo- onto the S-edge (1); rebuilding of the S-edge and migration of dissociatively adsorbed hydrogen from the S-edge into an H-reservoir (2); interaction of the S-edge with molecular hydrogen of gas phase (3).

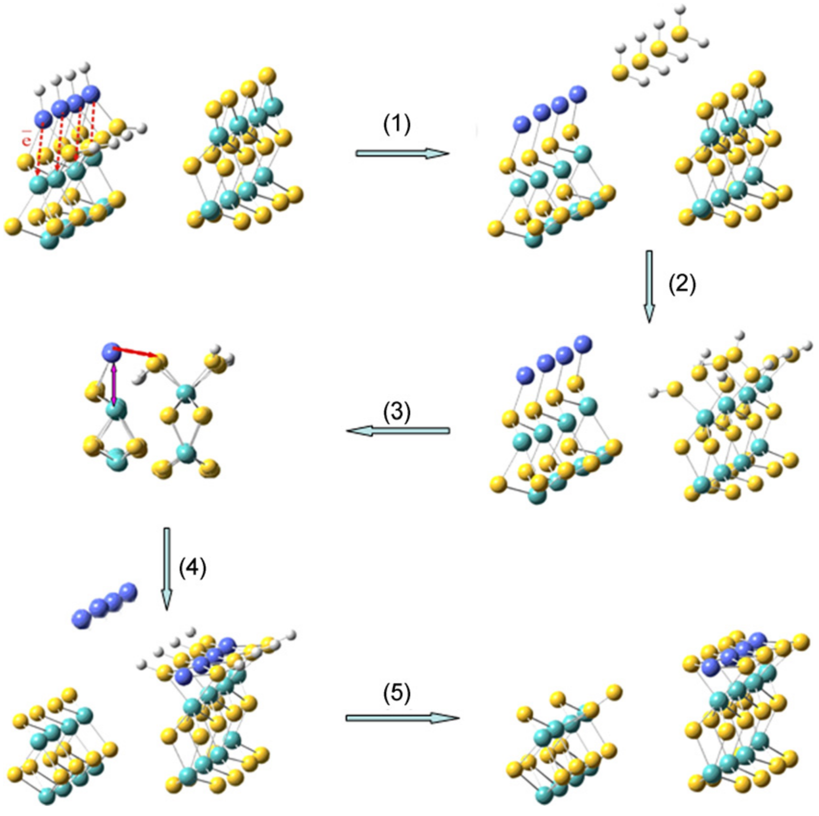


Fig. 9. Heterolytic dissociation of molecular hydrogen of the S-edge and the following transformations of the Mo and S-edges. Explanations are given in the text.

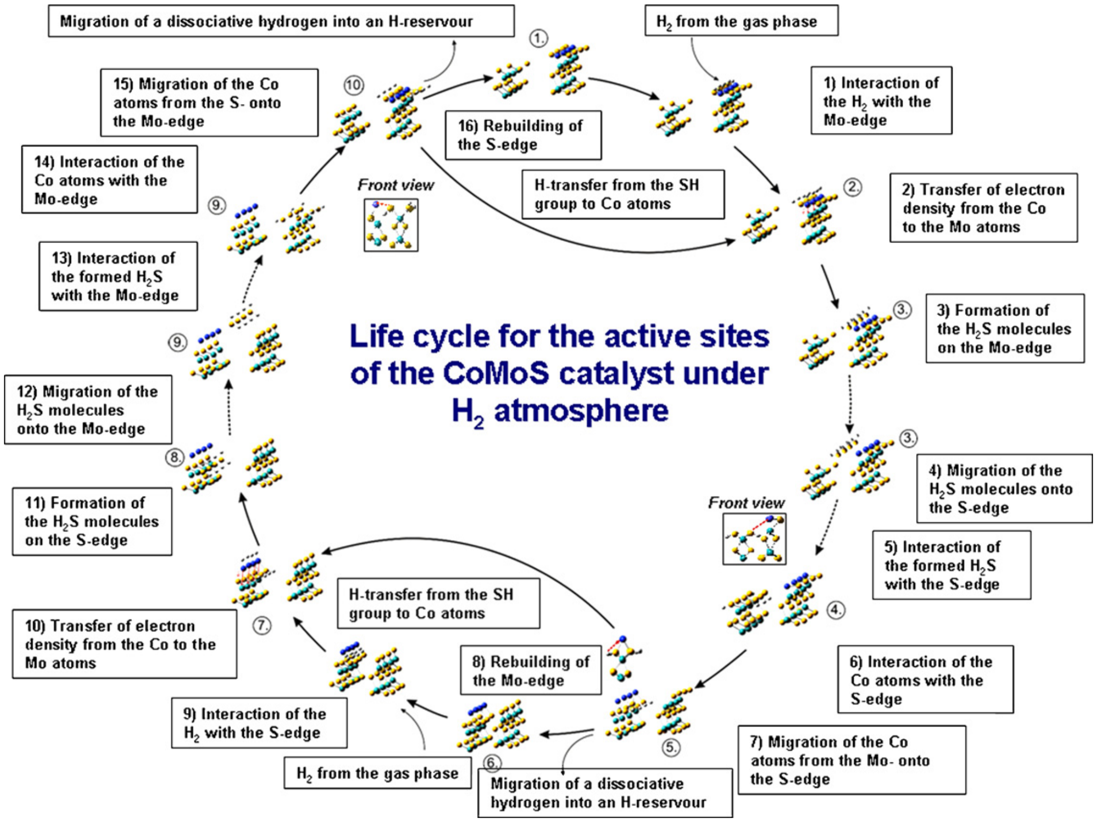


Fig. 10. Transformations of the Mo and S-edges of the promoted MoS_2 crystallite under hydrogen atmosphere.

this point of view [50, Table 2] and found that they do not contradict the supposition except the fact that the number of the “slow” sites rises with an increase of the promoter content at the same Mo loading.

This phenomenon needs special explanation. An increase of Co content in the Mo-sulfide slab leads to a change of its shape: the diameter of the slab grows whereas its height decreases (Fig. 3). As a result the number of unpromoted Mo sites increases. It helps to

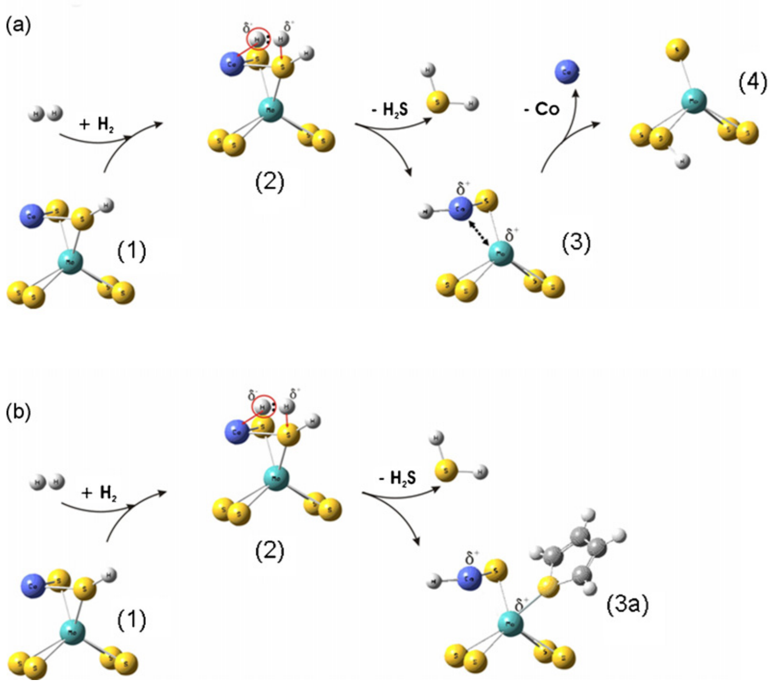


Fig. 11. Single CoMoS cluster transformations under H_2 atmosphere (a) without thiophene adsorption; (b) at thiophene adsorption. (1) Initial structure of the single CoMoS cluster; (2) heterolytic dissociation of H_2 on the SH group and Co atom with formation and following elimination of the H_2S; (3) repulsion of Co atom form Mo atom and its elimination from the cluster; (3a) disappearing of the Co–Mo repulsion as a result of compensation of the positive charge on the Mo atom by electron density of sulfur of the adsorbed thiophene; (4) formation of unpromoted single Mo-sulfide cluster.

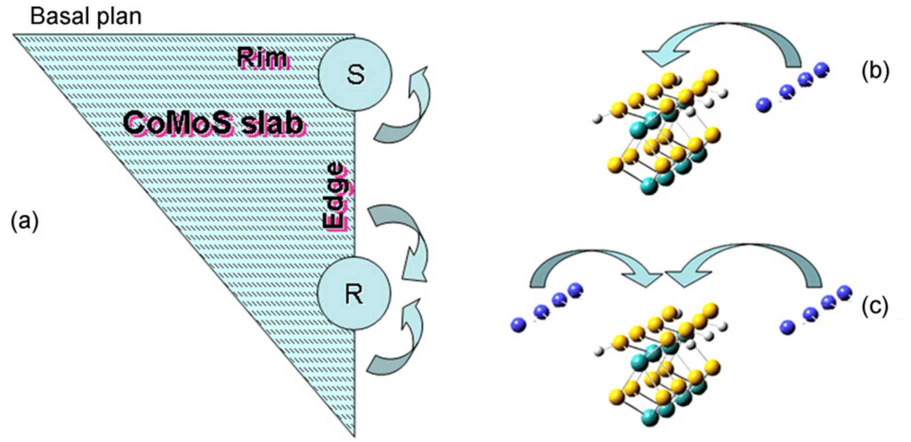


Fig. 12. Transformations of the "slow" Mo sites into the promoted CoMo "rapid" sites on the rim and the edge of the CoMoS slab. (a) Schematic illustration of promoting of the active sites located on the rim (S-site) and on the edge (R-site) by Co atoms; (b) atomic scale scheme of the Co atoms capture by the S-site located on the rim of the slab; (c) atomic scale scheme of the Co atoms capture by the R-site located on the edge of the slab.

understand it if to compare two virtual slabs with the fixed content of Mo and Co but of different diameters and heights. For the slab with a bigger diameter the number of unpromoted Mo sites is higher because the length of the rims (the places for location of unpromoted Mo "slow" sites) will be higher and the density of the promoted CoMo "rapid" sites on the edges of the slab is lower than for slab of smaller diameter. This explanation fully agrees with the data of Delmon [26, Fig. 4] about distribution of the sites responsible for hydrogenolysis and hydrogenation depending on the shape of the slab.

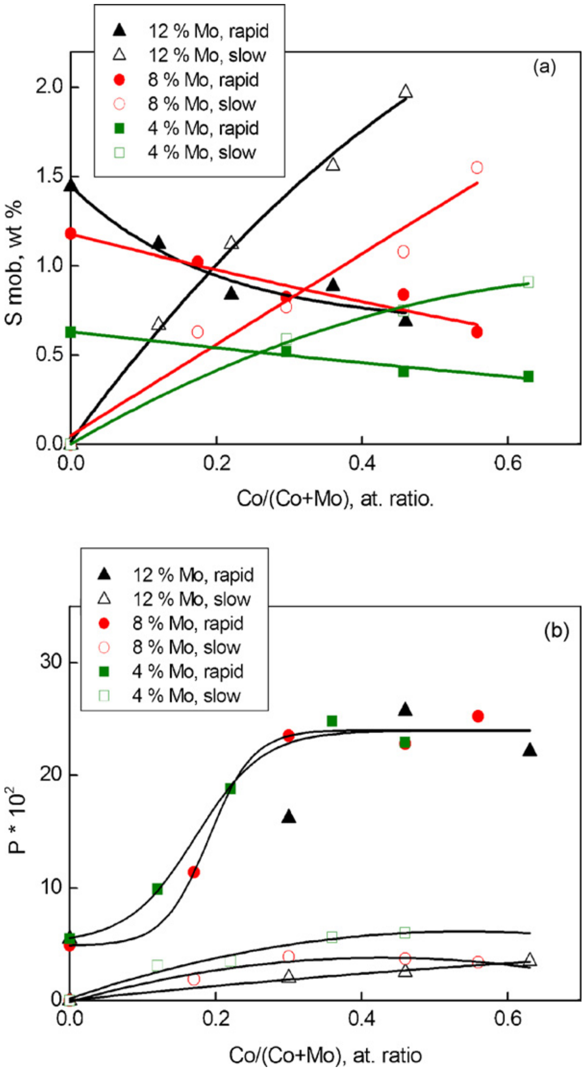


Fig. 13. Dependencies of mobile sulfur amount (a) and active sites productivities (b) on the Co/(Co + Mo) atomic ratio, obtained in the course of thiophene HDS over CoMo/Al_2O_3 catalysts of various composition.

4. Conclusions

According to the suggested model, neighboring layers of the multilayered MoS_2 crystallite exchange sulfur between Mo- and S-edges placed one under another in the course of permanent reduction–sulfidation processes under hydrogen atmosphere. When the sulfur atoms bonded to Co atoms leave the reduced edge of the layer, the atoms of the promoter also move along the sulfur atoms from one layer to an adjacent layer of higher sulfidation state. Then the process reverses. Such oscillations occur until the sulfur organic compound adsorbs on the vacancy on the reduced edge. The frequency of the oscillations determines catalytic activity of the CoMoS slab. Thiophene adsorption makes transfer of a promoter to the neighboring slab improbable because the electron density of thiophene sulfur compensates the extra positive charge on the Mo atom that appears after H_2S removal. When thiophene adsorbs on the vacancy of the CoMoS site the proton linked to Co moves to the SH group of the neighboring layer forming the H_2S which desorbs from this layer and a new vacancy is formed. This model explains the reasons for an electron transfer from an atom of the promoter to Mo and different locations of the active sites responsible for hydrogenation and desulfurization on a promoted Mo-sulfide slab.

References

[1] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel, S. Morup, J. Catal. 68 (1981) 433.
[2] C. Wivel, R. Candia, B.S. Clausen, S. Morup, H. Topsøe, J. Catal. 68 (1981) 453.
[3] B.S. Clausen, H. Topsøe, R. Candia, J. Villadsen, B. Lengeler, J. Als-Nielsen, F. Christensen, J. Phys. Chem. 85 (1981) 3868.
[4] N.-Y. Topsøe, H. Topsøe, J. Catal. 84 (1983) 386.
[5] M. Breysse, B.A. Bennett, D. Chadwick, M. Vrinat, Bull. Soc. Chim. Belg. 90 (1981) 1271.
[6] S. Harris, R.R. Chianelli, J. Catal. 98 (1986) 17.
[7] R.R. Chianelli, G. Berhault, P. Raybaud, S. Kasztelan, J. Hafner, H. Toulhoat, Appl. Catal. A: Gen. 227 (2002) 83.
[8] M. Daage, R.R. Chianelli, A.F. Ruppert, Stud. Surf. Sci. Catal. 75 (1993) 571.
[9] R.R. Chianelli, M. Daage, M.J. Ledoux, Adv. Catal. 40 (1994) 177.
[10] M. Daage, R.R. Chianelli, J. Catal. 149 (2) (1994) 414.
[11] J.V. Lauritsen, S. Helveg, E. Lægsgaard, I. Stensgaard, B.S. Clausen, H. Topsøe, F. Besenbacher, J. Catal. 197 (2001) 1.
[12] J.V. Lauritsen, M. Nyberg, R.T. Vang, M.V. Bollinger, B.S. Clausen, H. Topsøe, K.W. Jacobsen, E. Lægsgaard, J.K. Norskov, F. Besenbacher, Nanotechnology 14 (2003) 385–389.

[13] S. Helveg, J.V. Lauritsen, E. Lægsgaard, I. Stensgaard, J.K. Nørskov, B.S. Clausen, H. Topsøe, F. Besenbacher, Phys. Rev. Lett. 84 (2000) 951.
[14] J.V. Lauritsen, M.V. Bollinger, E. Lægsgaard, K.W. Jacobsen, J.K. Nørskov, B.S. Clausen, H. Topsøe, F. Besenbacher, J. Catal. 221 (2004) 510.
[15] H. Topsøe, B. Hinnemann, J.K. Nørskov, J.V. Lauritsen, F. Besenbacher, P.L. Hansen, G. Hytoft, R.G. Egeberg, K.G. Knudsen, Catal. Today 107–108 (2005) 12.
[16] F. Besenbacher, M. Brorson, B.S. Clausen, S. Helveg, B. Hinnemann, J. Kibsgaard, J.V. Lauritsen, P.G. Moses, J.K. Nørskov, H. Topsøe, Catal. Today 130 (2008) 86.
[17] P. Raybaud, J. Hafner, G. Kresse, H. Toulhoat, Surf. Sci. 407 (1998) 237.
[18] H. Toulhoat, P. Raybaud, S. Kasztelan, G. Kresse, J. Hafner, Catal. Today 50 (3–4) (1999) 629.
[19] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, H. Toulhoat, J. Catal. 189 (1) (2000) 129.
[20] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, H. Toulhoat, J. Catal. 190 (1) (2000) 128.
[21] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, J. Hafner, F. Hutschka, Stud. Surf. Sci. Catal. 127 (1999) 327.
[22] A. Travert, H. Nakamura, R.A. van Santen, S. Cristol, J.F.E. Payen, J. Am. Chem. Soc. 124 (2002) 7084.
[23] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, S. Clémendot, F. Hutschka, J. Phys. Chem. B 104 (2000) 11220.
[24] S. Cristol, J.-F. Paul, E. Payen, D. Bougeard, S. Clémendot, F. Hutschka, J. Phys. Chem. B 106 (2002) 5659.
[25] J.-F. Paul, E. Payen, J. Phys. Chem. B 107 (2003) 4057.
[26] B. Delmon, Bull. Soc. Chim. Belg. 104 (1995) 173.
[27] Y.W. Li, B. Delmon, J. Mol. Catal. A: Chem. 127 (1997) 163.
[28] P. Gajardo, P. Grange, B. Delmon, J. Catal. 63 (1) (1980) 201.
[29] Y.-W. Li, X.-Y. Pang, B. Delmon, J. Mol. Catal. A: Chem. 169 (2001) 259.
[30] G. Hagenbach, Ph. Courty, B. Delmon, J. Catal. 23 (2) (1971) 295.
[31] G. Hagenbach, Ph. Courty, B. Delmon, J. Catal. 31 (2) (1971) 264.
[32] M. Sun, J. Adjaye, A.E. Nelson, Appl. Catal. A: Gen. 263 (2004) 131.
[33] F. Dumeignil, J.-F. Paul, E.W. Qian, A. Ishihara, E. Payen, T. Kabe, Res. Chem. Intermed. 29 (6) (2003) 589.
[34] Ch. Song, Catal. Today 86 (2003) 211.
[35] E. Benavente, M.A. Santa Ana, F. Mendizábal, G. Gonza.lez, Coord. Chem. Rev. 224 (2002) 87.
[36] J.A. Spirko, M.L. Neiman, A.M. Oelker, K. Klier, Surf. Sci. 542 (2003) 192.
[37] M. Sun, J.A.E. Nelson, Adjaye, J. Catal. 226 (2004) 32.
[38] L. Vradman, M.V. Landau, Catal. Lett. 77 (1–3) (2001) 47.
[39] G. Berhault, L. Cota Araiza, A.D. Moller, A. Mehta, R.R. Chianelli, Catal. Lett. 78 (1–4) (2002) 81.
[40] H. Shimada, Catal. Today 86 (2003) 17.
[41] Y. Okamoto, T. Kubota, Catal. Today 86 (2003) 31.
[42] G. Murali Dhar, B.N. Srinivas, M.S. Rana, M. Kumar, S.K. Maity, Catal. Today 86 (2003) 45.
[43] B. Pawelec, R.M. Navarro, J.M. Campos-Martin, A. Lopez Agudoa, P.T. Vasudevan, J.L.G. Fierro, Catal. Today 86 (2003) 73.
[44] J.J. Lee, S. Han, H. Kim, J.H. Koh, T. Hyeon, S.H. Moon, Catal. Today 86 (2003) 141.
[45] H. Orita, K. Uchida, N. Itoh, Appl. Catal. A: Gen. 258 (1) (2003) 115.
[46] H. Farag, K. Sakanishi, M. Kouzu, A. Matsumura, Y. Sugimoto, I. Saito, J. Mol. Catal. A: Chem. 206 (2003) 399.
[47] V.M. Kogan, in: T. Weber, R. Prins, R. van Santen (Eds.), Transition Metal Sulfides, Chemistry and Catalysis NATO ASI Series, Kluwer Academic Publishers, 3, High Technology, 1998, 60, p. 235.
[48] V.M. Kogan, Nguen Thi Đung, V.I. Yakerson, Bull. Soc. Chim. Belg. 104 (1995) 303.
[49] V.M. Kogan, N.M. Parfenova, Stud. Surf. Sci. Catal. 106 (1997) 449.
[50] V.M. Kogan, N.N. Rozhdestvenskaya, I.K. Korshevets, Appl. Catal. A: Gen. 234 (2002) 207.
[51] H. Schweiger, P. Raybaud, G. Kresse, H. Toulhoat, J. Catal. 207 (2002) 76.
[52] J.-F. Paul, S. Cristol, E. Payen, Catal. Today 130 (2008) 139.
[53] V.M. Kogan, G.V. Isaguliants, Catal. Today 130 (2008) 243.
[54] R.R. Chianelli, Oil Gas Sci. Technol. – Rev. IFP 61 (4) (2006) 503.
[55] Th. Weber, J.A. Rob van Veen, Catal. Today 130 (2008) 170.
[56] 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.
[57] V.M. Kogan, N.N. Rozhdestvenskaya, Oil Gas Sci. Technol. – Rev. IFP 61 (4) (2006) 547.