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Catalytic Processing Dimethyl Disulphide into Dimethyl Sulphide

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Abstract

Regularities were studied concerning dimethyl disulphide transformation in an atmosphere of helium in the presence of solid catalysts those differ from each other in the acid-base properties. The catalysts containing mainly Brønsted acidic centres or strong basic centres on the surface exhibit a low activity level. Under the action of weak Lewis acidic centres, the dimethyl sulphide is formed at a low rate, however with increasing the strength of these centres the rate of dimethyl sulphide formation increases. For a catalyst to exhibit a high activity level in the formation of dimethyl sulphide, it is required for the presence of strong Lewis and Brønsted centers, as well as basic centres with a moderate strength on the surface. The results of kinetic studies indicate that before 200 °C there is a parallel reaction scheme realized, whereas at a higher temperature the reaction scheme is consecutive. The reaction kinetic type varies from the first-order kinetics to zero-order one depending on the concentration of the substrate. The rate of dimethyl sulphide formation increases with increasing the temperature, the apparent activation energy amounts to (55±1) kJ/mol. The selectivity level of dimethyl sulphide formation in the case of complete conversion level of the substrate reaches 50–60 %.

Key words: catalysts, dimethyl disulphide, dimethyl sulphide

INTRODUCTION

The scale of production and processing mercaptane-containing gas condensates, crude oil and petroleum products are steadily increasing. In connection with the fact that in the course of their production, processing, transportation and storage there are a number of environmental and technological problems, the products are subjected to demercaptanization, for the last time with the use of oxidation methods [1]. The disposal of great amounts of lower dialkyl disulphides (R = C_1–C_4) generated in the course of oxidation of is not an easy task. In the process of the incineration of the mentioned compound, evolving hydrogen sulphide, sulphur dioxide, carbonyl compounds and others observed, which results in a significant pollution of atmosphere.

Attempts are being made for utilizing non-destructed disulphides. Thus, dimethyl disulphide (DMDS) isolated from the mixture is proposed to use as an odorant for natural gas, as an inhibitor coke-forming in the pyrolysis of hydrocarbons and as a sulphiding agent for hydrofining catalysts [2]. At the same time the DMDS obtained in the course of desulphurization could be used as available and cheap raw material for synthesizing thio compounds under demand, in particular dimethylsulphide (DMS). The latter is widely used, for example in the production of dimethyl sulphoxide being a solvent required for a number of industries, a pharmaceutical preparation, an extracting agent for metals and aromatic hydrocarbons.

There is information concerning DMS formation *via* DMDS decomposition in the presence of solid catalysts. The conversion level of

DMDS in hydrogen environment at 180–260 °C in the presence of supported Pd, Rh, Ru, Ni, Co, Mo, W, Ni (Co) Mo sulphides results in hydrogenolysis with the predominant formation of methanethiol (MT); whereas DMS as a byproduct is formed with the yield lower than 5 mol. % [3–5]. At a low content of H_2 in N_2 (2 : 1), the DMS yield increases up to 11.7 mol. % [6]. A significant increase in the yield of DMS is observed in the case of carrying out the reaction in an inert atmosphere at 350 °C in the presence of zeolite, Al_2O_3 either pure or modified with Mo, K, Na oxides [7]. The reaction of DMS synthesis *via* decomposing the DMDS under the action of solid catalysts is not completely understood.

In this paper, in order to identify the conditions for obtaining a higher yield of DMS we investigated the patterns of heterogeneous catalytic DMDS conversion in a helium environment.

EXPERIMENTAL

In our work, we used purity grade reagents. As the catalysts, we used ready-made compounds such as γ-Al_2O_3 (S_{sp} = 275 m^2/g), zeolite NaX (S_{sp} = 800 m^2/g) and a HZSM-5, Si/Al = 17 (S_{sp} = 500 m^2/g). Before measuring the activity level, the catalysts were calcined in a flow of dry air at 400–500 °C for 5 h. Supported catalysts were prepared by means of carrier (γ-Al_2O_3 and SiO_2, S_{sp} = 310 m^2/g) impregnation according to water-absorbing capacity with aqueous solutions of different compounds such as H_2SO_4, H_3PO_4, $H_4SiW_{12}O_{40}$ HSiW, K_2WO_4, NaOH, $Cr(NO_3)_3$, and $Co(CH_3CO_2)_2$. The samples were air-dried at a room temperature for 12 h, further for 5 h at 110–120 °C to be then heat treated during 5 h. The samples of HSiW, H_3PO_4 applied onto a carrier were calcined in an environment of He at 300 °C, the samples impregnated with K_2WO_4 were calcined at 400 °C, whereas the other samples were calcined in a flow of air at 500 °C. The content of acids on the carriers amounted to (%): HSiW 25, H_3PO_4 30, H_2SO_4 10, K_2WO_4 20, Na 0.02 and 1.7.

Catalytic experiments were performed in a flow-through apparatus at atmospheric pressure. To a thermostated saturator filled with DMDS, was helium supplied the gas then was fed to a heated reactor with the catalyst having the grain size ranging within 0.25–0.5 mm. When 30 passed min after starting to feed the mixture into the reactor, the initial mixture and reaction products were sampled for analysis. By default, the initial concentration of DMDS was equal to (1.6±0.2) vol. %.

The reaction products were identified by means of a Varian Saturn2000 gas chromatograph-mass spectrometer (the USA) with an ion trap using a quartz capillary column (3 m × 25 mm LSP CP-Sil 8 CB) with temperature programming from 50 to 250 °C, the temperature of the evaporator being equal to 300 °C. Quantitative chemical analysis was performed by means of a LHM-8MD chromatograph (Russia) with a catharometer (column 2 m × 3 mm, filled with sorbent Porapak Q + R (1 : 1), carrier gas helium). Measurement error was within the range of ±5 rel. %.

As the contact time value, we took the ratio between the catalyst volume to the gas flow rate (in cm^3/s) at a room temperature and atmospheric pressure. Basing on the analysis we calculated the DMDS conversion level (X), the yield of the reaction products, the selectivity level (S) from the ratio between the product yield and DMDS conversion level, the rate of DMDS conversion and the rate of DMS formation (w_{DMDS} and w_{DMS}, respectively, in mmol/h as calculated per 1 g of catalyst).

RESULTS AND DISCUSSION

Initially, the experiments were carried out without a catalyst at T = 190–350 °C and the rate of helium amounting to 1 L/h in a reactor with the volume capacity of 3 mL filled with broken glass. The conversion level of DMDS was less than 2 %, the reaction products were found to contain MT with the yield ranging within 0.3–1.5 mol. % and the traces of methane. In the presence of a catalyst, the process of DMDS decomposition demonstrated a significant yield of DMS, as well as the formation of other sulphur-containing products such as MT, H_2S, CS_2; with the yield ranging within 1–6 mol. %, and evolving C_1–C_2 hydrocarbons was observed.

For each catalyst, the experiments were carried out at a constant temperature and at a

TABLE 1

Activity of catalysts in the formation of dimethyl sulphide from dimethyl disulphide, and the selectivity level with respect to sulphur-containing products

Catalysts	T, °C	$w_{DMC,}$ mmol/(h · g_{cat})	Selectivity level, %			
			$(CH_3)_2S$	CH_3SH	H_2S	CS_2
K_2WO_4/SiO_2	190	0.002	1.5	74	5	14
	250	0.09	3.2	68	10	12
NaX	190	0.013	0.6	69	11	15
	250	0.22	6.0	50	10	24
NaX + H_2S	250	0.43	9.0	51	6	27
HSiW/SiO_2	190	0.05	28	31	20	17
Cr/SiO_2	250	0.04	12	38	20	22
HZSM-5	190	2.50	44	24	20	10
	250	7.90	36	42	18	6
γ-Al_2O_3	190	0.92	46	24	12	15
	250	3.28	40	29	11	18
γ-Al_2O_3 + H_2S	250	6.10	50	24	14	20
0.02 Na/γ-Al_2O_3	250	1.71	30	45	15	9
H_2SO_4/γ-Al_2O_3	250	0.08	14	42	15	26
Cr/γ-Al_2O_3	190	0.04	8	68	7	14
	250	0.67	17	45	16	20
Cr/γ-Al_2O_3 + H_2S	250	6.43	34	32	10	18
Co/γ-Al_2O_3	250	1.29	28	47	10	14
Co/γ-Al_2O_3 + H_2S	250	9.03	43	34	10	11

constant substrate concentration and at different contact time values. Basing on the kinetic curves we determined the contact time value whereat the conversion level was equal to 60 % to calculate the selectivity level for the formation of sulphur-containing products, as well as the rate of DMS formation that was used for characterizing the activity of the catalyst (Table 1).

The catalysts used such as zeolites, supported acids, bases and oxides differed from each other in acid-base properties of the surface. The acid-base properties of the catalysts were earlier studied by means of infrared adsorption of probe molecules [8], data concerning the values of acid-base strength and the concentration of active centres therein are presented in [8–12]. The strength of Lewis acidic centres (LAC) was determined from the heat of CO adsorption (Q_{CO}); the strength of basic centres (BC) resulted from the deuterium affinity in $CDCl_3$ with respect to BC (PA^b) that ranges within 800–900 kJ/mol for the BC of moderate strength, the strength of Brønsted acidic centres (BAC) was estimated *via* the proton affinity with respect to pyridine (PA^a) that amounts to 1170–1200 kJ/mol for strong BAC.

The catalysts investigated in this work were different in the nature, strength and the concentration of acidic and basic centres on the surface thereof (Table 2).

The catalyst K_2WO_4/SiO_2 does not contain BAC, contains weak LAC and strong BC. The presence of this catalyst resulted in a low rate of the DMS formation at 190 and 250 °C, whereas the main reaction product was presented by MT. On the surface of zeolite NaX there are also no BAC, the LAC thereon are weak and BC exhibit a lower strength. In the reaction of DMS formation at 190 °C, the NaX demonstrated very low activity and selectivity level, those slightly increased with increasing the temperature up to 250 °C. At the same time, the rate of DMS formation on NaX exceeded the formation rate in the case of a supported alkaline catalyst. In the course of the reaction, the zeolite NaX promoted a decrease of the

TABLE 2

Acid-base properties of the catalysts [8–12]

Catalysts	BAC		LAC		BC	
	PA[a], kJ/mol	C, μmol/m^2	Q_{CO}, kJ/mol	C, μmol/m^2	PA[b], kJ/mol	C, μmol/m^2
K_2WO_4 /SiO_2	1170–1190	0	19	2.1	830–930	2.4
NaX	<1200	0	20	3.0	800–900	0.5
H_3PO_4/SiO_2	~1300	1.2	0	0	<800	н/д
HSiW/SiO_2	<1200	1.0	0	0	800–900	н/д
Cr/SiO_2	<1200	0.25	28	0.4	800–900	2.0
HZSM-5	1170–1180	0.33	33–37	0.16		
			42–54	0.013	800–900	1.1
γ-Al_2O_3	1170–1270	0.03	32–34	2.2		
			41–56	0.2	800–900	4.0
0.02 Na/γ-Al_2O_3	<1200	0	27–32	4.2	850–915	2.2
			920–960	0.8		
Cr/γ-Al_2O_3	1245–1270	0.15	36	2.4	900	2.8
γ-Al_2O_3 + H_2SO_4	1170–1180	0.1	37–48	0.5	0	0

Note. ND – no data.

initial activity at 190 °C almost by 3 times for 3 h, and almost by 10 times at 250 °C. When K_2WO_4/SiO_2 catalysts and zeolite NaX are processed with H_2S + H_2 mixture at 400 °C for 1 h, then a number of strong BAC to appear on the surface (C = 0.01–0.03 μmol/m^2), which results in an increase in the activity and selectivity level of catalysts.

The catalyst H_3PO_4/SiO_2, with no LAC containing only weak BAC and weak BC is completely inactive with respect to the formation of DMS. On the surface of a supported heteropoly acid of the 12th series (HSiW/SiO_2) there are also no LAC, BC containing thereon are weak, but there is a significant number of strong BAC. In the presence of this catalyst at 190 °C, the decomposition of DMDS proceeded to form approximately equal amounts of MT and DMS and H_2S in somewhat fewer amounts. The rate and the selectivity level of DMS formation were low. After the experiment, on the surface of the catalyst there were sulphur and carbon detected. Under the influence of strong BAC there occurred, to all appearance the formation of polymeric compounds such as (CH_2S_n) [13], those were deposited on the surface. Increasing the experimental temperature up to 250 °C resulted in a considerable destruction of the heteropoly acid. The catalyst Cr/SiO_2 containing strong BAC, weak LAC and BC of medium strength, demonstrated a low activity with respect to the formation of DMS. A significantly higher activity in the formation of DMS was exhibited by zeolite HZSM-5 in hydrogen form containing strong BAC, strong LAC and BC with moderate strength.

On the surface of γ-Al_2O_3 calcined at 500 °C, there is a small number of strong BAC, as well as strong LAC and the BC of moderate strength. The catalyst is active with respect to the formation of DMS. After processing the γ-Al_2O_3 with the H_2S + H_2 mixture at 400 °C for 1 h, increasing the amount of strong BAC (C = 0.08 μmol/m^2) on the surface is observed, whereby the strength of the LAC and BC does not change, however their density is somewhat reduced. As to compare with the initial γ-Al_2O_3 the activity demonstrates an increase. Adding 0.02 mass % Na to γ-Al_2O_3 causes suppressing the BAC, reducing the strength of LAC and a certain increase in the basicity of the surface. The formation rate of DMS in this case is almost twice lower than that inherent in pure γ-Al_2O_3. Sulphuric acid addition the to γ-Al_2O_3 results in increasing the concentration of strong BAC, increasing the strength of LAC and suppressing the BC; thus, the activity of this catalyst is low.

Transition metal oxides applied onto γ-Al_2O_3 exhibit an activity with respect to DMS formation. The activity of the oxides increases with sulphiding them by a mixture of hydrogen sulphide with hydrogen at 400 °C. The acid-base properties of such catalysts are poorly understood, but it is known [14] that metal sulphides formed in the course of sulphurization are partially reduced to result in appearing coordinately unsaturated cations on the surface those represent strong acceptor centres. Furthermore, resulting from treatment of these catalysts by H_2S at elevated temperature values, an increase in strong BAC concentration on the surface is observed.

TABLE 3

Selectivity level of DMS formation from pure DMDS the mixture with methanol (γ-Al_2O_3, T = 350 °C, molar ratio methanol/DMDS = 2 : 1)

Initial raw	Selectivity level of DMS formation, %						
	DMDS conversion level, %						
	30	45	60	75	84	92	100
Pure DMDS	21	28	35	46	50	53	54
DMDS + methanol	95	96	95	94	97	94	96

Basing on these data concerning the influence of acid-base properties of the catalysts on their activity one could conclude that the reaction of DMS formation from DMDS with a high rate requires that the surface of the catalyst simultaneously contained strong BAC, strong LAC and BC with medium strength. Taking this into account, as well as the information about the properties of organic disulphides [13] and the data concerning the adsorption [15, 16], we could assume that the conversion of DMDS proceeds according to the scheme as it

TABLE 4

Effect of temperature and contact time on the conversion level of dimethyl disulphide and product yield in the presence of sulphided catalyst 10 % Co/γ-Al_2O_3

T, °C	Contact time, s	X, %	Yield, mol. %			
			CH_3SH	$(CH_3)_2S$	CS_2	H_2S
160	0.8	45	9	26	5	5
	2.0	63	13	36	6	6
	4.1	87	17	50	9	9
180	0.5	58	12	29	7	9
	0.9	84	17	42	10	13
	2.1	99	20	49	12	16
200	0.34	39	13	15	7	3
	0.48	72	16	34	11	10
	0.86	91	14	46	14	15
220	0.13	38	13	14	5	2
	0.32	84	17	39	13	10
	0.45	98	12	48	16	20
250	0.07	55	18	20	8	7
	0.20	85	16	43	11	15
	0.37	99	14	54	14	18
270	0.06	51	21	15	9	4
	0.10	69	26	27	10	6
	0.23	90	27	41	9	14
300	0.02	45	21	11	7	4
	0.05	69	25	25	10	8
	0.09	95	21	48	13	13
330	0.03	70	20	27	11	6
	0.04	83	24	34	14	10
	0.05	98	20	46	15	20
350	0.016	40	20	11	7	1
	0.03	83	25	33	15	8
	0.046	100	22	46	15	17

follows. In the course of DMDS interaction with a solid catalyst, a donor-acceptor bond is formed between a sulphur atom of the disulphide and an acceptor centre of the surface. The complex formation results in breaking a weak S–S bond in the disulphide as well as in appearing thiomethane groups (CH_3S) on the surface. Owing to the coordination of the sulphur atom of the second disulphide with the LAC and of the carbon atom of methyl group with the BC, breaking the C–S bond occurs to release sulphur to form the CH_3 group. The CH_3S and CH_3 groups undergo various transformations those result in the formation of MT, H_2S, CS_2, methane, tioformaldehyde and resins. The formation DMS to all appearance could occur as a result of the condensation of two CH_3S groups accompanied by a release of sulphur. However, a more likely mechanism for the DMS formation consists in the interaction between CH_3S and CH_3 groups *via* a mechanism similar to the formation of dimethyl ether through methanol dehydration [17]. Somehow confirming the participation of surface CH_3 groups in the formation of DMS consists in the results of experiments concerning DMDS transformation in the presence of methanol that is readily performs the methoxylation of solid acidic catalyst surface [18]. We have found that in the case of aluminum oxide in the presence of methanol the DMDS undergoes conversion to form mainly DMS; MT is formed in small amounts as a side sulphur-containing product; the selectivity level of DMS under certain conditions amounts up to 95–97 % (Table 3).

It can be seen that with increasing the conversion level of substrate the selectivity level with respect to DMS formation in the experiments with pure DMDS increases to be equal to 54 % at $X = 100$ %, whereas in the presence of methanol it is almost unchanged amounts to 95–97 %. A high selectivity with respect to DMS formation could be, to all appearance, caused

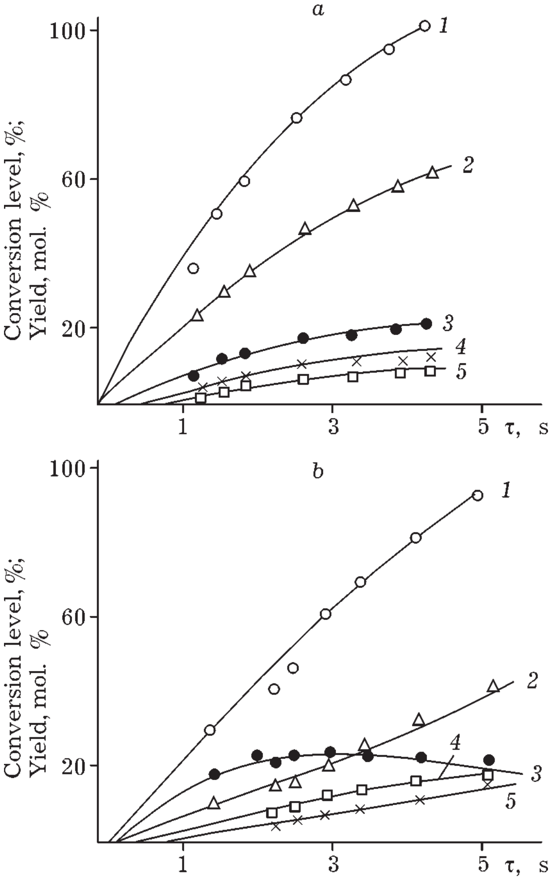

Fig. 1. Effect of the contact time on the conversion level of DMDS (*1*) and the yield of DMS (*2*), MT (*3*), H_2S (*4*), CS_2 (*5*). Temperature, °C: 150 (*a*) and 320 (*b*).

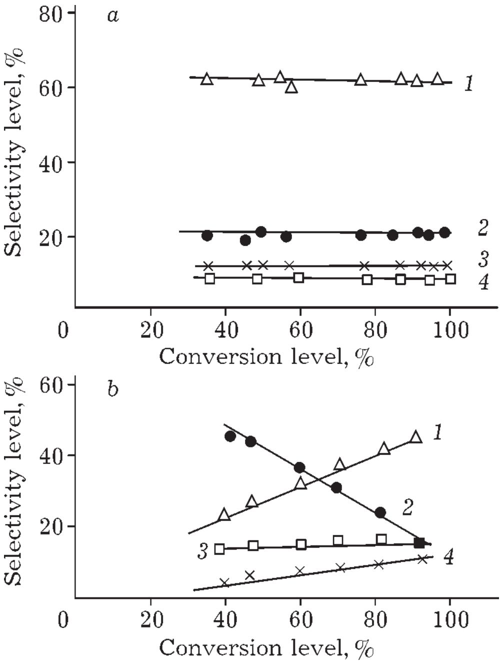

Fig. 2. Selectivity level for the formation of DMS (*1*), MT (*2*), H_2S (*3*), CS_2 (*4*) at different DMDS conversion level values. Temperature, °C: 150 (*a*), 320 (*b*).

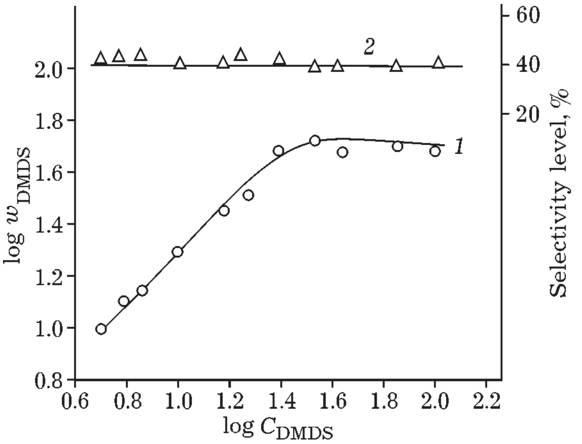

Fig. 3. DMDS conversion rate (*1*) and selectivity of DMS formation (*2*) depending on the concentration of DMDS.

by the fact that methanol being adsorbed mainly on active centres prevents DMDS from profound decomposition. Detailed experimental results concerning the catalytic conversion of DMDS in the presence of methanol are to be published in a separate paper, whereas a detailed study of the reaction mechanism should be the subject of further research work.

The conversion of DMDS under different conditions was investigated in the presence of a sulphidized catalyst 10 % Co/Al_2O_3 within the temperature range of 150–350 °C, at the DMDS concentration values amounting to 0.8–14 vol. % and at the contact time ranging within 0.02–4.0 s. The experimental results are presented in Table 4 and in Figs. 1–4.

At a constant temperature and with the initial concentration of DMDS amounting to (1.6±0.2) vol. %, increasing the contact time value resulted in an increase of the conversion level and of the yields of DMS, CS_2, H_2S and hydrocarbons on the contrary, whereas the yield of MT at the temperature above 200 °C exhibited a decrease (see Table 4 and Fig. 1). The selectivity levels with respect to the formation of all the products (see Fig. 2) at the temperature values ranging within 150–190 °C did not depend on the conversion level, which allows us to suggest that the mentioned products could be formed from DMDS *via* independent pathways. At the temperature higher than 200 °C, the increase in the conversion level did not result in changing the selectivity level with respect to CS_2, but there was a drop of selectivity level with respect to MT and the growth of this parameter concerning DMS and H_2S. To all appearance, the CS_2 is formed directly from the disulphide, whereas DMS and H_2S are yielded (at least partially) *via* the condensation of MT formed in the course of DMDS decomposition.

In order to determine the effect of DMS concentration on the reaction rate we conducted experiments at 250 °C with varying the initial DMDS concentration values within the range of 0.8–14 vol. %. For the case of $X = 50$ % we calculated the current value of DMDS concentration, the total rate of DMDS conversion and selectivity level with respect to DMS (see Fig. 3). It is seen that varying the concentration of DMDS does not result in changing the selectivity level with respect to DMS. With increasing the concentration of DMDS from 0.5 to about 3.3 % the reaction rate exhibits a linear increase (first order); in the case of a higher concentration the reaction rate did not change (zero order), to all appearance, in connection with the inhibition of the process by disulphide. The overall conversion rate of DMDS at $X =$ 70 %, and the initial concentration of the disulphide of about 1.6 % exhibited an increase with increasing the temperature (see Fig. 4). The selectivity level with respect to DMS formation at a complete conversion level of the substrate ranges within 50–60 %. The apparent activation energy determined from the logarithmic dependence of the reaction rate on the reciprocal temperature value amounted to (55±0.1) kJ/mol.

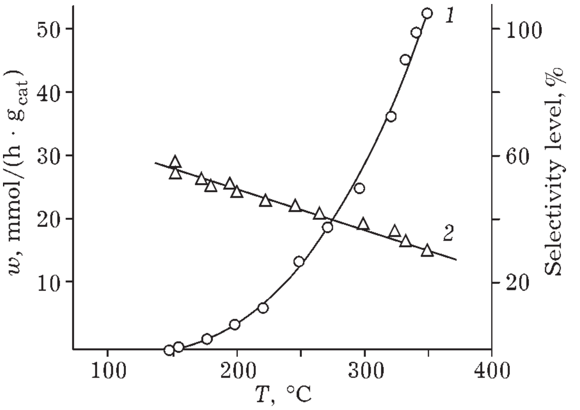

Fig. 4. Effect of reaction temperature on the rate (*1*) and the selectivity level (*2*) of DMS formation.

CONCLUSION

Under the action of solid catalysts the DMDS decomposes to produce DMS, MT, CS_2, H_2S, ethylene and methane in an inert atmosphere, at 150–350 °C. Catalysts containing predominantly of the BAC or strong BC on the surface exhibit a low activity level with respect to the formation of DMS. The reaction rate and the selectivity level with respect to DMS formation exhibit a substantial increase in the case when strong BAC, strong LAC and moderate strength BC are simultaneously present on the catalyst surface. The kinetic data indicate that at the temperature values below 200 °C the change in DMDS conversion level does not affect the selectivity of the reaction products formation, *i. e.*, they are formed from DMDS via independent patterns. At higher temperature values the selectivity level with respect to DMS increases with increasing the conversion level, *i. e.* there takes place a consecutive reaction process, and the DMS is mainly formed *via* the condensation of MT. Within the range of the values of current substrate concentration from 0.5 to 3.3 vol. %, there occurs a first order reaction kinetics, whereas at a higher concentration zero order kinetics is observed. The selectivity with respect to DMS does not depend on the substrate concentration. With increasing the temperature the rate of DMS demonstrates an increase, whereas the selectivity level somewhat decreases. In the case of complete substrate conversion the selectivity level with respect to DMS ranges within 50–60 %.

These results open up the prospects for a novel process of DMS production from available raw materials, the products of demercaptanizing sulphur-containing hydrocarbon mixtures.

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REFERENCES

1 Mazgarov A. M., Vildanov A. F., *Neftekhimiya*, 39, 5 (1999) 371.

2 Sharipov A. X., *Khim. i Tekhnol. Topliv i Masel*, 4 (2002) 50.

3 Mashkina A. V., Khairulina L. N., *Neftekhim.*, 44, 1 (2004) 57.

4 Mashkina A. V., Khairulina L. N., *Kinetika i Kataliz*, 46, 6 (2005) 921.

5 Mashkina A. V., Khairulina L. N., *Kinetika i Kataliz*, 48, 1 (2007) 132.

6 Cadot E., Lakroix E., Breysse M., Arretz E., *J. Catal.*, 164, 1 (1996) 490.

7 Mashkina A. V., Yakovleva V. N., Sakhaltueva L. G., Khairulina L. N., *Neftekhim.*, 41, 1 (2001) 54.

8 Paukshtis E. A., Infrakrasnaya Spektroskopiya v Geterogennom Kislotno-Osnovnom Katalize, Nauka, Novosibirsk, 1992.

9 Mashkina A. V., Kataliz Reaktsiy Organicheskikh Soyedineniy Sery, Izd-vo SO RAN, Novosibirsk, 2005.

10 Desyatov I. V., Paukshtis E. A., Mashkina A. V., *React. Kinet. Catal. Lett.*, 51, 1 (1993) 45.

11 Krivoruchko O. P., Anufrienko V. F., Paukshtis E. A., Larina T. V., Burgina E. B., Yashnik S. A., Ismagilov Z. R., Parmon V. N., *Dokl. RAN*, 398, 8 (2001) 356.

12 Malysheva L. V., Shmachkova V. G., Paukshtis E. A., Kotsarenko N. S., *Kinetika i Kataliz*, 32, 4 (1991) 940.

13 Oae S., in: Khimiya Organicheskikh Soyedineniy Sery, in E. N. Prilezhaeva (Ed.), Khimiya, Moscow, 1975.

14 Pecorard T. A., Chianelli R. R., *J. Catal.*, 67, 2 (1988) 430.

15 Halevi B., Vohs J. M., *J. Phys. Chem. B.*, 109, 50 (2005) 23976.

16 Kang D. H., Friend C. M., *Langmuir*, 20, 26 (2004) 11443.

17 Kzanskiy V. B., *Usp. Khim.*, 57, 12 (1988) 1937.

18 Krylov O. V., Matyshak V. A., *Usp. Khim.*, 63, 7 (1994) 585.