Kinetics and Catalysis, Vol. 41, No. 2, 2000, pp. 216–221. Translated from Kinetika i Kataliz, Vol. 41, No. 2, 2000, pp. 239–244.
Original Russian Text Copyright © 2000 by Mashkina.

Dimethyl Disulfide Catalytic Conversion into Methanethiol in the Presence of Water

A. V. Mashkina[1]

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Received May 5, 1998

Abstract—The processes of dimethyl disulfide conversion yielding methanethiol, ethylene and hydrogen sulfide, and the disproportionation of methanethiol formed in this reaction into hydrogen sulfide and dimethyl sulfide proceed on acid–base type catalysts at 350°C in the presence of water. Catalysts with weak proton sites exhibit low activity, which increases with the increasing surface acidity. Catalysts with weak Lewis acid sites and strong basic sites are most active and selective in the reaction of methanethiol formation. The presence of water inhibits the side reaction of disproportionation, thus enhancing the methanethiol formation selectivity.

INTRODUCTION

Dialkyl disulfides (mainly dimethyl and diethyl disulfides) are formed in considerable amounts in the industrial process of hydrocarbon raw material demercaptanization. Presently, they cannot find practical application, and their destruction by combustion leads to the formation of sulfur dioxide and carbonyl compounds polluting the atmosphere. Nevertheless, disulfides can be used to manufacture alkanethiols, which can serve as starting materials in the synthesis of a number of valuable thiocompounds. For example, methanethiol is widely used on a large scale in the production of methionine, which is a medicine and a poultry feed additive. Earlier [1, 2], we had established the possibility of thiol formation in the catalytic conversion of dimethyl and diethyl disulfides. In the helium atmosphere, the reaction proceeds with insufficient selectivity, and the catalyst shows fast deactivation. Hydrogen sulfide addition to the reaction mixture enhances the catalyst stability and increases the reaction rate and the selectivity to methanethiol or ethanethiol, but the process is complicated by the formation of H_2S and sulfur. It is known [3] that heating of the diethyl disulfide mixture with water up to 170–210°C for 4–5 h in a sealed ampoule or in a copper autoclave leads to the formation of ethanethiol and unstable ethanesulfenic acid, which decomposes into acetaldehyde, ethanesulfinic acid, and H_2S. No information is available on the influence of water on the catalytic conversion of dialkyl disulfides in a helium atmosphere.

The regularities of dimethyl disulfide decomposition on acid–base catalysts in the presence of water were investigated in this work.

EXPERIMENTAL

Dimethyl disulfide (DMDS) and dimethyl sulfide (DMS) used in this work were of the reagent grade. Methanethiol (MT) was obtained by methylisothiourea decomposition in the presence of an alkali. Catalysts used and their acid–base properties were described earlier in [4–7].

The experiments on DMDS catalytic decomposition were performed in a flow-type reactor at an atmospheric pressure. A helium flow was passed through constant-temperature saturators with DMDS and water for the supply of the reagents into the reactor filled with a catalyst. The composition of the initial mixture and reaction products was controlled by chromatography [1, 2]. A fresh portion of the catalyst with a particle size of 0.25–0.5 mm was used in each experiment.

The duration of each experiment on determining the catalyst activity was 1 h. The contact time (τ, s) is assumed to be equal to the ratio of the catalyst volume (cm^3) to the gas flow rate (cm^3/s) at room temperature and atmospheric pressure. For describing the experimental results, the following characteristics were used: the DMDS conversion (x, %) and water conversion calculated `on the basis of the initial DMDS (x_{H_2O}); yield (y, mol %); the yields of etylene, H_2S, and DMS were set equal to the number of moles of the product formed, whereas the yield of MT was set equal to the half number of MT moles calculated on the basis of the number of moles of initial DMDS; the selectivity ($S = y/x$, %); and the average DMDS conversion rate, calculated per 1 g of the catalyst (w, mol g^{-1} h^{-1}) at $x = 70\%$. The value of x was estimated using the dependence of the DMDS conversion on the contact time.

RESULTS AND DISCUSSION

Preliminary experiments showed that, when a gas mixture containing 2.5 vol % DMDS and 6 vol % H_2O

---

[1] V. N. Yakovleva and L. G. Sakhaltueva participated in the experimental part of this work.

in helium (flow rate 0.5–3 l/h) was passed through the reactor filled with glass chips heated to 200–350°C, the DMDS conversion did not exceed 3%. The reaction products were ethylene, H_2S, and traces of MT. Noticable DMDS conversion was observed only in the presence of catalysts, and the reaction products were MT, DMS, ethylene, and H_2S. Slow DMDS decomposition can be observed on all the catalysts under study already at 200°C, and the reaction rate increased with rising temperature. In the case of the K_2WO_4/Al_2O_3 catalyst at 350°C, $\tau = 0.07$ s, and the initial DMDS concentration $[DMDS]_0 = 2.5$ vol %, an increase in the H_2O : DMDS molar ratio from 0.2 to 1.4 led to an increase in the DMDS conversion from 52 to 66%, and the selectivity to MT changed from 68 to 76%. A further increase in the water content had no effect on the process parameters. All other experiments were performed at 350°C; $[DMDS]_0 = 2.5 \pm 0.1$ vol %, H_2O : DMDS = (2.2–2.4) : 1. The yield of products and their ratio depended on the catalyst nature and contact time (Table 1). For all catalysts under study, the DMDS conversion and the ethylene and DMS yields increased with the contact time. For some catalysts, the yield of MT changes in parallel with τ, while the selectivity is independent of x. This fact may be considered as an argument in favor of MT formation directly from DMDS. In other cases, the MT yield increased to a certain limit with increasing τ, and then remained unchanged or even diminished presumably as a result of MT conversion into DMS and H_2S. Catalytic decomposition of MT and DMS is usually accompanied by methane evolution [5], but under conditions chosen in this work, no methane was detected in the products of DMDS decomposition. As found from the elemental analysis data, the catalyst after the experiment contained 0.5–2 mol % of sulfur and 1–4 mol % of carbon as calculated on the basis of decomposed DMDS (at $x = 90\%$). This indicates the occurrence of the cracking reaction.

The ethylene yield increased in parallel with τ for all catalysts, while the selectivity of ethylene formation remained virtually unchanged at any DMDS conversion. Ethylene was probably formed directly from DMDS. In the case of catalysts characterized by low DMS formation, the H_2S yield was close to the ethylene yield and increased with τ, whereas the selectivity to H_2S was almost independent of x. For the catalysts active in DMS formation, the H_2S yield exceeded the ethylene yield by a value equal to the DMS yield.

Water added to the reaction mixture was consumed only in catalytic processes. In the case of the γ-Al_2O_3 and K_2WO_4/Al_2O_3 catalysts, after passing water through the catalyst (0.03–0.3 g) in the concentration $[H_2O]_0$ = 5.5–6.5 vol % for 3 h in the absence of DMDS, less than 5% of water was consumed at 250–400°C. In all catalytic experiments, the DMDS conversion coincided with the water conversion within the limits of the experimental error (5–10%) (Table 1).

The catalyst activities were compared using the DMDS conversion rate at $x = 70\%$. The results obtained are presented in Table 2. The pathways of DMDS transformation were discriminated using the selectivity dependence on the DMDS conversion (Table 1).

The SiO_2 catalyst contains weak Brönsted acid sites (BAS) with proton affinity $PA^a = 1390$ kJ/mol and concentration $C = 2.8$ μmol/m^2, no Lewis acid sites (LAS), and weak basic sites (BS) with $PA^b < 800$ kJ/mol. DMDS conversion on this catalyst in the presence of water proceeds at a low rate. Since an increase in the DMDS conversion does not lead to essential changes in the selectivity to MT and ethylene, it could be supposed that these products are formed from DMDS through an independent route. No DMS formation was observed on SiO_2.

Enhancement of the catalyst proton acidity favors the reaction rate growth. This is supported by the data on DMDS conversion over decationized high-silica HZSM-5 zeolite (Si/Al = 100), which contains strong BAS ($PA^a = 1180$ kJ/mol, $C = 0.4$ μmol/m^2), a low concentration of strong LAS (CO adsorption heat Q_{CO} = 41–55 kJ/mol, $C = 0.1$ μmol/m^2), and BS with a moderate strength (PA^b = 800–900 kJ/mol, $C = 1.1$ μmol/m^2). The reaction rate on this catalyst was two orders of magnitude higher than that on SiO_2. The dependence of the MT yield on the contact time shows a maximum, while the yields of other products gradually increase with contact time (Fig. 1). The selectivity to MT formation decreases and the selectivities to DMS and H_2S increase with increasing x (Table 1). The process of MT disproportionation most likely occurs in this case:

$$2CH_3SH \rightleftharpoons (CH_3)_2S + H_2S.$$

It was established earlier [4] that HZSM-5 zeolite reveals high activity in this process. The fact that S_{H_2S} does not considerably exceed S_{DMS} indicates that H_2S is mostly formed as a result of MT disproportionation. Besides disproportionation, DMDS decomposition also takes place to some extent.

NaX zeolite does not contain BAS, but it does contain BS (with PA^b = 800–900 kJ/mol, $C = 0.3$ μmol/m^2) and a significant concentration of weak LAS (Na^+ cations with $Q_{CO} = 20$ kJ/mol, $C = 0.3$ μmol/m^2). The reaction on this catalyst proceeds in approximately the same way as on HZSM-5 zeolite, but the initial activity and selectivity of MT formation on NaX are higher than on HZSM-5. However, NaX is unstable under these conditions and the reaction rate and selectivity to MT after 2 h of the experiment decrease by a factor of four as compared to the results obtained after 1 h.

The data obtained on acidic alumina catalysts show that the enhancement of Lewis acidity has a negative effect on the DMDS conversion. Thus, for γ-Al_2O_3, which contains very weak BAS ($PA^a = 1420$ kJ/mol), a considerable concentration of strong LAS (Q_{CO} = 34 kJ/mol, $C = 2.3$ μmol/m^2, and Q_{CO} = 41 kJ/mol,

Table 1. Dependence of the DMDS conversion and selectivities to the products on the contact time for different catalysts at 350°C, $[DMDS]_0 = 2.5 \pm 0.1$ vol %; H_2O : DMDS = (2.2–2.4) : 1

Catalyst	τ, s	x, %	x_{H_2O}, %	S, %			
				MT	DMS	C_2H_4	H_2S
SiO_2	2.3	8	9	75	0	23	20
	7.1	30	27	70	0	28	26
	11.3	48	46	67	0	31	28
	17.0	70	74	68	0	29	30
HZSM-5	0.01	18	21	83	7	1	8
	0.04	38	35	65	15	2	16
	0.09	57	63	49	24	3	26
	0.14	70	67	40	26	4	32
	0.20	76	78	38	30	6	33
	0.29	86	81	28	34	4	39
	0.35	91	93	22	40	4	41
NaX zeolite	0.035	32	27	68	12	8	0
	0.04	44	35	63	15	12	0
	0.10	70	63	60	17	14	5
	0.35	100	100	71	17	11	2
γ-Al_2O_3	0.12	21	19	76	5	15	20
	0.24	43	40	68	10	14	22
	0.39	63	69	63	12	13	25
	0.60	75	70	56	16	16	30
	0.78	84	81	51	14	18	33
	0.95	94	90	47	19	16	35
1% B/Al_2O_3	0.26	47	45	70	2	22	24
	0.53	65	72	64	5	20	27
	0.79	86	94	60	9	18	25
5% Mo/Al_2O_3	0.04	16	15	80	3	14	18
	0.12	48	43	70	11	8	19
	0.25	76	71	64	12	6	18
	0.39	96	87	60	15	7	20
0.3% Na/Al_2O_3	0.12	38	39	67	6	20	25
	0.25	58	59	59	9	20	27
	0.40	70	66	60	12	16	28
1.7% Na/Al_2O_3	0.12	46	41	73	2	19	23
	0.20	70	67	72	4	20	24
	0.32	98	90	70	5	18	25
2.9% Na/Al_2O_3	0.04	14	13	79	0	22	21
	0.08	30	33	80	0	20	21
	0.12	56	62	78	0	21	20
	0.15	70	76	76	0	20	23
	0.19	86	79	77	0	21	23
	0.24	96	100	77	0	24	22
	0.38	98	95	75	0	22	23
15% K_2WO_4/Al_2O_3	0.03	32	29	80	0	18	20
	0.05	52	46	78	1	19	20
	0.07	66	71	76	3	17	22
	0.18	90	92	70	4	20	25
6.4% K_2CO_3/SiO_2	0.15	20	18	79	0	21	20
	0.45	69	63	77	0	22	23
	0.68	85	82	75	0	25	23

$C = 0.2$ μmol/m^2) and basic sites with a moderate strength ($PA^b = 800$–900 kJ/mol, $C = 4$ μmol/m^2), the rate of DMDS conversion is four times lower than for the zeolite catalyst, whereas the selectivities are approximately the same. The MT yield on γ-Al_2O_3 increases with increasing contact time up to a certain limit and then does not change. On the contrary, the yields of other products gradually increase (Fig. 2). As x increases, the selectivity to MT diminishes, S_{DMS} is increased, and $S_{C_2H_4}$ remains constant (Table 1).

The enhancement of LAS ($Q_{CO} = 36$ kJ/mol) in the case of alumina–boria catalysts leads to activity diminution as compared to γ-Al_2O_3. The alumina–molibdena catalyst containing both strong LAS ($Q_{CO} = 36$ kJ/mol) and BAS ($PA^a = 1200$ kJ/mol, $C = 0.2$ μmol/m^2) is about two times more active than γ-Al_2O_3, while their selectivities are close.

Sodium hydroxide addition to γ-Al_2O_3 suppresses BAS activity and enhances the basicity ($PA^b = 830$–915 kJ/mol, $C = 2.3$–4.4 μmol/m^2 and $PA^b = 920$–960 kJ/mol, $C = 1.0$–1.5 μmol/m^2), while the strength of LAS decreases (for the 0.3–2.9% Na/Al_2O_3 catalysts, $Q_{CO} = 29$–18 kJ/mol). Such changes in the acid–base properties favor DMDS conversion: the reaction rate and the MT and ethylene yields, as well as the selectivity to MT, grow, and the DMS yield diminishes as the Na^+ concentration increases (Fig. 3). At the same time, S_{DMS} decreases. DMS is not formed at all on the 2.9% Na/Al_2O_3 catalyst (Table 1).

The potassium-modified alumina–tungstena catalyst is characterized by stronger Lewis acidity than the 2.9% Na/Al_2O_3 catalyst ($Q_{CO} = 31$ kJ/mol, $C = 0.5$ μmol/m^2). The rates of DMDS conversion and the selectivities to MT are practically the same for both catalysts, but in case of K_2WO_4/Al_2O_3, the process of MT disproportionation into DMS proceeds to some extent. On γ-Al_2O_3 modified by an alkali, the MT, H_2S, and ethylene yields increase as the contact time grows (Fig. 2); moreover, the selectivities to ethylene and H_2S are equal and do not depend on the DMDS conversion (Table 1). Along with DMDS decomposition into MT and ethylene, the process of MT conversion into DMS and H_2S proceeds on the alumina catalyst with a low alkali content. A growth in the concentration of basic sites suppresses the MT disproportionation process.

Table 2. Activity and selectivity of different catalysts in the reaction of DMDS conversion in the presence of water

Catalyst	w, mmol g^{-1} h^{-1}	S, %			
		MT	DMS	C_2H_4	H_2S
NaX zeolite	51.3	60	17	14	5
HZSM-5 zeolite	41.5	40	26	4	32
2.9% Na/Al_2O_3	37.1	76	0	20	23
15% K_2WO_4/Al_2O_3	37.2	74	3	22	23
1.7% Na/Al_2O_3	28.1	72	4	20	24
5% Mo/Al_2O_3	25.8	65	14	7	20
0.3% Na/Al_2O_3	16.0	60	12	16	28
6.4% K_2CO_3/SiO_2	14.5	78	0	20	22
γ-Al_2O_3	11.4	57	14	15	29
1% B/Al_2O_3	6.4	65	8	16	24
SiO_2	0.5	68	0	29	30

The K_2CO_3/SiO_2 catalyst contains strong BS ($PA^b = 860$ kJ/mol, $C = 2.4$ μmol/m^2 and $PA^b = 925$–950 kJ/mol, $C = 1.4$ μmol/m^2) and weak LAS ($Q_{CO} = 29$ kJ/mol, $C = 1.6$ μmol/m^2). The reaction pattern on this catalyst is much the same as on γ-Al_2O_3 modified by a larger amount of an alkali, but the reaction rate is lower in this case.

Some catalytic experiments on DMDS conversion were performed in a dry helium atmosphere. Like DMDS conversion in the presence of water, the reaction products at 350°C were MT, DMS, H_2S, and ethylene. The selectivity to DMS for the catalysts under study increases with enhancement of the surface acidity. The rates of DMDS conversion were very close in both processes; in dry helium, the yield of DMS was

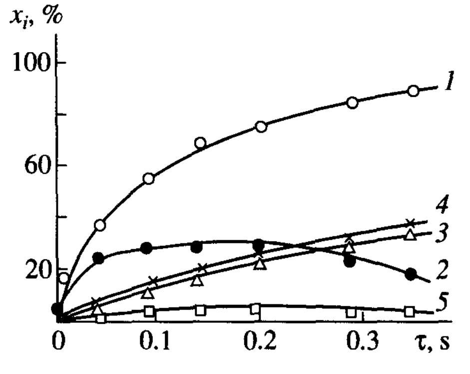

Fig. 1. Influence of the contact time on (*1*) the DMDS conversion, yields of (*2*) MT, (*3*) DMS, (*4*) H_2S, and (*5*) ethylene on the HZSM-5 zeolite.

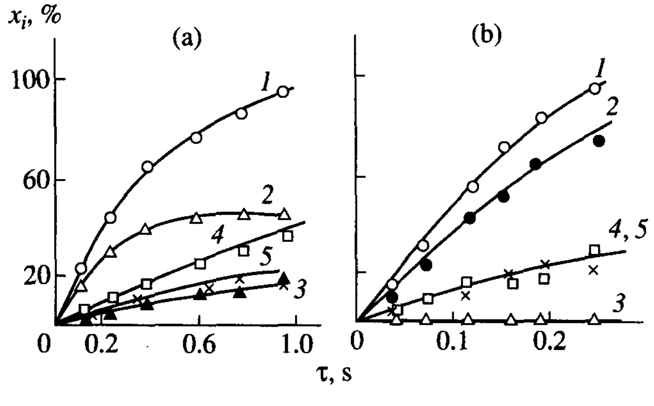

Fig. 2. Influence of the contact time on (*1*) the DMDS conversion, yields of (*2*) MT, (*3*) DMS, (*4*) H_2S, and (*5*) ethylene on (a) γ-Al_2O_3 and (b) 2.9% Na/Al_2O_3 catalysts.

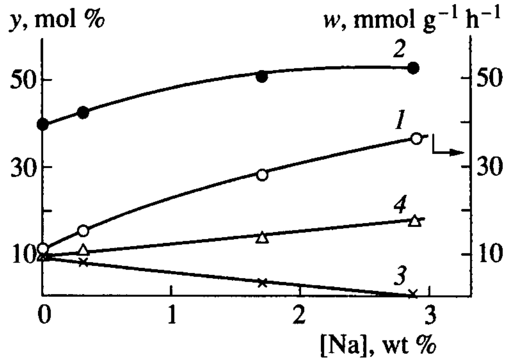

Fig. 3. Dependence of the (*1*) DMDS conversion rate, yields of (*2*) MT, (*3*) DMS, and (*4*) ethylene on the potassium content in the Na/Al_2O_3 catalyst (x = 70%).

higher, whereas the selectivity to MT was lower (Table 3). Acid catalysts are unstable in DMDS conversion in a dry helium atmosphere, and the concentration of sulfur and carbon deposited on the surface is 3–5 times higher as compared to the process performed in wet helium. After 2 h of the experiment at $\tau = 0.5$ s in dry helium, the initial activity of γ-Al_2O_3 halved. On the contrary, the catalysts with strong BAS or LAS retained their activity after 4 h of the experiment in wet helium. The activity of the alkali-modified catalysts after 4 h decreased by 60–70%.

It could be assumed that the route of DMDS conversion in the presence of water is very much the same as in dry helium [1]. The course of this reaction is defined by disulfide ability to form complexes. Dissolved dialkyl disulfides are known [8, 9] to form a hydrogen bond with a proton site; their interaction with Al, Ti, B, Sn, and Ga halides results in coordination followed by electron migration from sulfur in disulfides toward a cation. A similar complex formation process takes place in the case of the interaction of disulfides with solid catalysts. Thus, the formation of the bond between a sulfur atom in a disulfide and a hydrogen atom of an OH group on the surface of a SiO_2 or Al^{3+} cation in aluminum oxide was proved in [10]. Complex formation on the acid catalyst at an elevated temperature is accompanied by destruction of the unstable S–S bond in DMS leading to MT formation. The possibility for disulfide conversion to thiol as a result from its coordination with SH groups of a homogeneous Mo complex containing SH ligands was discussed in [11]. The S–S bond activation is not favorable in the case of weak BAS (SiO_2); therefore, the rate of DMDS decomposition is low. The enhancement of BAS (in HZSM-5) leads to the acceleration of the MT formation process. DMDS coordination by LAS results in the buildup of the surface methylthio groups. If OH or SH groups are present on the surface, they can interact with CH_3S groups yielding MT. Due to the conjugation of 3*d*-orbitals of dithiogroups, the α hydrogen atom in the methyl group becomes quite mobile, and its interaction with all possible basic sites on the catalyst surface results in its detachment with the formation of OH groups. The CH_2S groups formed as a result of such an interaction undergo further changes yielding ethylene and H_2S.

Table 3. Activity and selectivity of catalysts in the reaction of DMDS conversion in a dry helium atmosphere or in the presence of water at 350°C and x = 70%

Catalyst	w, mmol g^{-1} h^{-1}		S, %			
			MT		DMS	
	dry He	He + H_2O	dry He	He + H_2O	dry He	He + H_2O
γ-Al_2O_3	23	11	20	57	46	14
2.9% Na/Al_2O_3	43	37	53	76	25	0
15% K_2WO_4/Al_2O_3	22	37	61	74	20	3
6.4% K_2CO_3/SiO_2	20	15	67	78	18	0

Water consumption in the course of catalytic DMDS decomposition could be explained by the participation of water in surface hydration. We cannot a priori exclude the possibility of MT formation due to DMDS hydrolysis [3]. But no sulfinic acid and aldehyde were found among the reaction products. The rate of DMDS decomposition in the presence of water is close to that in dry helium. Under conditions when the reaction of disproportionation does not proceed or the rate of this process is rather low, the number of moles of MT formed is 1.3–1.6 times higher than that of DMDS consumed. That is why there is no reason to conclude that hydrolysis contributes substantially to the consumption of DMDS in the case of acid–base catalysts studied.

Hydrogen sulfide evolved in the course of DMDS decomposition undergoes dissociative chemisorption and forms surface OH and SH fragments. H_2S adsorption at 300°C on NaX zeolite, which does not possess proton acidity in the original state, leads to the appearance of BAS with $PA^a < 1300$ kJ/mol and $C = 0.03$ μmol/m^2. H_2S dissociative chemisorption yielding OH and SH groups takes place also on the other acid–base catalysts [5]. An additional amount of H_2S that is necessary for the generation of surface BAS is formed by MT disproportionation. It is known [4, 5, 7] that in the case of acid–base catalysts, MT is responsible for the surface methoxylation. CH_3O-group interaction with the second MT molecule activated on the basic sites leads to DMS formation. The stronger the surface acidity, the higher the rate of the disproportionation process. Methoxylation of the catalyst surface by methanethiol is hardly possible in the case of the catalysts with weak acid sites, and thus DMS is not formed. In the case of the catalysts with strong acid sites, such a problem does not exist and DMDS decomposition is followed by the formation of a considerable DMS amount along with MT formation. This in turn leads to a decrease in the selectivity to MT. Water is known to adsorb on the acid surface sites, thus inhibiting thiol adsorption [12]. Thus, the disproportionation of MT formed by DMDS decomposition in the presence of water is complicated. In such a case, S_{MT} increases and S_{DMS} decreases. The blocking of strong acid sites by water molecules inhibits coke formation on the surface, thus contributing to the improvement of the catalyst stability.

REFERENCES

1. Mashkina, A.V., Borodin, B.P., and Mashkin, V.Yu., *Kinet. Katal.*, 1995, vol. 36, no. 2, p. 275.
2. Mashkina, A.V., Yakovleva, V.N., and Sarhaltueva, L.G., *React. Kinet. Catal. Lett.*, 1994, vol. 53, no. 2, p. 363.
3. Challenger, F. and Rawlings, A.A., *J. Chem. Soc.*, 1937, p. 871.
4. Mashkina, A.V., Grunval'd, V.R., Borodin, B.P., *et al.*, *Kinet. Katal.*, 1991, vol. 32, no. 4, p. 866.
5. Mashkina, A.V., *Sulfur Rep.*, 1991, vol. 10, no. 4, p. 279.
6. Mashkina, A.V., Desyatov, I.V., and Mashkin, V.Yu., *Kinet. Katal.*, 1996, vol. 37, no. 1, p. 104.
7. Mashkina, A.V., *Usp. Khim.*, 1995, vol. 64, no. 12, p. 1210.
8. Oae, S., *Khimiya organicheskikh soedinenii sery* (Chemistry of Organosulfur Compounds), Moscow: Khimiya, 1975.
9. Ganyushina, L.A., Gur'yanova, E.N., Romm, M.P., and Lobanova, A.A., *Zh. Obshch. Khim.*, 1979, vol. 49, no. 9, p. 2090.
10. Lyapina, N.K., Lygin, V.I., and Ulendeeva, L.D., *Usp. Khim.*, 1980, vol. 49, no. 6, p. 998.
11. Coucouvanis, D., Hadyikyiacou, A., Draganyao, M., *et al.*, *Polyhedron*, 1986, vol. 5, nos. 1–2, p. 349.
12. Kamanaka, T., Sugioka, M., and Aomura, K., *Bull. Jpn. Petrol. Inst.*, 1977, vol. 19, no. 1, p. 41.