A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
International Edition
www.angewandte.org

Title: 33S label tracing for hydrodesulfurization process: insights into the reaction mechanism, catalyst characterization and improvement

Authors: Vitaly L. Sushkevich, Andrey G. Popov, and Irina I. Ivanova

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201704027
Angew. Chem. 10.1002/ange.201704027

Link to VoR: http://dx.doi.org/10.1002/anie.201704027
http://dx.doi.org/10.1002/ange.201704027

WILEY-VCH

^{33}S label tracing for hydrodesulfurization process: insights into the reaction mechanism, catalyst characterization and improvement

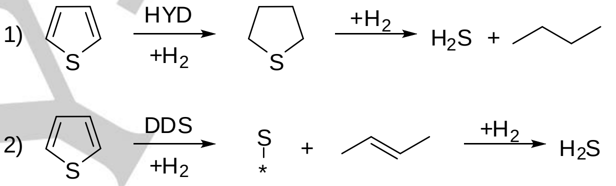
Vitaly L. Sushkevich,*[ab] Andrey G. Popov[a] and Irina I. Ivanova[a]

Abstract: The novel approach based on ^{33}S label tracing is proposed for the elucidation of hydrodesulfurization (HDS) mechanisms and characterization of molybdenum sulfide catalysts. The technique involves sulfidation of the catalyst with dihydrogen sulfide labeled with the ^{33}S isotope, followed by monitoring the fate of ^{33}S label in the course of hydrodesulfurization reaction by on-line mass spectrometry and characterization of the catalyst after the reaction by TPO-MS. The results point to different pathways of thiophene transformation over Co or Ni promoted and unpromoted molybdenum sulfide catalysts, provide information on the role of promoter and give a key for the design of new efficient HDS catalysts.

Hydrodesulfurization (HDS) is one of the most important refinery processes, with the annual capacity close to 4 billion tons.[1] Nowadays, strict refinery regulations on the sulfur content in the final feedstock require significant improvements in the composition of catalyst and the process technology.[2] In addition, the trends to use heavy oil for the fuel production demand new approaches to refine high-temperature boiling and sour oil.[1] These challenges motivate research in the field of hydrodesulfurization, revealing several directions aimed at the increase of the efficiency of the MoS_2 based catalysts.[3-6] In the general case, the efficiency can be increased by using different supports,[4] variation of the dispersion of the MoS_2 phase, using different precursors for the catalyst preparation[5] and promoting with various dopants.[6] For the industrial catalysts promoting with cobalt or nickel is commonly used resulting in the 2-5 fold increase of catalysts activity. However, the nature of this promotion effect is still the subject of debate.

It is generally accepted that doping the MoS_2 catalysts with Co and Ni leads to the formation of (Co or Ni)-Mo-S surface species with higher intrinsic activity with respect to the unpromoted Mo-S samples.[7] These active species are located at the edges of the slabs, giving coordinatively unsaturated sites (CUS).[8] The basal planes are believed to be inactive. Another model of the active sites, proposed in the recent years, postulates the existence of the so-called “brim sites”. These sites are described as metal-like regions located near the edges of the sulfide slabs and suggested to be able to catalyze hydrogenation and the C−S bond cleavage.[9]

In the case of NiMo and CoMo catalysts the hydrodesulfurization of thiophene proceeds via two possible mechanisms (Scheme 1, pathways 1 and 2) that are generally accepted in the literature. The first one corresponds to the hydrogenation route (HYD) implying the stepwise addition of hydrogen to thiophene with the subsequent S-C scission. The second one includes an irreversible direct desulfurization (DDS) via a direct break of the S-C bond leading to the formation of sulfur S* surface species and butane, followed by the hydrogenation of sulfur species into H_2S. The impact of each pathway is governed by the reaction conditions, hydrogen pressure and catalyst composition.[10]



Scheme 1. Main pathways of thiophene hydrodesulfurization over (Co,Ni)-MoS_2 catalysts. First route corresponds to hydrogenation (HYD) and second to direct desulfurization (DDS) of thiophene molecules over the catalyst.

The active sites of HDS catalysts are usually characterized by STM and TEM microscopy.[11] These techniques give important information on the structure of the active sites and the location of a promoter over fresh and used catalysts. However, to get a deeper insight into the mechanism of the HDS process, the information on the catalyst and promoters and their interaction with substrate under real reaction conditions is highly desirable. This information can be best obtained by the *in situ* isotope tracing technique, which allows following the fate of different atoms of the catalyst and substrate directly during the catalytic reaction. Thus, in the case of the HDS reaction, tracing of S-isotopes could be particularly useful since sulfur atoms are contained both in the catalyst and the reactants and are involved in their interaction.

Kabe et al. and Dobrovolsky et al. have used the ^{35}S radioactive isotope tracing for the investigation of hydrodesulfurization of dibenzothiophene over (Co,Ni)-MoS_2.[12] Their experiments confirmed the lability of sulfur atoms, and pointed to sulfur exchange between the catalyst and the reaction products. However, the application of the ^{35}S radioactive isotope tracing experiments was limited to several examples[12] due to the low resolution of this technique, large characteristic time for the measurements and difficulties in determination of the contributions from the different compounds into the total radioactivity. In addition, these experiments require special expensive equipment to protect the environment from strong

---

[a] Dr. V.L. Sushkevich, Dr. A.G. Popov and Prof. I.I. Ivanova,
Chemistry Department of Lomonosov Moscow State University
119991, Leninskye Gory, 1, bld, 3, Moscow, Russia
[b] Dr. V. L. Sushkevich, Paul Scherrer Institut, 5232 Villigen, Switzerland
Email: vitaly.sushkevich@psi.ch

Supporting information for this article is given via a link at the end of the document.

10.1002/anie.201704027

irradiation.

Herein we propose to use the ^{33}S isotope, which is commercially available and not radioactive and can be easily monitored by on-line mass spectrometry. The application of mass spectrometry appears to be beneficial with respect to radioactivity measurements since it allows accessing the sulfur distribution in the reactants and products, which is extremely important for analyzing the mechanism of the sulfur exchange between the catalyst and the substrate. Furthermore, for the quantitative determination of the contents of labile and rigid sulfur in different catalysts, we propose to examine the samples obtained after tracing experiments by the TPO-MS technique.

By using this novel approach, this study is aimed to clarify the mechanism of sulfur exchange over the unpromoted and the cobalt and nickel promoted MoS_2/Al_2O_3 catalysts that are the most commonly used catalysts for hydrodesulfurization. The results point to the existence of a new undiscovered pathway of thiophene transformation over MoS_2/Al_2O_3 catalysts implying the reversible S exchange in the aromatic ring. Furthermore, they provide information on the role of Co and Ni promoters and give hints for characterization and improvement of molybdenum sulfide catalysts.

Table 1. Catalysts characteristics

Catalyst	Metal content in oxide precursor, wt%		Surface area, m^2/g	Sulfur content, wt% [a]
	Mo	Co, Ni		
Mo	11.0	0	165	6.90
CoMo	12.6	2.6	190	8.10
NiMo	10.3	3.0	205	6.90

[a] After sulfidation in a flow of H_2/H_2S

The catalysts were prepared by the insipient wetness impregnation of the commercial alumina with the solutions of corresponding metal salts followed by the calcination at 773K (for details see Supporting Information). The catalysts characteristics are summarized in Table 1. Metal loadings were selected basing on the compositions reported in the literature.[12]

Before the catalytic tests the oxide precursors were preliminary sulfidized in a flow of H_2S/H_2 mixture at 673K for 1 h. The H_2S enriched with the ^{33}S isotope was synthesized *in situ* by reacting the ^{33}S sulfur powder with paraffin (see Supporting Information). Catalytic properties were studied in the thiophene hydrodesulfurization reaction under atmospheric pressure in a continuous flow fixed bed reactor at 633K using the hydrogen to thiophene molar ratio of 13.

The results pointed to 2-3 fold higher activity of Co and Ni promoted catalysts in the HDS reaction of thiophene with respect to the unpromoted MoS_2 catalyst (Table 2). The main products observed were H_2S, linear butenes and n-butane. The selectivity and the alkane to alkene molar ratio were similar for all studied catalysts. In the case of the NiMo sample a slightly higher content of n-butane was observed due to the considerable hydrogenation properties of nickel.[13]

Table 2. Hydrodesulfurization of thiophene over MoS_2 based catalysts.

Catalyst	Mo	CoMo	NiMo
Yield of H_2S*, %	8.9	33.7	29.1
Alkane to alkene ratio*	0.20	0.19	0.24
Yield of [^{33}S]thiophene**, %	62.9	0	0
Labile sulfur content***, wt%	4.39	5.13	4.32
Rigid sulphur content***, wt%	2.51	2.97	2.58

* calculated from GC data

** calculated from MS-data

*** calculated from TPO-MS data

For the ^{33}S label tracing experiments oxide precursors were sulfidized in $H_2[^{33}S]$ yielding the catalysts with the ^{33}S-labeled active phase. After sulfidation all physically adsorbed $H_2[^{33}S]$ was purged with hydrogen at 663K for 1h and then the flow was switched to the $[^{32}S]C_4H_4/H_2$ mixture. The $H_2[^{32}S]$ and $H_2[^{33}S]$ zero time corrected MS responses observed after the switch are shown in Fig. 1. Before the introduction of thiophene, the evolution of $H_2[^{33}S]$ was not detected. After the switch, the formation of both labeled and unlabeled hydrogen sulfide was observed hence confirming the lability of the surface sulfur atoms of the catalysts. The response of the unlabeled H_2S for CoMo and NiMo catalysts was ca. 3 times higher than in the case of MoS_2 catalyst, which confirms a higher hydrodesulfurization activity of promoted catalysts (Table 2). The yield of labeled $H_2[^{33}S]$ passed through the maxima after ca. 1 min on stream indicating a fast exchange process. It is important to mention that the MS response of $H_2[^{33}S]$ for Mo catalyst did not decrease to zero, stabilizing at a considerable level. This behavior could point to several different mechanisms of sulfur exchange over MoS_2 catalysts.

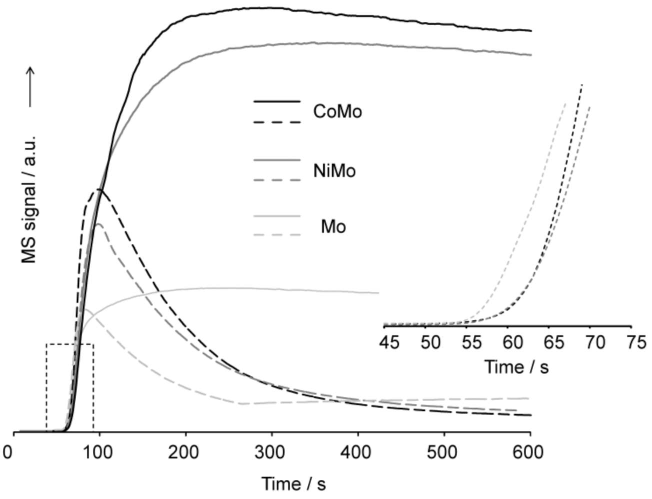


Figure 1. Variation of intensities of the MS molecular ions of $H_2[^{33}S]$ (solid lines) and $H_2[^{33}S]$ (dashed lines) with time on stream during the hydrodesulfurization of unlabelled thiophene over the catalysts sulfidized with $H_2[^{33}S]$. Inset: zoomed fragment from 45 to 75 s region.

The position of the $H_2[^{33}S]$ response maximum is different for promoted and unpromoted catalysts. The detailed examination of this region (see inset) shows that for Mo catalysts the sulfur exchange process is much faster with respect to CoMo and NiMo samples despite the higher activity of the latter. The difference in behavior could be associated with several reasons: i) different amount of labile sulfur and ii) different mechanisms of the S exchange over the MoS_2 and (Co,Ni)-MoS_2 catalysts.

The information on the amount of labile sulfur can be obtained by examination of the catalysts used in the HDS reaction. To estimate the amount of ^{32}S and ^{33}S retained by the catalysts after the reaction, the catalysts were oxidized *in situ* in a temperature programmed regime and the formation of $[^{32}S]O_2$ and $[^{33}S]O_2$ was monitored by on-line mass spectrometry. The results are presented in Fig. 2.

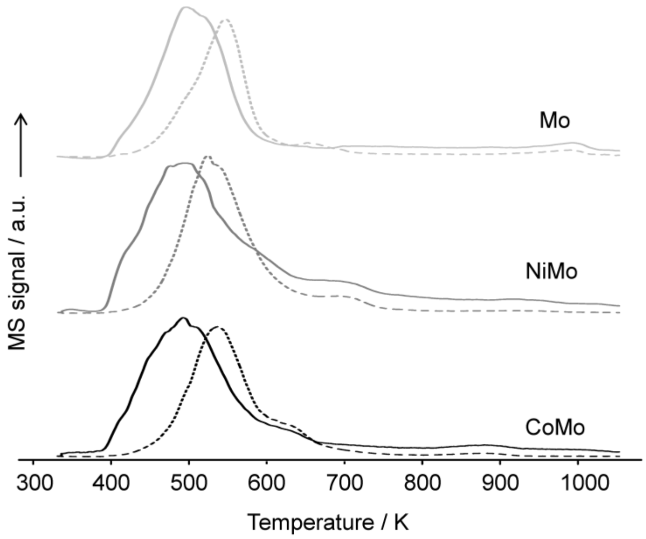


Figure 2. TPO-MS profiles observed over the catalysts sulfidized with $H_2[^{33}S]$ and subjected to HDS reaction of unlabelled thiophene for 1h. Solid lines correspond to the evolution of $[^{32}S]O_2$, dashed lines correspond to the evolution of $[^{33}S]O_2$.

All catalysts demonstrated similar TPO curves both for the $[^{32}S]O_2$ and $[^{33}S]O_2$ evolution. This observation suggests that the promoters do not influence the oxidation properties of the catalysts significantly. In the case of CoMo and NiMo small peaks in the range of 600-750K were also observed due to the individual phases of metal sulfides.[14]

The temperature of the ^{32}S species oxidation was ca. 50K lower with respect to ^{33}S indicating that labile sulfur undergoes easier oxidation. It could be suggested that labile sulfur is located at the edges of the slabs, which facilitates the exchange and oxidation. Integration of the $[^{32}S]O_2$ and $[^{33}S]O_2$ TPO curves gives the content of labile and rigid sulfur for all considered catalysts (Table 2). The values calculated for promoted catalysts are very close to those of unpromoted pointing to the similar content of labile S in all catalysts. Thus, although the amount of $H_2[^{33}S]$ originating from the unpromoted catalyst during the HDS reaction was found to be much lower as compared to the promoted catalyst, the amount of labile and rigid sulfur was found to be the same in both cases (Table 1). This observation implies different pathways of the sulfur exchange over the promoted and unpromoted catalysts and points to the possibility of a reversible sulfur exchange in thiophene over the latter.

The sulfur exchange in aromatic compounds was not reported previously for MoS_2 catalyst. Such process was found to proceed over Al_2O_3 at the temperatures higher than 700K by the Juriev reaction.[15] Under the conditions used in the present study the impact of this process is negligible. It is generally assumed that once adsorbed on the active sites, the S-containing aromatics undergo irreversible hydrogenation or/and the C-S cleavage forming the hydrogenation products and hydrogen sulfide.[7, 11d] However, our results suggest that MoS_2 catalysts can reversibly exchange S atoms in thiophene.

To get more details on this pathway, the MS responses of thiophene isotopomers were studied during the HDS over the Mo, CoMo and NoMo catalysts preliminary sulfidized with $H_2[^{33}S]$ The results are shown in Fig. 3.

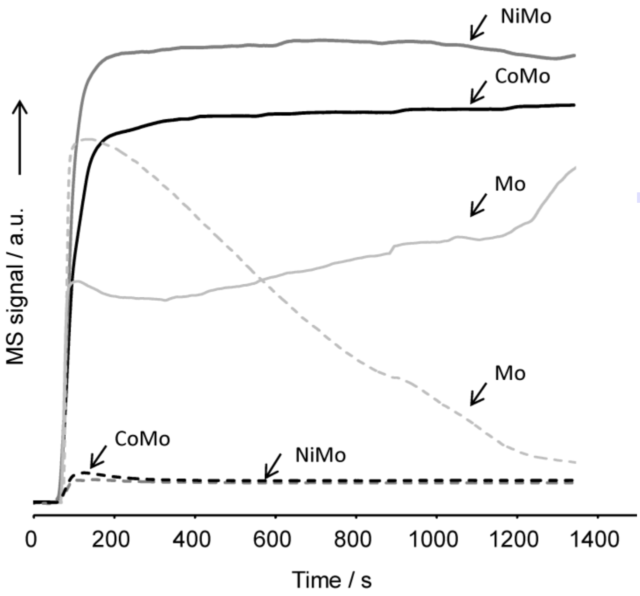


Figure 3. Variation of intensities of the MS molecular ions of the $[^{32}S]$ and $[^{33}S]$ thiophene with time on stream during the hydrodesulfurization of unlabelled thiophene over the catalysts sulfidized with $H_2[^{33}S]$. Solid lines correspond to m/z = 84 ($[^{32}S]$ thiophene), dashed lines - to m/z = 85 ($[^{33}S]$ thiophene).

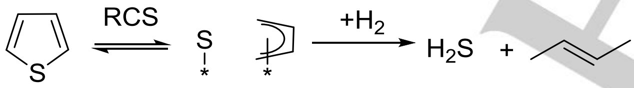
The results show that in the case of the CoMo and NiMo catalysts the molecular ion at 84 m/z corresponding to unlabeled thiophene is mostly observed. Slight ramp for 85 m/z after the introduction of thiophene could be associated with the ^{13}C natural abundance impact arising from unlabeled thiophene. This observation suggests that sulfur from the active sites of the

Ni or Co promoted catalysts does not undergo the reversible exchange with thiophene. Once adsorbed on the active site, thiophene molecule decomposes into C_4 hydrocarbons and sulfur species as shown in Scheme 1. The latter can exchange with the surface Mo[^{33}S]$_2$ species giving H_2[^{33}S] observed during the HDS reaction (Fig. 1).

A rather different result is observed over the Mo catalyst without a promoter. The relative intensity of 85 m/z peak increases immediately after the introduction of unlabeled thiophene and then passes through the maximum. Simultaneously, the unlabeled thiophene concentration reaches the lowest value and then gradually increases. This behavior clearly evidences the sulfur exchange between the catalyst surface and thiophene molecules. Comparing the intensities for 84 and 85 m/z ions right after the introduction of thiophene, the conversion of [^{32}S] into [^{33}S]-thiophene could be estimated. The value obtained is close to 63%, which is significantly higher (Table 2) than the conversion of thiophene into hydrogen disulfide (8.9%).

Summarizing, our data suggest that Mo catalyst demonstrates rather high activity in the sulfur exchange in thiophene, providing the reversible C-S cleavage reaction (RCS, Scheme 2). However, after the cleavage only a small part of the newly formed S* and C_4* surface species undergo further hydrogenation into H_2S and C_4 hydrocarbons, accounting for low hydrodesulfurization activity of this catalyst.

The mechanism of reversible C-S cleavage might include the acid-mediated steps similar to observed for Paal-Knorr synthesis of thiophene. However, basing on the present results the conclusions about the detailed mechanism of the reversible C-S cleavage can not be delivered and further study in this field is required.



Scheme 2. Reversible C-S cleavage (RCS) pathway accounting for thiophene hydrodesulfurization over unpromoted MoS_2 catalysts

On the contrary, CoMo and NiMo catalysts show high activity in the HDS reaction, but they are not active in sulfur exchange with thiophene. Furthermore, a promoted catalysts exhibits a total yield of H_2[^{33}S] and [^{33}S]thiophene of ca. 30%, which is more than 2 times lower than that of the unpromoted MoS_2 (Table 2). The reasons of such a behavior are associated with the decoration of MoS_2 active species with Ni and Co promoters highly active in hydrogenation reactions. It could be suggested that Ni or Co atoms are important in the promotion of an irreversible hydrogenation via HYD and DDS pathways and their role should be carefully revisited. This implies completely different mechanisms of thiophene transformation over unpromoted and Co, Ni-promoted MoS_2 catalysts.

In conclusion, our results demonstrate that the ^{33}S label tracing techniques can be successfully applied for the elucidation of the hydrodesulfurization mechanisms as well as for the characterization of the MoS_2 based catalysts and predicting their catalytic properties. Most importantly, the current results emphasize the crucial role of the metal promoter, which is able to change the chemical environment of the MoS_2 active sites and thus influence the mechanism of the HDS reaction. This opens an exciting possibility of using the metals with different electronic structures to not only tune the catalytic activity but even to change the entire reaction mechanism. This specifically renders the MoS_2-based catalyst a natural choice for rational design of novel catalytic materials with engineered properties.

Another important issue arises from the application of the TPO-MS technique for the analysis of the catalysts labeled with ^{33}S isotope and subjected to the HDS reaction. This approach allows for quantitative determination of the amount of labile and rigid sulfur atoms in the catalyst, which could be related to the dispersion of an active phase. Assuming that the rigid sulfur atoms are located on the top of the slabs, the stacking of MoS_2 species can be estimated and related to the accessibility of active sites and the catalyst activity in the HDS reaction. This novel tool can be easily used to control the quality of the HDS catalyst at industrial scale and evaluate the feasibility of novel MoS_2-based catalysts.

We believe that the proposed approach opens new perspectives for the improvement of existing hydrodesulfurization catalysts and the development of novel efficient heterogeneous catalysts for this process.

Acknowledgements

The authors gratefully acknowledge the Russian Science Foundation for the financial support (Grant №14-23-00094).

Keywords: hydrodesulfurization • isotope tracing • heterogeneous catalysis • mass spectrometry • ^{33}S

[1] V. C. Srivastava, *RSC Advances*, **2012**, *2*, 759–783.

[2] a) USEPA. http://www.epa.gov/sbrefaldocuments/pnl13f.pdf; b) European Standard for Gasoline EN 228/1999 and for diesel EN 590/1999, **1999**.

[3] a) T. Kabe, W. H. Qian, S. Ogawa, A. Ishihara, *J. Catal*., **1993**, *143*, 239–248; b) D. Yitzhaki, M. V. Landau, D. Berger, M. Herskowitz, *Appl. Catal., A*, **1995**, *122*, 99–110; c) L. Vradman, M. V. Landau, M. Herskowitz*, Catal. Today*, **1999**, *48*, 41–48; d) F. T. T. Ng, I. K. Milad, *Appl. Catal., A*, **2000**, *200*, 243–254; e) N. Kunisada, K. H. Choi, Y. Korai, I. Mochida, K. Nakano*, Appl. Catal., A*, **2004**, *269*, 43–51.

[4] a) Y. Okamoto, K. Ochiai, M. Kawano, K. Kobayashi, T. Kubota, *Appl. Catal., A*, **2002**, *226*, 115–127; b) T. Klimova, J. Reyes, O. Gutierrez, L. Lizama, *Appl. Catal., A*, **2008**, *335*, 159–171; c) T. A. Zepeda, B. Pawelec, J. L. G. Fierro, T. Halachev, *Appl. Catal., B*, **2007**, *71*, 223–236; d) U. T. Turaga, C. Song, *Catal. Today*, **2003**, *86*, 129–140; e) O. Y. Gutiérrez, S. Singh, E. Schachtl, J. Kim, E. Kondratieva, J. Hein, J. A. Lercher, *ACS Catal*., **2014**, *4*, 1487-1499.

[5] a) A. M. Venezia, V. L. Parola, G. Deganello, D. Cauzzi, G. Leonardi G. Predieri, *Appl. Catal., A*, **2002**, *229*, 261–271; b) C. Papadopoulou, J. Vakros, H. K. Matralis, C. Kordulis, A. Lycourghiotis, *J. Colloid Interface Sci.*, **2003**, *261*, 146–153.

[6] a) M. Egorova, R. Prins, *J. Catal*., **2004**, *224*, 278–287; b) P. Grange, X. Vanhaeren, *Catal. Today*, **1997**, *36*, 375–392; c) W. R. A. M. Robinson, J. A. R. van Veen, V. H. J. de Beer, R. A. van Santen, *Fuel Process. Technol.*, **1999**, *61*, 103–116; d) W. Qian, Y. Yoda, Y. Hirai, A. Ishihara, T. Kabe, *Appl. Catal. A,* **1991**, *184*, 81–88.

[7] a) Torres, B.; Berhault, G.; Chianelli, R. R. Metal Sulfides. Encyclopedia of Catalysis; Wiley: New York, **2002**; b) Topsøe, H.; Clausen, B.; Massoth, F. Hydrotreating Catalysis Science and Technology; Springer-Verlag: New York, **1996**.

[8] a) Sun, M.; Adjaye, J.; Nelson, A. E., *Appl. Catal. A*., **2004**, *263*, 131−143; b) Moreau, C.; Joffre, J.; Saenz, C.; Geneste, P. *J. Catal*. **1990**, *122*, 448−451.

[9] a) Topsøe, H. *Appl. Catal. A.,* **2007**, *322*, 3−8; b) Kibsgaard, J.; Tuxen, A.; Knudsen, K. G.; Brorson, M.; Topsøe, H.; Laegsgaard, E.; Lauritsen, J. V.; Besenbacher, F., *J. Catal*., **2010**, *272*, 195−203.

[10] Schulz, H., Böhringer, W., Waller, P., Ousmanov, F., *Cat. Today*, **1999**, *49*, 87-97.

[11] a) C. Kisielowski, Q. M. Ramasse, L. P. Hansen, M. Brorson, A. Carlsson, A. M. Molenbroek, H. Topsøe, S. Helveg, *Angew. Chem. Int. Ed*. **2010**, *49*, 2708 – 2710; b) L. P. Hansen, Q. M. Ramasse, C. Kisielowski, M. Brorson, E. Johnson, H. Topsøe, S. Helveg, *Angew. Chem. Int. Ed*. **2011**, *50*, 9994 – 9994; c) Y. Zhu, Q. M. Ramasse, M. Brorson, P. G. Moses, L. P. Hansen, C. F. Kisielowski, S. Helveg, , *Angew. Chem. Int. Ed*., **2014**, *53*, 10723-10727; d) 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*, **2008**, *130*, 86-96.

[12] a) T. Kabe, A. Ishihara, W. Qian, *Catal .Surv. Japan*, **1999**, *3*, 17-25; b) V.M Kogan, N.N Rozhdestvenskaya, I.K Korshevets, *Appl. Catal. A. Gen.*, **2002**, 207-219; c) T. Kabe, W.H. Qian, S. Ogawa, A. Ishihara, *J. Catal.,* **1993**, *143*, 239-248; d) W. Qian, Y. Hachiya, D. Wang, K. Hirabayashi, A. Ishihara, T. Kabe, H. Okazaki, M. Adachi, *Appl. Catal. A. Gen.*, **2002**, *227*, 19-28; e) M. Dobrovolszky, K. Matusek, Z. Paal, P. Tetenyi, *J. Chem.Soc., Faraday Trans*., **1993**, *89*, 3137; f) M. Dobrovolszky, Z. Paal, P. Tétényi, *Appl. Catal.,* **1996**, *142*, 159.

[13] J. Laine, F. Severino, R. Golding, *J. Chem. Tech. Biotechnol*., **1984**, *34A*, 387-393

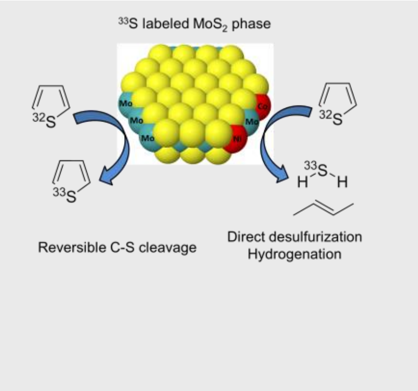
[14] a) J. van Doorn, J.L. Bosch, R.J. Bakkum, J.A. Moulijn, *Catalyst Deactivation*, **1987**, 391-402; b) J. Bartholdy, P. Zeuthen, F.E. Massoth, *Appl Catal. A: Gen*., **1995**, *129*, 33-42; c) P. Zeuthen, P. Blom, B. Muegge, F.E. Massoth, *Appl. Catal*., **1991**, *68*, 117-130.

[15] I. V. Desyatov, E. A. Paukshtis, A. V. Mashkina, *React. Kinet. Catal. Lett.,* **1993**, *51*, 45-50.

Entry for the Table of Contents

COMMUNICATION

The novel approach based on ^{33}S label tracing is proposed for the elucidation of hydrodesulfurization (HDS) mechanisms and characterization of molybdenum sulfide catalysts. The results point to different pathways of thiophene transformation over Co or Ni promoted and unpromoted molybdenum sulfide catalysts, provide information on the role of promoter and give a key for the design of new efficient HDS catalysts.



Vitaly L. Sushkevich, Andrey G. Popov and Irina I. Ivanova*

Page No. – Page No.

^{33}S label tracing for hydrodesulfurization process: insights into the reaction mechanism, catalyst characterization and improvement