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Activity of Zeolites in Dimethyl Sulfide Synthesis

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Abstract—Dimethyl disulfide conversion into dimethyl sulfide over various zeolites in an inert medium at atmospheric pressure and $T = 190–330°C$ is reported. A significant activity in dimethyl sulfide formation is shown by the decationized zeolites HNaY and HZSM-5, whose surface has strong protonic and nonprotonic acid sites. Cobalt-containing faujasite is more active than HNaY, and the activity of CoHZSM-5 is comparable with the activity of its decationized counterpart.

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Dimethyl sulfide (DMS) is the starting chemical in the synthesis of dimethyl sulfoxide, which is used as a medicine, a solvent in polysulfone production and acrylonitrile polymerization, a complexing agent in the extraction of noble and rare metals, and an extractant of aromatic hydrocarbons from petroleum products. DMS to be converted into dimethyl sulfoxide is synthesized by reacting methanol with hydrogen sulfide or by methyl mercaptan (MM) condensation [1]. A readily available and cheap DMS precursor is dimethyl disulfide (DMDS), which is obtained in large amounts in the removal of mercaptans from gases [2]. It was established earlier that DMDS decomposition in an inert medium at atmospheric pressure and $T = 190–350°C$ on zeolites HNaY and HZSM-5 yields DMS along with other products [3]. However, the activity and selectivity of zeolite catalysts was not studied as a function of their composition.

Here, we report the activity of a variety of unsubstituted and cobalt-containing zeolites in DMDS conversion into DMS in an inert medium.

EXPERIMENTAL

The catalysts were zeolites NaX (Si/Al = 1.5), NaY (Si/Al = 2.25), HNaY, and HZSM-5 (Si/Al = 17 and 35) without a binder and zeolite HZSM-5 (Si/Al = 35) with a binder (20% Al_2O_3), all calcined in flowing dry air at 300–400°C. Cobalt (2–5 wt %) was introduced into zeolites by impregnating them with an aqueous solution of cobalt acetate. The impregnated samples were dried in air at room temperature (12 h) and at $T = 110°C$ (5 h) and were then calcined in flowing dry air at $T = 400°C$ (5 h). The acid–base properties of the zeolites were determined earlier by IR spectroscopy of adsorbed probe molecules [1, 4, 5].

All chemicals were reagent grade or pure grade.

Catalytic tests were performed using an earlier reported procedure [3]. Reaction products were identified by the GC/MS method. Quantitative analyses were made on an LKhM-8MD chromatograph with a thermal-conductivity detector (2 m × 3 mm column packed with Porapak Q + Porapak R (1 : 1), helium as the carrier gas).

The residence time (τ, s) was taken 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. The results of the analyses were used to calculate the DMDS conversion (X, %), product yields (Y, mol %), DMS selectivity (S, %) as Y/X, and the total DMDS conversion rate (w, mmol/h) and DMS formation rate at $X = 70\%$ per gram of catalyst (w_1, mmol/h) or per gram of cobalt (w_2, mmol/h).

RESULTS AND DISCUSSION

DMDS conversion was studied in helium at atmospheric pressure and $T = 190–350°C$ over NaX, NaY, HNaY, HZSM-5, and cobalt-containing zeolites. Each catalyst was tested at a fixed temperature and different residence times. From experimental data, we derived the DMDS conversion and the yields of sulfur-containing products, namely, DMS, MM, hydrogen sulfide, and carbon disulfide. Small amounts (1–3 mol %) of methane were also observed. In the presence of the sodium form of zeolites—NaX and NaY—the DMS yield was 1.1 mol % or below ($T = 200°C$, $\tau = 0.1$ or 2.0 s, $X = 70–76\%$). The main product in this case was MM. Hydrogen sulfide and carbon disulfide were also detected among the sulfur-containing products. At 350°C, the reaction needed a much shorter residence time of 0.15 s, but the DMS yield did not exceed 4.2 mol % at $X = 62–70\%$.

Table 1. DMDS conversion and product yield data for decationized and cobalt-containing zeolites Y and ZSM-5

Zeolite	Reaction temperature, °C	τ, s	*X*, %	Yield, %			
				DMS	MM	H_2S	CS_2
HNaY	200	1.0	74	17	35	11	7
	250	0.2	75	20	32	12	9
HZSM-5	200	0.5	60	29	14	10	6
	260	0.2	75	27	23	15	8
	350	0.14	90	33	34	18	3
5% Co/HZSM-5	200	0.37	66	34	12	11	5
	250	0.22	70	32	18	10	9
	350	0.08	77	37	27	9	3
5% Co/HNaY	200	0.25	61	18	36	1	5
	250	0.2	78	26	29	11	12
	340	0.09	82	36	24	8	10

A much higher DMS yield was attained with the decationized zeolites HNaY and HZSM-5 and with cobalt-containing zeolites (Table 1).

The activity of the zeolites in DMDS conversion at $T = 200–330°C$ decreases in the following order:

$$\text{HZSM-5} > \text{HNaY} \gg \text{NaX} > \text{NaY}.$$

As for the DMS formation rate, the decationized zeolites are 1–2 orders of magnitude more efficient than NaX or NaY.

The DMS selectivity of the sodium zeolites at $X =$ 70% does not exceed 5.5%, while that of the decationized zeolites is 25–48% (Table 2). The rate of DMS formation over HZSM-5 (Si/Al = 35) with alumina binder is 2.3 times higher than is observed for the same zeolite without a binder. This is likely due to alumina being involved in the process since this compound is known to be very active in DMDS conversion [3]. Reducing the Si/Al ratio in zeolite HZSM-5 from 35 to 17 raises the DMS formation rate at 250°C by a factor of 1.8.

These findings can be explained in terms of the difference between the acid properties of the catalysts. All of the zeolites contain medium-strength basic sites ($PA^b = 800–900$ kJ/mol) and differ in the strength of acid sites. Zeolites NaX and NaY have low acidity: they do not contain strong protonic sites (PS's) with $PA^a < 1300$ kJ/mol and have only weak Lewis sites (L-sites) associated with Na^+ cations with $Q_{CO} \sim$ 20 kJ/mol. The decationized zeolites are much more acidic: they contain both strong PS's with $PA^a <$ 1200 kJ/mol and strong L-sites associated with Al^{3+} cations ($Q_{CO} = 32–54$ kJ/mol)[1] [1, 4, 5]. Earlier [3], we deduced from the results of DMDS decomposition on various oxide catalysts that, for DMS formation from DMDS, it is necessary that the surface have both medium-strength basic sites and strong protonic and nonprotonic acid sites. When DMDS is in contact with a catalyst, the sulfur atom of one CH_3S group binds to a PS; the sulfur atom of the other methanethio group, to an L-site; and the carbon atom of a CH_3 group, to a basic site. The decomposition of the resulting surface complex yields sulfur and DMS. A possible cause of the low catalytic activity of zeolites NaX and NaY in DMS formation is that they contain only weak L-sites.

The fact that NaY is less active than NaX is likely due to NaY having a lower concentration of delocalized Na^+ cations in NaY [6], which are involved in DMDS activation. It is also very significant that the sodium zeolites have no strong PS's. It is possible, however, that these sites appear under the action of the reaction medium, including H_2S resulting from DMDS decomposition. The interaction between H_2S and a zeolite generates strong PS's on the surface [1], and this process is enhanced by increasing temperature. It was established by IR spectroscopy of adsorbed pyridine that treatment of zeolite NaX with hydrogen sulfide at an elevated temperature produces strong PS's on its surface at a concentration of 12–24 μmol/g [7, 8]. This may increase *w* and *S*. We indeed found that passing a 15% H_2S + 85% H_2 mixture through zeolite NaX at $T = 400°C$ for 1 h raises the w_1 value at $T = 200$ and 250°C by a factor of 1.7–4. However, because the catalyst has no strong L-sites, the w_1 value remains very low.

The increased activity of the decationized versus sodium zeolites in DMS formation is likely due to the fact that the former have a higher concentration of strong protonic and nonprotonic acid sites on their surface. For example, HNaY contains PS's with $PA^a \leq$ 1200 kJ/mol ($C = 0.2$ μmol/m^2) and L-sites (Al^{3+})

[1] Hereafter, *C* is the site concentration (μmol/m^2) and PA^b, PA^a, and Q_{CO} are the powers of basic sites, PS's, and L-sites, respectively (kJ/mol).

Table 2. Activity and selectivity of zeolites in DMDS conversion

Zeolite	Reaction temperature, °C	w, mmol/(h (g Cat))	w_1, mmol/(h (g Cat))	S, %
NaY	200	1.7	0.005	0.3
	240	3.2	0.032	1.0
	300	6.9	0.10	1.6
	330	12.6	0.35	2.8
NaX	200	2.0	0.02	1.1
	200*	2.8	0.08	3
	250	3.6	0.22	6
	250*	4.6	0.37	8
	300	12.6	0.5	4
	330	25.0	1.38	5.5
	350	36.4	2.2	6.0
HNaY	200	4.0	1.0	25
	240	11.2	3.2	29
	300	25.1	9.0	36
	330	31.6	12.0	38
HZSM-5 (Si/Al = 17)	200	6.3	2.9	46
	250	14.1	6.4	40
	300	31.6	12.9	41
	330	56.2	21.9	39
HZSM-5 (Si/Al = 35)	190	4.8	2.3	48
	250	8.0	3.6	45
	250**	19.1	8.4	44

* Catalyst was treated with an $H_2S + H_2$ mixture at $T = 400$°C before the test.
** Zeolite with a binder.

with $Q_{CO} = 32–35$ kJ/mol ($C = 0.16$ μmol/m^2). Zeolite HZSM-5 with Si/Al = 17 contains PS's with PA[a] = 1700–1800 kJ/mol ($C = 0.33$ μmol/m^2) and L-sites (Al^{3+}) with $Q_{CO} = 33–54$ kJ/mol ($C = 0.19$ μmol/m^2). Owing to its higher surface acidity, HZSM-5 is somewhat superior to HNaY in DMS formation activity. Raising the Si/Al ratio in HZSM-5 from 17 to 35 reduces the concentration of strong acid sites. The concentrations of PS's and nonprotonic sites decrease to 0.16 μmol/m^2 and 0.04 μmol/m^2, becoming lower than those in the Si/Al = 17 zeolite by a factor of 2.1 and 4.8, respectively. It is likely this fact that is responsible for the lower DMS formation activity of the Si/Al = 35 zeolite.

The initial activity of the sodium zeolites decreases during the reaction. At $T = 200$°C, the initial DMDS conversion and S decrease by a factor of ~3 in 3 h; at $T = 340$°C, these parameters decrease in 3 h by a factor of 35 and 12, respectively. The low performance stability of these catalysts is likely due the long residence times, which are favorable for the formation of substances blocking the active sites of the catalyst. With the decationized zeolites at $T = 200–250$°C, the initial conversion and DMS selectivity do not decrease at least during 3-h-long continuous operation. At higher temperatures, the initial catalytic activity decreases in the course of the reaction, and deactivation increases progressively as the temperature is raised. For example, at $T = 340$°C the initial DMDS conversion on HNaY and HZSM-5 (Si/Al = 17) decreases by a factor of 5–30 and S by a factor of 20–30 in 3 h. The low performance e stability of these catalysts is likely explained by the high concentration of strong PS's, which are favorable for the formation of polymers like $(CH_2S)_n$ at elevated temperatures [9]. These polymers accumulate in the pores of the zeolites, thus reducing their activity.

The introduction of cobalt into the decationized zeolites changes the DMS formation rate relative to that observed with the initial zeolite (compare the data listed in Tables 2 and 3). The CoHNaY catalyst is 2.3–3.6 times more active than HNaY, and 2%CoHZSM-5 (Si/Al = 17) is ~2 times more active than HZSM-5. The catalysts richer in cobalt are similar in activity to pentasil or are inferior to it.

The difference between the activities of the cobalt-containing and cobalt-free zeolites with Si/Al = 17 can be explained as follows. The Co^{2+} cations intro-

Table 3. Activity and selectivity of cobalt-containing zeolites in DMDS conversion

Catalyst	Reaction temperature, °C	Catalyst pretreatment* temperature, °C	w, mmol/(h (g Cat))	w_1, mmol/(h (g Cat))	S, %
5% CoHNaY	200	200	12.0	3.6	30
	250	–	22.7	7.3	32
	250	200	25.3	8.6	34
	250	400	42.0	13.4	32
	340	400	58.1	19.1	33
2% CoHZSM-5 Si/Al = 17	190	–	6.1	2.8	46
	190	190	12.3	5.9	48
2.5% CoHZSM-5 Si/Al = 17	250	200	14.0	6.4	46
	250	400	24.2	10.9	45
	300	400	35.5	13.5	38
5% CoHZSM-5 Si/Al = 17	190	–	0.5	0.2	38
	250	200	6.3	2.4	38
	250	400	12.7	5.3	42
	300	400	27.8	11.1	40
5% CoHZSM-5 Si/Al = 35	250	–	3.6	1.1	30
	250	200	6.4	2.0	32
	250	400	7.2	2.2	31
5% CoHZSM-5 Si/Al = 35 with a binder	250	400	13.3	5.6	42

* 15% H_2S + 85% H_2.

duced into the channels of zeolite HZSM-5 bind to extraframework Al^{3+}; as a result, the zeolites containing 2 or 5% Co have a lower acidity: the concentration of strong PS's decreases by a factor of 1.6–1.7 and the L-sites due to Al^{3+} disappear completely, but strong L-sites with Q_{CO} = 37.7–59.5 kJ/mol due to Co^{2+} appear at the same time [5, 10, 11]. This raises the DMDS decomposition rate and DMS selectivity. The difference between the activities of the Si/Al = 35 and Si/Al = 17 HZSM-5 catalysts is likely due to the fact that the concentration of Al^{3+} L-sites decreases as the Si/Al ratio is increased. Accordingly, the introduction of cobalt into the Si/Al = 35 zeolite generates a smaller number of strong Co^{2+} L-sites.

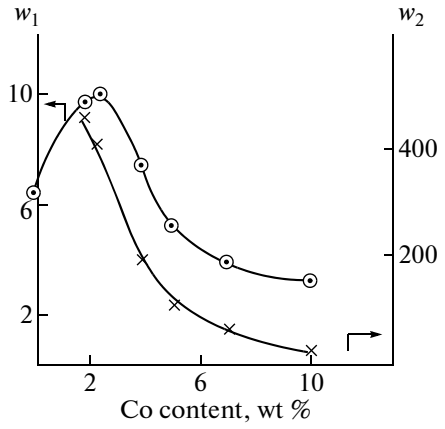

Fig. 1. w_1 and w_2 as a function of the cobalt content of zeolite HZSM-5 (Si/Al = 17).

An important parameter of the cobalt-containing zeolites is the temperature of their activation with hydrogen sulfide: the rate of DMS formation on the catalysts treated with an $H_2S + H_2$ mixture at T = 200–400°C is ~2 times higher than that observed for the nonsulfided catalysts. As compared to the decationized zeolites, the cobalt-containing zeolites show 2–3 times more stable catalytic activity during the reaction. This is likely due to the lower PS concentration in the latter.

Variation of the cobalt concentration in HZSM-5 demonstrated that the catalysts in which HZSM-5 contains up to 2.5 wt % Co are 1.5–2 times more active at T = 250°C than the decationized zeolite; however, at higher Co contents of 3–10 wt %, w_1 and w_2 decrease (Fig. 1). In the high-silica zeolite containing up to 3 wt % Co, the metal is almost entirely located in zeolite channels as isolated Co^{2+} ions or one-dimensional CoO or $CoAl_2O_3$ nanoparticles. Two- and three-dimensional particles appear at higher Co contents. In addition, Co^0 nanoparticles form in a reductive medium [10]. Treating CoHZSM-5 with an $H_2S + H_2$ mixture at an elevated temperature gener-

Table 4. Effects of the residence time and initial DMDS concentration on the DMDS conversion and product selectivities for the 2.5%CoHZSM-5 (Si/Al = 17) catalyst at 250°C

τ, s	$[DMDS]_0$, vol %	*X*, %	*S*, %			
			DMS	MM	H_2S	CS_2
0.18	1.2	65	42	25	16	14
0.15	1.6	68	44	27	14	14
0.16	1.9	72	47	26	16	11
0.17	3.1	68	45	24	14	16
0.10	1.6	48	37	41	11	10
0.13	1.7	61	40	35	12	11
0.16	1.6	70	44	29	14	12
0.21	1.8	84	46	20	17	15
0.36	1.5	98	50	16	19	14

ates fine CoS particles containing coordinatively unsaturated Co cations, which are acceptor sites.

The effect of the reaction conditions on the outcomes of the process were studied on the 2.5%CoHZSM-5 catalyst. At a constant temperature and residence time, variation of the initial DMDS concentration has no effect on the DMDS conversion (Table 4). The product selectivities of the reaction are also independent of the initial DMDS concentration. As the DMDS conversion, which depends on the residence time, is increased, the MM selectivity decreases and the DMS selectivity increases to reach its thermodynamic limit at complete disulfide conversion. This suggests that DMS forms via a consecutive route: DMDS decomposes to MM, which then condenses into DMS, releasing hydrogen sulfide. Similar trends were observed earlier for DMDS conversion into DMS under the action of other catalysts [3]. As the reaction temperature is raised, the DMS formation rate increases and the DMS selectivity falls (Fig. 2).

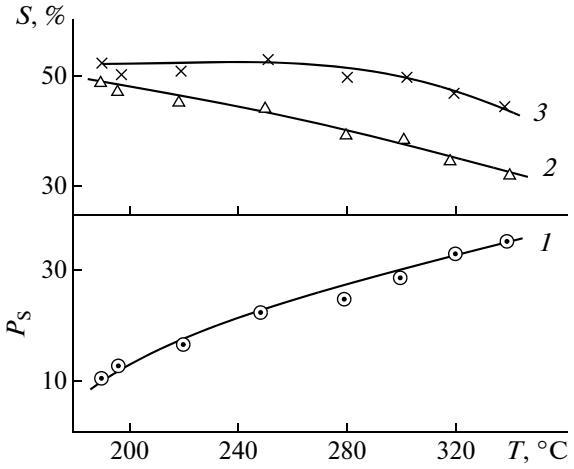

Fig. 2. (*1*) DMS formation rate (P_S) and (*2*, *3*) DMS selectivity at *X* = (*2*) 70 and (*3*) 98% as a function of temperature for the 2.5%CoHZSM-5 (Si/Al = 17) catalyst. [DMDS] = 3.2 vol %.

Thus, the decationized and cobalt-containing zeolites are active catalysts for DMDS conversion into DMS. The most efficient catalyst is 2.5%CoHZSM-5 (Si/Al = 17).

REFERENCES

1. Mashkina, A.V., *Kataliz reaktsii organicheskikh soedinenii sery* (Catalysis of Reactions of Organosulfur Compounds), Novosibirsk: Sib. Otd. Ross. Akad. Nauk, 2005.

2. Mazgarov, A.M. and Vil'danov, A.F., *Neftekhimiya*, 1999, vol. 39, no. 5, p. 371 [*Pet. Chem.* (Engl. Transl.), vol. 39, no. 5, p. 336].

3. Mashkina, A.V. and Khairulina, L.N., *Kinet. Katal.*, 2009, vol. 50, no. 3, p. 434 [*Kinet. Catal.* (Engl. Transl.), vol. 50, no. 3, p. 414].

4. Paukshtis, E.A., *Infrakrasnaya spektroskopiya v geterogennom kislotno-osnovnom katalize* (Infrared Spectroscopy in Heterogeneous Acid–Base Catalysis), Novosibirsk: Nauka, 1992.

5. 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*, 2001, vol. 398, no. 3, p. 356 [*Dokl. Phys. Chem.* (Engl. Transl.), vol. 398, no. 3, p. 226].

6. Karge, H.G., Ziolek, M., and Laniecke, M., *Zeolites*, 1987, vol. 7, no. 3, p. 197.

7. Masthihin, V.M., Mudrakovsky, I.L., Nosov, A.V., and Mashkina, A.V., *J. Chem. Soc., Faraday Trans. 1*, 1989, vol. 85, no. 9, p. 2819.

8. 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].

9. *Organic Chemistry of Sulfur*, Oae, S., Ed., New York: Plenum, 1977.

10. Krivoruchko, O.P., Gavrilov, V.Yu., Molina, I.Yu., and Larina, T.V., *Kinet. Katal.*, 2008, vol. 49, no. 2, p. 300 [*Kinet. Catal.* (Engl. Transl.), vol. 49, no. 2, p. 285].

11. Kazansky, V.B., Serykh, A.J., and Bell, A.T., *Catal. Lett.*, 2002, vol. 83, nos. 3–4, p. 191.