

Conversion of Dimethyl Disulfide in the Presence of Zeolites

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Abstract—Dimethyl disulfide conversion in the presence of zeolites was studied at atmospheric pressure and $T = 190\text{--}350^\circ\text{C}$. For all catalysts, the products of the reaction at $T = 190^\circ\text{C}$ —methanethiol, dimethyl sulfide, and hydrogen sulfide—result directly from dimethyl disulfide. The relative reaction rate and the dimethyl sulfide selectivity decreases in the order HZSM-5 \geq CoHZSM-5 $>$ HNaY $>$ NaX, NaY. The methanethiol formation selectivity changes in the reverse order. The highest methanethiol selectivity at $T = 190^\circ\text{C}$ is shown by the sodium zeolites; the highest dimethyl sulfide selectivity, by the high-silica zeolite HZSM-5. Raising the reaction temperature increases the reaction rate and changes the process route: at high temperatures, dimethyl disulfide decomposes to methanethiol, which then condenses to yield dimethyl sulfide and hydrogen sulfide. The observed regularities are explained in terms of the different acidic properties of the zeolite surfaces.

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The processing of sulfur-containing gases from some gas-condensate oil fields yields large amounts of dialkyl disulfides, which have found only limited application to date. At the same time, dialkyl disulfides could be converted into valuable thio compounds. In particular, they could be decomposed on acid catalysts to obtain alkanethiols and dialkyl sulfides, which are employed as odorants, starting compounds for the synthesis of physiologically active substances, solvents, and extracting agents. Zeolites possessing acidic properties are widely used in various syntheses and conversions of organic compounds. There is information that some reactions of sulfur compounds take place on zeolites in cationic or decationized form. These include alkylmercaptan and dialkyl sulfide synthesis by the reaction between H_2S and an alcohol or an olefin, thiolane synthesis from tetrahydrofuran and H_2S , and thiophene synthesis by furan recyclization in an H_2S medium or by alkylthiophene dealkylation. A significant role in these reactions is played by the acidity of the zeolites [1]. The literature data relevant to the conversion of dialkyl disulfides under the action of zeolites are very scarce. It was found that dimethyl disulfide (DMDS) decomposes into methanethiol (MT), dimethyl sulfide (DMS), and hydrogen sulfide in the presence of the high-silica zeolite HZSM-5 in helium (pure or containing water or hydrogen sulfide) at $T = 350^\circ\text{C}$ and $P = 0.1 \text{ MPa}$ [2]. In dry helium at a contact time of $\tau = 0.12 \text{ s}$, the MT yield is 6.3 mol %. The introduction of 6 vol % water or 9 vol % H_2S into the system, raises the MT yield to 22 and 55 mol %, respectively, while the DMS yield changes in the reverse order. The reaction performed on zeolite NaX at $T = 350^\circ\text{C}$ and $\tau = 0.04 \text{ s}$ in helium containing 9 vol % H_2S affords MT

and DMS in 60 and 27 mol % yields, respectively. This is all the data available on disulfide conversion over zeolites.

In this work, which was aimed at finding active catalysts for disulfide conversion into alkanethiols and dialkyl sulfides, we studied DMDS conversion in the presence of various catalysts.

EXPERIMENTAL

The following catalysts without a binder were used: NaX (Si/Al = 3, [Na] = 8 wt %), NaY (Si/Al = 4.5, [Na] = 9 wt %), HNaY obtained by exchanging sodium ions in NaY for ammonium ions followed by calcination in flowing dry air at $T = 500^\circ\text{C}$ for 1 h ([Na] = 3 wt %), and HZSM-5 in hydrogen form (Si/Al = 17, [Na] = 0.05 wt %). The zeolites were pre-heat-treated for 2–5 h at the following temperatures: NaX and NaY, 400°C ; HNaY, 350°C ; and HZSM-5, 300°C . Zeolite HZSM-5 was loaded with cobalt cations by incipient-wetness impregnation with an aqueous CoCl_2 solution at room temperature [3]. Next, the zeolite was treated with aqueous NH_3 with pH 9.0 for 16 h, filtered, washed with distilled water at room temperature, air-dried, and heated in air at 250°C for 2 h and at 450°C for 6 h. The resulting powder was pelletized and crushed, and the 0.25–0.5 mm size fraction was separated. The acidic properties of zeolites were characterized by IR spectroscopy using adsorbed probe molecules. The strength of protonic sites was evaluated as the pyridine affinity of the proton (PA^a , kJ/mol); the strength of Lewis acid sites (L-sites), as the heat of CO

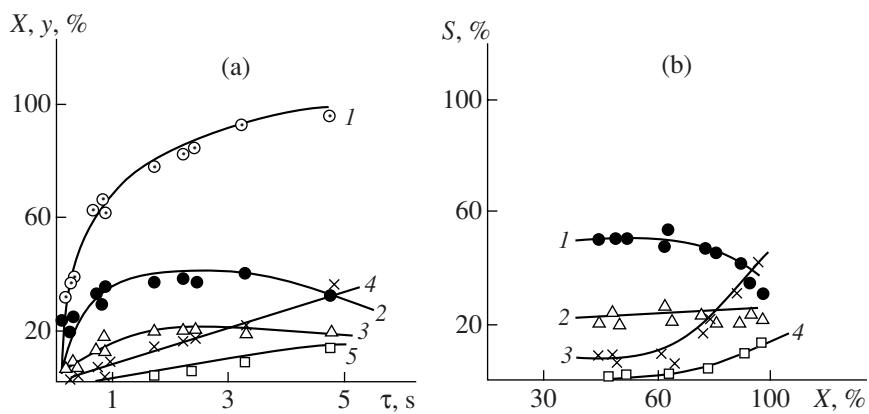


Fig. 1. DMDS conversion in the presence of zeolite HNaY at $T = 190^\circ\text{C}$: (a) (1) DMDS conversion, (2) MT yield, (3) DMS yield, (4) H_2S yield, and (5) methane yield as a function of the contact time; (b) DMDS conversion effect on the (1) MT, (2) DMS, (3) H_2S , and (4) methane selectivities.

adsorption (Q_{CO} , kJ/mol); the strength of basic sites, as CDCl_3 deuterium affinity (PA^b , kJ/mol) [1, 3, 4].

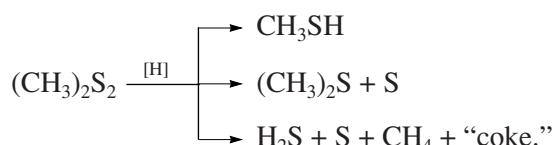
DMDS conversion experiments were carried out at atmospheric pressure and $T = 190\text{--}350^\circ\text{C}$ in a flow reactor connected to a chromatograph. Hydrogen from a cylinder was passed through a temperature-controlled DMDS-filled bubbler and was then fed into the heated reactor containing a catalyst. In each experiment, we used a fresh catalyst sample with a particle size of 0.25–0.5 mm. Prior to catalytic activity measurements, the catalyst was treated with a 15% H_2S + 85% H_2 mixture for 1 h. Thereafter, hydrogen was passed through the catalyst bed at 190°C for 30 min. After this activation procedure, a DMDS + hydrogen mixture was passed through the catalyst (the initial DMDS concentration in hydrogen was 1.6 ± 0.2 vol %). Half an hour after the admission of the mixture into the reactor, the initial mixture and the reaction products were sampled for analysis. In catalyst stability measurements, sampling was done at intervals over a period of 2–3 h. Analyses were carried out on an LKhM-8MD chromatograph with a thermal-conductivity detector (2 m × 3 mm column packed with Porapak Q + R (1 : 1), helium as the carrier gas). The accuracy of chromatographic analysis was ± 5 rel. %.

The contact time (τ) was taken to be equal to the ratio of the catalyst bed volume (cm^3) to the gas flow rate (cm^3/s) at room temperature and atmospheric pressure. It was controlled by varying the catalyst bed volume and the gas flow rate. From chromatographic data, we derived the DMDS conversion (X , %), the product yields (y , mol %), the selectivity of the reaction ($S = y/X$, %), and the DMDS conversion rate at $X = 60\%$ per gram of the catalyst (w , $\text{mmol h}^{-1} (\text{g Cat})^{-1}$). The stability of the catalyst was characterized by the ratio of the reaction rate at a given point in time (w) to the reaction rate determined 30 min after the beginning of the run (w_0).

RESULTS AND DISCUSSION

By investigating DMDS conversion on zeolite NaX as an example, we ascertained that the process parameters in hydrogen and helium are the same. DMDS conversion on all catalysts yielded MT, DMS, H_2S , and, under certain conditions, small amounts of methane. Variation of τ changed the DMDS conversion and the product yields (Tables 1–3, Fig. 1).

As is clear from the data presented in Table 1, the reaction conducted at $T = 190^\circ\text{C}$ in the presence of zeolite NaX or NaY yields MT, H_2S , and DMS traces. As the DMDS conversion increases, the MT selectivity decreases and the H_2S selectivity grows. As distinct from the reaction over the sodium zeolites, the reaction over the decationized zeolites HNaY and HZSM-5 yields not only MT and H_2S , but also DMS (in a yield of up to 40%) and minor amounts of methane. The product selectivities are invariable up to a DMDS conversion of 60%. Under these conditions, the reaction likely proceeds according to the following scheme:



With these catalysts at $X > 60\%$ (this conversion is achieved by increasing τ), the MT selectivity somewhat decreases and the H_2S selectivity grows. One might think that this is due to MT condensation [1]. However, DMS selectivity remains invariable as the DMDS conversion increases under these conditions. It is likely that the increase in the H_2S yield observed at high DMDS conversions is caused by partial MT cracking. With cobalt-exchanged HZSM-5, the DMDS conversion is nearly the same as in the presence of the original zeolite, but the MT yield is somewhat higher and the DMS yield is lower. The introduction of cobalt does not change the route of the process.

According to the data listed in Table 4, the zeolites can be arranged in the following order according to the

relative rate of overall DMDS conversion at $T = 190^\circ\text{C}$ and $X = 60\%$:



w _{rel}	3.6	3.3	3.3	1.8	1.3	1.0
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The lowest DMDS conversion rate is observed for zeolites NaY and NaX. The conversion rate on HNaY is 1.4–1.8 times higher, and the conversion on HZSM-5 (either unmodified or modified with 2 or 5% Co) is higher by a factor of ~2.7–3.6. The MT selectivity changes in the reverse order: it has the highest value for NaX and NaY and is 1.4 times lower for HNaY and 2.2–3.0 times lower for HZSM-5 and CoHZSM-5. The DMS selectivity of the reaction over NaX and NaY is <2% and is higher for the reactions over HNaY, HZSM-5, and CoHZSM-5. At $T = 190^\circ\text{C}$, the reaction proceeds more rapidly over HZSM-5 than over the Co-

containing zeolites, but the selectivities of these catalysts are nearly equal.

For all catalysts, raising the reaction temperature to 250–350°C increases the DMDS conversion rate. The MT selectivity either remains unchanged or increases, and the DMS selectivity increases for NaX and decreases for the other zeolites.

For the reaction on NaY and HNaY at $T = 250^\circ\text{C}$, varying the DMDS conversion has no significant effect on the product selectivities and the H_2S selectivity is much lower than the DMS selectivity (Table 2), indicating that the products result mainly from DMDS decomposition. For HZSM-5 and CoHZSM-5 at $T = 250^\circ\text{C}$

Table 1. Effects of the contact time on DMDS conversion and on the MT and DMS yields and selectivities at $T = 190^\circ\text{C}$ in the presence of various zeolites

Zeolite	τ, s	$X, \%$	Yield, mol %			Selectivity, mol %		
			MT	DMS	H_2S	MT	DMS	H_2S
NaX	0.60	32	24	0	2	75	0	6
	1.40	60	41	0	6	69	0	10
	3.30	82	51	1	14	62	2	27
	4.20	92	55	1	18	60	2	33
NaY	1.20	50	41	0	2	82	0	4
	1.56	62	43	0	6	70	0	10
	2.45	75	48	1	11	64	2	15
	4.74	86	48	1	17	56	2	20
HNaY	0.33	39	20	8	3	51	20	8
	0.82	62	29	17	5	47	27	8
	2.42	82	36	20	21	44	24	26
	4.78	93	31	19	33	33	20	35
HZSM-5	0.27	39	10	21	8	25	50	20
	0.45	57	14	27	12	25	48	21
	0.74	70	16	40	17	23	57	24
	1.84	83	17	40	23	19	48	28
2% CoHZSM-5	0.24	50	14	24	10	28	48	20
	0.73	65	18	31	15	28	48	23
	1.30	78	19	41	19	24	52	24
	3.30	95	23	50	25	22	50	30
5% CoHZSM-5	0.23	44	14	20	8	32	45	18
	0.53	67	23	28	19	34	42	19
	0.76	73	23	35	19	32	48	26
	1.40	86	24	38	24	28	44	28

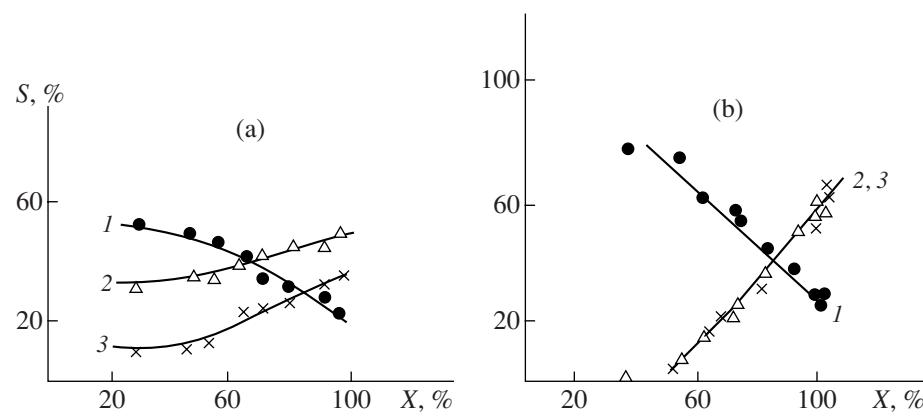


Fig. 2. (1) MT, (2) DMS, and (3) H₂S selectivities versus the DMDS conversion on (a) zeolite 2% CoHZSM-5 at $T = 250^\circ\text{C}$ and (b) zeolite 5% CoHZSM-5 at $T = 350^\circ\text{C}$.

(Table 2, Fig. 2), this process route is observed only at low DMDS conversions (<50%). At higher conversions, the MT selectivity increases and the DMS and H₂S selectivities increase, suggesting that part of the products result from the consecutive reaction scheme including DMDS decomposition to MT and the condensation of the latter yielding DMS and H₂S:



At $T = 350^\circ\text{C}$, the consecutive scheme yielding MT and equimolar amounts of DMS and H₂S is realized in the presence of all zeolites (Table 3, Fig. 2).

An important characteristic of a catalyst is the stability of its activity in time. At $T = 190^\circ\text{C}$, the activity of NaX changes with time: as the duration of the run is extended from 0.5 to 2–2.5 h, the DMDS conversion decreases by a factor of ~2. At $T = 350^\circ\text{C}$, the complete deactivation of this catalyst is observed in 45 min. The

Table 2. DMDS conversion on zeolites at $T = 250^\circ\text{C}$

Zeolite	τ , s	X, %	Yield, mol %			Selectivity, mol %		
			MT	DMS	H ₂ S	MT	DMS	H ₂ S
NaY	0.50	48	31	<1	0.4	64	<2	0.8
	0.74	66	44	1	0.6	67	2	1
	1.0	72	47	1	0.8	65	2	1
	1.2	75	48	1	1.0	64	2	1.3
HNaY	0.10	54	24	14	8	44	28	15
	0.18	72	32	24	12	44	33	17
	0.31	81	33	21	12	41	26	15
	0.65	95	41	28	25	43	27	26
HZSM-5	0.09	44	23	15	6	52	35	14
	0.18	69	26	24	16	38	35	23
	0.24	82	25	38	22	30	46	27
	0.40	94	21	44	22	22	47	28
2% CoHZSM-5	0.06	30	16	9	3	53	30	10
	0.11	47	24	17	6	51	36	12
	0.22	71	24	30	14	34	42	20
	0.32	90	25	40	25	28	44	28
5% CoHZSM-5	0.10	40	20	10	8	51	25	20
	0.14	51	27	13	10	53	26	22
	0.22	66	27	24	14	41	37	22
	0.97	96	25	46	25	26	48	26

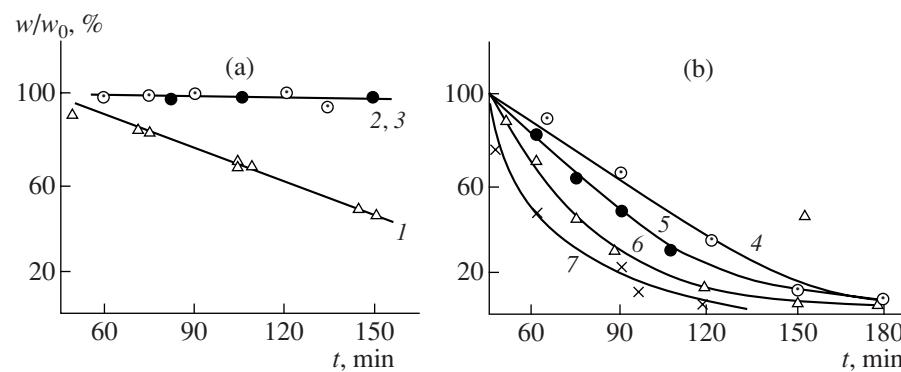


Fig. 3. Relative activity of zeolites (w/w_0) at $T = (a)$ 190 and (b) 350°C as a function of the time on stream: (1) NaX, (2, 4) HNaY, (3, 7) HZSM-5, (5) 5% CoHZSM-5, and (6) 2% CoHZSM-5.

activity of the hydrogen forms of the zeolites at $T = 190^\circ\text{C}$ does not change over 2.5 h. At 350°C , the initial activity of these catalysts decreases by a factor of 2 in 45–60 min. The introduction of cobalt makes the catalysts more stable. For example, the activity of the 2% CoHZSM-5 and 5% CoHZSM-5 catalysts at $T = 350^\circ\text{C}$ begins to decrease after 80 and 98 min, respectively. Zeolite HNaY is somewhat more stable (Fig. 3). It is likely that the deactivation of the catalysts is due to the blocking of their surface by the resulting polymers, such as $(\text{CH}_2\text{S})_n$ [5], sulfur, or other deep DMDS decomposition products, as well as by DMS decomposition products, whose yield is known to increase with increasing temperature [6].

Dialkyl disulfide conversion into alkanethiols is a heterolytic process occurring under the action both protonic sites and L-sites, which are involved in the formation of DMDS complexes [2]. The interaction of dialkyl disulfides with protonic acids; Al, B, Ga, and Sn halides; group VIII metal complexes; and solid catalysts yields a donor–acceptor bond between one sulfur atom of the disulfide and the acceptor site [1]. Even at a low temperature, the formation of a complex with a solid catalyst breaks the weak S–S bond in the disulfide and yields alkanethio groups on the surface. In the case of DMDS, this process yields methanethio groups (CH_3S). According to adsorption data [7–11], these groups undergo various conversions at elevated temperatures. For example, basic sites can abstract a proton

Table 3. DMDS conversion on zeolites at $T = 350^\circ\text{C}$

Zeolite	τ , s	X, %	Yield, mol %			Selectivity, mol %		
			MT	DMS	H_2S	MT	DMS	H_2S
NaX	0.02	28	21	0.9	1.6	75	4	5
	0.07	64	46	3.7	1.3	72	6	4
	0.10	70	50	4.2	4.2	71	6	6
	0.26	88	58	20	8	66	23	9
HZSM-5	0.05	54	53	0.3	0.5	98	0.5	1
	0.08	71	50	3	16	70	4	22
	0.10	80	46	5	26	58	6	32
	0.15	91	39	13	38	43	14	42
2% CoHZSM-5	0.07	26	21	2	2	81	8	8
	0.18	63	26	18	16	41	29	25
	0.31	80	30	22	22	38	28	28
	0.35	90	27	30	29	30	33	32
5% CoHZSM-5	0.02	35	28	2	2.5	80	6	7
	0.04	55	42	4.5	5	76	8	9
	0.05	70	42	14	9	60	20	13
	0.06	92	36	30	27	39	33	29

from the methanethio fragment to form an OH group and a CH_2S group. Acceptor sites can cleave the C–S bond to yield sulfur atoms and CH_3 fragments on the surface. The interaction between hydrogen and sulfur yields H_2S , and the interaction between hydrogen and CH_3S produces MT. The regeneration of protonic sites on the surface can partly be due to the deep cracking of the organosulfur compounds, but, more likely, this process is due to the dissociative chemisorption of H_2S (which results from heterolytic DMDS decomposition) and MT condensation. Dimethyl sulfide can result from the condensation of two CH_3S groups, which is accompanied by the release of sulfur, and from the interaction of CH_3S and CH_3 groups. If the surface has both protonic sites and pair sites (basic site + strong L-site pairs), DMS and H_2S can result from MT condensation, which proceeds via the methoxylation of the surface with methanethiol and the interaction of the resulting CH_3O groups with MT (either gaseous or activated on basic sites) [12, 13]. The reaction of CH_3 fragments with protons gives methane. DMDS decomposition can yield thioformaldehyde, which can partially polymerize into $(\text{CH}_2\text{S})_n$ [5]. What reactions actually take place will depend on the type, strength, and concentration of acid sites and on the process temperature. When discussing the regularities that we observed in DMDS

conversion on the zeolites, it is necessary to take into account the acid–base properties of the zeolite surface.

All zeolites have basic sites of moderate strength ($PA^b = 800\text{--}900 \text{ kJ/mol}$), but their surface acidities are very different.

The similar zeolites NaY and NaX have weak L-sites (Na^+) with $Q_{\text{CO}} = 20 \text{ kJ/mol}$, and the concentration of these sites is $C = 2400\text{--}2850 \mu\text{mol/g}$. Protonic sites are initially absent. However, after the treatment of the zeolite with hydrogen sulfide at an elevated temperature, a low concentration of protonic sites ($C = 12\text{--}14 \mu\text{mol/g}$) with $PA^a < 1300 \text{ kJ/mol}$ appears on the surface owing to hydrogen sulfide decomposition [14, 15]. The interaction of DMDS with the acid sites of zeolites NaX and NaY at $T = 190^\circ\text{C}$ yields CH_3S fragments on the surface, which then react with a proton to turn into MT. The formation of H_2S , which is necessary for proton regeneration, is hampered because of the absence of strong acceptor sites on the surface. This leads to a low rate of DMDS conversion into MT. The reaction products contain a small amount of DMS because, owing to the low acidity of the surface, MT condensation into DMS and CH_3S decomposition to CH_3 structures are hampered. Zeolite NaX is superior to NaY in overall activity. However, the selectivities of these catalysts are similar, suggesting that the DMDS

Table 4. DMDS conversion rates and MT and DMS selectivities at various temperatures

Catalyst	$w, \text{mmol}/(\text{h (gCat)})$ ($X = 60\%$)	Selectivity, % ($X = 60\%$)		Selectivity, % ($X = 95\%$)	
		MT	DMS	MT	DMS
$T = 190^\circ\text{C}$					
NaY	1.7	67	<2	46	<2
NaX	2.2	70	<2	60	<2
HNaY	3.0	48	27	33	22
HZSM-5	6.1	23	54	16	50
2% CoHZSM-5	6.0	30	50	23	50
5% CoHZSM-5	5.9	28	42	24	43
$T = 250^\circ\text{C}$					
NaY	4	65	<1	–	–
HNaY	8	44	28	43	27
HZSM-5	20	43	40	22	48
2% CoHZSM-5	16	42	36	24	48
5% CoHZSM-5	12	49	30	30	48
$T = 350^\circ\text{C}$					
NaX	31	74	7	60	5
HNaY	30	38	27	–	–
HZSM-5	51	87	6	38	26
2% CoHZSM-5	20	52	28	26	35
5% CoHZSM-5	48	63	15	40	32

conversion routes on these catalysts may be identical. Raising the reaction temperature to 350°C facilitates the activation of the substrate and the dissociative chemisorption of the resulting H₂S, thus increasing the DMDS conversion rate. As this takes place, the DMS selectivity somewhat increases but remains low. It is possible that, on the sodium zeolites at $T = 350^\circ\text{C}$, DMS results from MT condensation. This is suggested by the fact that, as the DMDS conversion increases, the MT selectivity decreases and the DMS and H₂S selectivities increase (Table 3). However, MT condensation proceeds slowly because of the absence of strong L-sites.

As compared to the sodium zeolites, zeolite HNaY is much more acidic (the strength of its protonic sites is $PA^a \leq 1200 \text{ kJ/mol}$, and their concentration is $C = 800 \mu\text{mol/g}$) and contains L-sites. Specifically, it contains a large number ($C = 700 \mu\text{mol/g}$) of weak L-sites (Na^+ , $Q_{\text{CO}} \sim 20 \text{ kJ/mol}$) and much smaller numbers of strong L-sites (Al^{3+} , $Q_{\text{CO}} = 45\text{--}55 \text{ kJ/mol}$, $C = 80 \mu\text{mol/g}$) and medium-strength L-sites ($Q_{\text{CO}} \sim 35 \text{ kJ/mol}$, $C = 60 \mu\text{mol/g}$).¹ Under the action of the strong acid sites of zeolite HNaY, DMDS decomposition at $T = 190\text{--}250^\circ\text{C}$ proceeds at a higher rate than DMDS decomposition over NaX or NaY. Due to the fact that the surface contains a comparatively large number of weak L-sites (from Na^+ ions), which favor the conversion of disulfides into thiols [1], the reaction has a high MT selectivity. HNaY, as distinct from the corresponding sodium zeolite, affords a high yield of DMS, which results from MT condensation on acid-base pair sites. At $T = 350^\circ\text{C}$, the DMDS conversion rates on HNaY and NaX are equal, but the MT and DMS selectivities are different (Table 4).

The original zeolite HZSM-5 contains strong protonic sites ($PA^a = 1170\text{--}1180 \text{ kJ/mol}$, $C = 165 \mu\text{mol/g}$) and weaker protonic sites associated with SiOH ($PA^a = 1390 \text{ kJ/mol}$, $C = 40 \mu\text{mol/g}$) and with AlOH ($PA^a = 1420 \text{ kJ/mol}$, $C = 50 \mu\text{mol/g}$). There are also strong L-sites associated with Al^{3+} ($Q_{\text{CO}} = 37.5\text{--}53.5 \text{ kJ/mol}$, $C = 54 \mu\text{mol/g}$) and medium-strength L-sites ($Q_{\text{CO}} = 32.5 \text{ kJ/mol}$, $C = 37 \mu\text{mol/g}$) [3]. Under the action of the acid sites of HZSM-5, DMDS decomposition at $T = 190^\circ\text{C}$ proceeds at a higher rate than in the case of HNaY and is highly DMS-selective. The MT selectivity is lower, possibly because the CH_3S groups undergo deeper conversion on the strong acid sites of HZSM-5 than on weak acid sites.

The introduction of 2 or 5 wt % Co into HZSM-5 causes a decrease in the surface acidity: the concentration of strong protonic sites decreases by a factor of 1.6–1.7; the concentration of weak protonic sites, by a factor of 3.0 and 3.7 for 2 and 5 wt % Co, respectively. The L-sites associated with Al^{3+} disappear entirely. Nevertheless, DMDS conversion on the cobalt-containing zeolites proceeds at a high rate and with a high

selectivity. DMDS can be activated both by the strong protonic sites remaining on the surface and by Co^{2+} ions. It was found by IR spectroscopic examination of molecular hydrogen adsorbed on Co-containing high-silica zeolites [16] that the Co^{2+} ions are Lewis acid sites. In the presence of cobalt catalysts supported on materials having no protonic sites (e.g., silica and carbon) or of alumina, which contains weak protonic sites and strong L-sites, DMDS decomposition at $T < 200^\circ\text{C}$ in hydrogen results mainly in MT: the MT selectivity of the reaction at $X \sim 90\%$ is close to 100%, while the DMS percentage in the products is very small [17]. The enhanced formation of DMS in the presence of the Co-containing zeolite catalysts is due to their surface having strong protonic sites.

Thus, the above data suggest that DMDS conversion into MT is favored by zeolites whose surface has weak L-sites and DMS formation requires strong acid sites. The highest DMDS conversion rate is observed at $T = 350^\circ\text{C}$, but the catalysts suffer from rapid deactivation at this temperature; therefore, it is advisable to conduct the synthesis of MT and DMS at a lower temperature. Under these conditions, the highest MT selectivity ($S = 60\text{--}70\%$) at high DMDS conversions is shown by the sodium forms of the zeolites; however, they are deactivated at low temperatures. In the presence of more stable hydrogen-containing zeolites, such as 5% CoHZSM-5, the MT selectivity at 350°C is 63%, which is much lower than the MT selectivity achieved on a nonzeolite catalyst [2, 16]. At the same time, CoHZSM-5 is superior to these catalysts in DMS selectivity ($S \approx 50\%$), so it is of interest as a catalyst for producing DMS, a practically important compound from the rather readily available compound DMDS.

REFERENCES

1. Mashkina, A.V., *Kataliz reaktsii organicheskikh soedinenii sery* (Catalysis of Reactions of Organosulfur Compounds), Novosibirsk: Sib. Otd. Ross. Akad. Nauk, 2005.
2. Mashkina, A.V., Yakovleva, V.N., Sakhaltueva, L.G., and Khairulina, L.N., *Neftekhimiya*, 2001, vol. 41, no. 1, p. 54 [*Pet. Chem. (Engl. Transl.)*, vol. 41, no. 1, p. 50].
3. Krivoruchko, O.P., Anufrienko, V.F., Paukshtis, E.A., Larina, T.V., Burgina, E.B., Yashnik, S.A., Ismagilov, Z.R., and Parmon, V.N., *Dokl. Akad. Nauk*, 2004, vol. 398, no. 3, p. 356 [*Dokl. Phys. Chem. (Engl. Transl.)*, vol. 398, no. 3, p. 226].
4. Paukshtis, E.A., *Infrakrasnaya spektroskopiya v geterogennom kislotno-osnovnom katalize* (Infrared Spectroscopy in Heterogeneous Acid–Base Catalysis), Novosibirsk: Nauka, 1992.
5. Coope, J.A.R. and Bryce, W.A., *Can. J. Chem.*, 1954, vol. 32, no. 8, p. 768.
6. Koshelev, S.N., Mashkina, A.V., and Paukshtis, E.A., *React. Kinet. Catal. Lett.*, 1991, vol. 44, no. 2, p. 367.
7. Batteas, J.D., Rufael, T.S., and Friend, C.M., *Langmuir*, 1999, vol. 15, no. 7, p. 2391.

¹ Estimated from the Na content of HNaY.

8. Carley, A.F., Davies, P.R., Joms, R.V., and Harikumar, K.R., *Top. Catal.*, 2002, vol. 22, nos. 3–4, p. 161.
9. Liu, G., Rodriguez, J.R., Chang, Z., Hrbek, J., and Gonzalez, L.J., *J. Phys. Chem. B*, 2002, vol. 106, no. 38, p. 9883.
10. Kang, D.H. and Friend, C.H., *Langmuir*, 2004, vol. 20, no. 26, p. 11443.
11. Halevi, B. and Vohs, J.M., *J. Phys. Chem. B*, 2005, vol. 109, no. 50, p. 23976.
12. Mashkina, A.V., *Kinet. Katal.*, 1991, vol. 32, no. 4, p. 885.
13. Mashkina, A.V., Grunval'd, V.R., Borodin, B.P., Nas- teka, V.I., Yakovleva, V.N., and Khairulina, L.N., *Kinet. Katal.*, 1991, vol. 32, no. 4, p. 866.
14. Mastikhin, V.M., Mudrakovskiy, I.L., Nosov, A.V., and Mashkina, A.V., *J. Chem. Soc., Farad. Trans. 1*, 1989, vol. 85, no. 9, p. 2819.
15. Mashkina, A.V., Desyatov, I.V., and Mashkin, V.Yu., *Kinet. Katal.*, 1996, vol. 37, no. 1, p. 104 [*Kinet. Catal.* (Engl. Transl.), vol. 37, no. 1, p. 98].
16. Kazansky, V.B., Serykh, A.I., and Bell, A.T., *Catal. Lett.*, 2002, vol. 83, nos. 3–4, p. 191.
17. Mashkina, A.V. and Khairulina, L.N., *Kinet. Katal.*, 2005, vol. 46, no. 6, p. 921 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 6, p. 873].