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## Selective Catalytic Dimethyl Disulphide Conversion into Dimethyl Sulphide

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### Abstract

Reaction between dimethyl disulphide and methanol at 250–400 °C was studied under the influence of catalysts having strong acidic centers on the surface thereof such as amorphous aluminosilicate, zeolites HNaY and HZSM-5, and aluminochromium catalysts. In the presence of these catalysts, the major product of the reaction is presented by dimethyl sulphide that is formed via the interaction of one disulphide molecule with two molecules of methanol. Among aluminosilicate catalysts, the greatest activity is exhibited by pure zeolite HZSM-5; in the case of modifying the zeolite by cobalt or chromium oxides the catalytic performance thereof is not improved. Catalysts containing chromium oxide on aluminum oxide appeared to be efficient in the formation of dimethyl sulphide, whereas the activity thereof increases with increasing the content of chromium in the catalyst. The rate of the reaction in the presence of chromium catalysts increases in direct proportion with increasing the concentrations of methanol and dimethyl disulphide, as well as with increasing the temperature. The apparent activation energy is equal to  $(67 \pm 2)$  kJ/mol. The reaction between methanol and dimethyl disulphide in the presence of aluminochromium catalysts occurs selectively and with a high productivity with respect to DMS.

**Key words:** catalysts, dimethyl disulphide, dimethyl sulphide, methanol

### INTRODUCTION

In the course of purifying gaseous condensates, crude oil and petroleum products from mercaptan, there is dimethyl disulphide (DMDS) formation in large amounts observed. A promising direction the processing thereof consists in obtaining dimethyl sulphide (DMS), an important sulphur-containing compound. Dimethyl sulphide is used as the extracting agent and gas odorant; as a starting material for the synthesis of a pharmaceutical preparation dimethylsulphoxide, as a solvent in the manufacture of polysulphones and in the course of acrylonitrile polymerization; as a complexation agent for the extraction of rare and noble metals, as well as for extracting aromatic hydrocarbons from petroleum.

Dimethyl sulphide is worthwhile to obtain with the use of a heterogeneous catalytic method. As demonstrated by the authors of [1–4], within the range of 150–350 °C in an inert medium there occurs breaking the S–S and the C–S bonds in DMDS under the action of solid oxide and sulphide catalysts with the formation of  $\text{CH}_3$  and  $\text{CH}_3\text{S}$  fragments, whose interaction leads to the formation of DMS. Besides, there proceed methanethiol (MT), hydrogen sulphide, carbon disulphide, methane, ethylene, resins formation reactions. As the result, the yield DMS is below 60 %, moreover, there is a problem of recycling large-scale volumes of environmentally hazardous wastes. Earlier, we revealed [5, 6] that in the course of using aluminum oxide as catalyst the yield of DMS could be substantially increased in the

case when the DMDS conversion reaction is conducted in the presence of methanol.

The fact is that the decomposition of methanol on the surface more readily results in the formation of  $\text{CH}_3$  groups (those are necessary for DMS to obtain) than the decomposition of DMDS. The studies on the reaction in the presence of catalysts with different acid-base properties have demonstrated [2, 7] that the conversion of DMDS represents a heterolytic process. In order to exhibit a high activity and selectivity, the catalyst surface should contain both strong Brønsted and Lewis acidic centers, and the basic centers of moderate strength. Such properties are inherent in some aluminosilicate and aluminum oxide catalysts.

In this paper, in order to develop a selective process of DMS synthesis we studied the features of the reaction between DMDS and methanol in the presence of a number of catalysts containing strong acidic centers on the surface.

## EXPERIMENTAL

For the experiments, we used chemical purity grade methanol and purity grade DMDS. As the catalyst carriers, we used ready-made samples  $\gamma\text{-Al}_2\text{O}_3$  samples ( $S_{\text{sp}} = 270 \text{ m}^2/\text{g}$ ), the amorphous aluminosilicate AlSi ( $S_{\text{sp}} = 310 \text{ m}^2/\text{g}$ ), zeolites HNaY ( $S_{\text{sp}} = 800 \text{ m}^2/\text{g}$ ) and HZSM-5 with Si/Al = 23 ( $S_{\text{sp}} = 500 \text{ m}^2/\text{g}$ ). Supported catalysts were prepared by means of impregnating the preliminary calcined carriers according to water-absorbing capacity with the use of cobalt acetate or chromic anhydride aqueous solutions. After impregnation, the samples were exposed to atmospheric air at a room temperature during 12 h, dried at  $110^\circ\text{C}$  (5 h) and then calcined in dry air for 5 h at  $T = 500\text{--}530^\circ\text{C}$ .

Catalytic experiments were conducted using a flow-through apparatus at atmospheric pressure. To saturators filled with DMDS and methanol placed in a thermostat, was supplied helium from a cylinder. After mixing, the gas with methanol and DMDS was supplied to a reactor heated up to a certain temperature packed with a catalyst (grain size 0.25–0.5 mm). Sampling was carried out for about 2 h with the time intervals of 45 min. The reaction products were an-

alyzed using a LCM-8MD chromatograph with a katharometer (a column  $2 \text{ m} \times 3 \text{ mm}$  packed with Porapak Q. Q + R (1 : 1); helium was used as the carrier gas).

As the contact time ( $\tau$ ), we took a ratio between the catalyst volume and the gas flow rate of at a room temperature and atmospheric pressure. Basing on the analysis, we calculated the DMDS conversion level ( $X$ ), and the yield of the reaction products as a ratio between the concentration of the product formed and the initial concentration of the substrate, as well as the rate of DMDS conversion ( $w$ ) at  $X = 70\%$ .

## RESULTS AND DISCUSSION

The features of the catalytic conversion of DMDS in a mixture with methanol was investigated at different temperature, reagent concentration and contact time values. The main conversion product of DMDS in the mixture with methanol for all the catalysts was presented by DMS; MT and hydrogen sulphide were formed in small amounts, as well. Increasing the contact time at a constant temperature and concentration of reactants led to increasing the conversion level of DMDS and the yield of DMS. Figure 1 presents the results concerning the DMDS conversion at  $350^\circ\text{C}$  in a mixture with methanol in the presence of

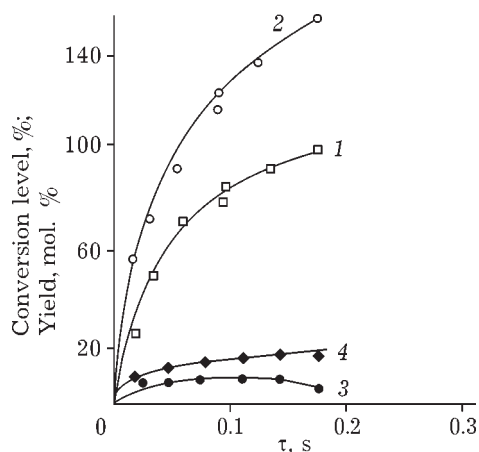


Fig. 1. Effect of contact time on the DMDS conversion level in the reaction with methanol (1) and on the yields DMS (2), MT (3),  $\text{H}_2\text{S}$  (4). Catalyst HZSM-5,  $T = 350^\circ\text{C}$ .

TABLE 1

Data concerning the concentrations of methanol was reacted with dimethyl disulphide (DMDS), and the resulting dimethyl sulphide (DMS) formed ( $X = 65-80\%$ )

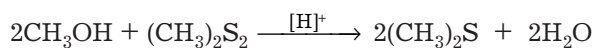
| Catalysts                               | Temperature, °C | Concentration, mmol/L |      |
|---|-----------------|-----------------------|------|
|   |                 | Methanol              | DMS  |
| HNaY                                    | 350             | 0.69                  | 0.73 |
| HZSM-5                                  | 350             | 0.60                  | 0.63 |
|   | 250             | 0.64                  | 0.65 |
| HZSM-5 + binding agent                  | 350             | 0.51                  | 0.55 |
| 2.5 % CoHZSM-5                          | 250             | 0.74                  | 0.68 |
|   | 350             | 0.71                  | 0.74 |
| 5 % CoHZSM-5                            | 250             | 0.75                  | 0.71 |
|   | 350             | 0.91                  | 0.84 |
| 10 % CoHZSM-5                           | 250             | 0.79                  | 0.82 |
| 1.5 % CrHZSM-5                          | 250             | 0.90                  | 0.94 |
|   | 350             | 0.71                  | 0.85 |
| 0.5 % Cr/Al <sub>2</sub> O <sub>3</sub> | 350             | 0.72                  | 0.80 |
| 1.5 % Cr/Al <sub>2</sub> O <sub>3</sub> | 350             | 0.84                  | 0.79 |
| 3.0 % Cr/Al <sub>2</sub> O <sub>3</sub> | 350             | 0.83                  | 0.87 |

HZSM-5 catalyst As one could see, the yield of DMS was significantly higher than the conversion level of DMDS. It is found that with increasing the methanol to DMDS molar ratio of ( $M$ ), the yield of DMS in the case of all the catalysts increased to reaches a maximum value at  $M \geq 2$ . For example, at 350 °C in the case of zeolite HZSM-5 for  $X = 70\%$  the following results were obtained:

|                   |    |     |     |     |     |     |
|-------------------|----|-----|-----|-----|-----|-----|
| $M$               | 1  | 1.5 | 1.8 | 2.1 | 2.5 | 3.0 |
| DMS yield, mol. % | 70 | 92  | 100 | 112 | 115 | 113 |

The amount of methanol reacted with DMDS, within experimental error, corresponded to the resulting concentration of DMS (Table 1).

Similar laws were obtained for the other investigated catalysts. Consequently, the following reaction takes place



The comparative analysis of catalysts with respect to the activity thereof in the reaction between methanol and DMDS was performed basing on the rates of disulphide conversion. For each catalyst, we carried out experiments under constant temperature and reactant concentration for different contact time values. According to kinetic curves, we determined the

contact time, wherewith the disulphide conversion level was equal to 70 %, calculated the reaction rate and the product yields. It was found that at a constant molar ratio between methanol and DMDS the DMDS conversion level does not depend on the initial concentration of the reagent. All the experiments were performed at the initial concentration of DMDS approximately equal to 1.4 % that of methanol being about 3.5 vol. %;  $M = 2.4-2.6$ . The results are demonstrated in Table 2.

Thus, in the presence of an amorphous aluminosilicate having a relatively weak acidity of the surface [8], the reaction of DMS formation at 350 °C proceeds at a low rate, and alongside with DMS, there is MT formation observed with a high yield. The HNaY zeolite with a high surface acidity level [3] exhibits an enhanced activity, but in the presence thereof the yield of MT is also considerable. The HZSM-5 zeolite containing strong acidic centers [3, 4], at 250 °C hardly differs from an amorphous aluminosilicate in the activity in the reaction of DMDS conversion into DMS. With increasing the temperature of the experiment (Table 3), an increase in the DMDS conversion level and in the yield of DMS are observed. The activity of zeolite HZSM-5 is reduced in the course of

TABLE 2

Effect of aluminosilicate catalysts on the reaction rate between dimethyl disulphide and methanol ( $w$ ), as well as on the yields of the reaction products ( $X = 70\%$ ,  $M = 2.4-2.6$ )

| Catalysts            | $T, ^\circ\text{C}$ | $w,$<br>mmol/(h · g <sub>cat</sub> ) | Yield, mol. %                     |                    |                  |
|----------------------|---------------------|--------------------------------------|-----------------------------------|--------------------|------------------|
|                      |                     |                                      | (CH <sub>3</sub> ) <sub>2</sub> S | CH <sub>3</sub> SH | H <sub>2</sub> S |
| AlSi                 | 350                 | 3.1                                  | 88                                | 23                 | 3                |
| HNaY                 | 350                 | 13.6                                 | 112                               | 14                 | 1                |
| HZSM-5               | 250                 | 4.1                                  | 100                               | 10                 | 8                |
|                      | 350                 | 28.0                                 | 117                               | 7                  | 5                |
| HZSM + binding agent | 250                 | 2.2                                  | 112                               | 7                  | 5                |
|                      | 350                 | 18.4                                 | 100                               | 18                 | 2                |
| 2.5 % Co/HZSM-5      | 250                 | 10.5                                 | 100                               | 20                 | 1                |
|                      | 250*                | 12.2                                 | 92                                | 22                 | 1                |
|                      | 350                 | 19.4                                 | 98                                | 15                 | 4                |
|                      | 350*                | 21.0                                 | 104                               | 14                 | 4                |
| 5 % Co/HZSM-5        | 250                 | 14.9                                 | 64                                | 36                 | 2                |
|                      | 350                 | 13.9                                 | 118                               | 8                  | 1                |
|                      | 350*                | 17.0                                 | 92                                | 20                 | 2                |
| 10 % Co/HZSM-5       | 250                 | 10.5                                 | 92                                | 23                 | 1                |
| 1.5 % Cr/HZSM-5      | 250                 | 3.8                                  | 100                               | 14                 | 2                |
|                      | 250*                | 4.5                                  | 104                               | 6                  | 10               |
|                      | 350                 | 20.9                                 | 120                               | 8                  | 1                |
|                      | 350*                | 15.5                                 | 116                               | 8                  | 2                |
| 1.5 % Cr/AlSi        | 350                 | 3.9                                  | 95                                | 21                 | 2                |

\*Prior to the experiment the catalyst was treated with a mixture of 15 % H<sub>2</sub>S + 85 % H<sub>2</sub> at  $T = 400^\circ\text{C}$  for 1 h.

the experiment, for example, at 350 °C, the DMDS conversion level and the yield of DMS during 2 h exhibited a 2.3-fold decrease. To all appearance, under the influence of strong Brønsted acidic centers there are polymeric compounds formed such as (CH<sub>2</sub> S<sub>n</sub>) [9].

For the practical purposes, it is necessary to use the zeolite in granular form, which is achieved via the introduction of an aluminum oxide binder thereto. However, we have found that after the introduction of the binder into the HZSM-5 zeolite the catalyst stability does not exhibit any increase, whereas the rate of DMS formation decreases by about 1.5 times (see Table 2).

The addition of 2.5–10 % of cobalt to the HZSM-5 zeolite causes increases the catalyst activity at 250 °C to exhibit a 2.6–3.6-fold increase. It is known [10] that, after the introduction of cobalt into the high-silica zeolite in the hydrogen form, the concentration of Brønsted and Lewis acidic centers on the surface

TABLE 3

Data concerning the dimethyl disulphide conversion level ( $X, \%$ ) and the yield of reaction products at different temperature and contact time values in the presence of zeolite HZSM-5 ( $M = 2.4-2.6$ )

| $T, ^\circ\text{C}$ | $\tau, \text{s}$ | $X, \%$ | Yield of products, mol. %         |                    |                  |
|---------------------|------------------|---------|-----------------------------------|--------------------|------------------|
|                     |                  |         | (CH <sub>3</sub> ) <sub>2</sub> S | CH <sub>3</sub> SH | H <sub>2</sub> S |
| 250                 | 0.30             | 40      | 54                                | 5                  | 6                |
|                     | 0.64             | 70      | 100                               | 8                  | 10               |
|                     | 0.85             | 83      | 120                               | 6                  | 15               |
| 300                 | 0.15             | 56      | 72                                | 12                 | 8                |
|                     | 0.18             | 70      | 110                               | 9                  | 6                |
|                     | 0.25             | 81      | 116                               | 7                  | 15               |
| 350                 | 0.03             | 44      | 74                                | 5                  | 2                |
|                     | 0.10             | 78      | 120                               | 8                  | 10               |
|                     | 0.15             | 95      | 146                               | 7                  | 14               |
| 400                 | 0.02             | 43      | 50                                | 10                 | 7                |
|                     | 0.04             | 70      | 96                                | 11                 | 12               |
|                     | 0.06             | 81      | 106                               | 8                  | 18               |

inherent in  $\text{Al}^{3+}$  exhibits a decrease, and new strong Lewis acidic centers ( $\text{Co}^{2+}$  cations) appear, those participate in the formation of DMS. However, the activity of cobalt-zeolite catalysts at  $350^\circ\text{C}$  demonstrates a 1.4-fold decrease as compared to pure zeolite, whereas the stability of the catalysts remains low.

After introducing the chromium oxide into the HZSM-5 zeolite in an amount of 1.5 mass % Cr the catalyst activity as compared with the pure zeolite exhibits no changing or even demonstrates a decrease. The addition of chromium oxide to the amorphous silica-aluminum oxide also does not promote any increase in the catalyst activity with respect to the reaction between methanol and DMDS. The treatment of cobalt-containing and chromium-containing zeolites with a mixture of 15 %  $\text{H}_2\text{S}$  + 85 %  $\text{H}_2$  at  $400^\circ\text{C}$  for 1 h exerts an insignificant effect on the catalyst activity. We have not revealed the cause of the mentioned phenomenon. To all appearance, owing to the fact that the process on the Co/HZSM-5 and Cr/HZSM-5 catalysts occurs to a considerable extent on the surface of the zeolite, the catalyst activity does not depend on the presence of Co and Cr therein.

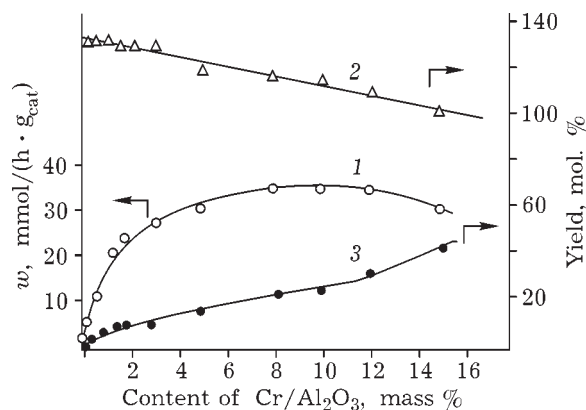


Fig. 2. Activity of aluminochromium catalysts in the reaction between dimethyl sulphide and methanol: 1 – DMDS conversion rate ( $w$ ); 2, 3 – DMS and MT yields, respectively.  $T = 350^\circ\text{C}$ .

Transition metal oxides applied onto  $\text{Al}_2\text{O}_3$ , contain strong acidic centers on the surface [4], and these catalysts are active in the reaction of DMS formation from DMDS and methanol. We investigated the features of the reaction between DMDS and methanol in the presence of chromium oxide applied in different amounts on aluminum oxide. It has been found that at a constant temperature, varying the contact time

TABLE 4

Effect of contact time on the dimethyl sulphide conversion level and on the yield of products in the presence of aluminochromium catalysts ( $T = 350^\circ\text{C}$ ,  $M = 2.4\text{--}2.6$ )

| Catalysts                          | $\tau$ , s | X, % | Yield, mol. %             |                        | Catalysts                          | $\tau$ , s | X, % | Yield, mol. %             |                        |
|------------------------------------|------------|------|---------------------------|------------------------|------------------------------------|------------|------|---------------------------|------------------------|
|                                    |            |      | $(\text{CH}_3)_2\text{S}$ | $\text{CH}_3\text{SH}$ |                                    |            |      | $(\text{CH}_3)_2\text{S}$ | $\text{CH}_3\text{SH}$ |
| 0.25 % Cr/ $\text{Al}_2\text{O}_3$ | 0.15       | 36   | 67                        | 2.2                    | 5.0 % Cr/ $\text{Al}_2\text{O}_3$  | 0.04       | 48   | 82                        | 5.8                    |
|                                    | 0.32       | 70   | 130                       | 4.2                    |                                    | 0.09       | 70   | 120                       | 8.4                    |
|                                    | 0.40       | 81   | 151                       | 4.9                    |                                    | 0.13       | 81   | 140                       | 9.7                    |
|                                    | 0.53       | 98   | 182                       | 5.9                    |                                    | 0.22       | 98   | 168                       | 12.1                   |
| 0.5 % Cr/ $\text{Al}_2\text{O}_3$  | 0.12       | 44   | 82                        | 2.1                    | 10.0 % Cr/ $\text{Al}_2\text{O}_3$ | 0.02       | 46   | 72                        | 6.9                    |
|                                    | 0.26       | 70   | 132                       | 3.5                    |                                    | 0.08       | 70   | 120                       | 7.7                    |
|                                    | 0.35       | 81   | 154                       | 4.0                    |                                    | 0.14       | 81   | 144                       | 8.8                    |
|                                    | 0.46       | 92   | 173                       | 4.5                    |                                    | 0.18       | 97   | 175                       | 8.2                    |
| 1.5 % Cr/ $\text{Al}_2\text{O}_3$  | 0.04       | 36   | 56                        | 7.0                    | 15 % Cr/ $\text{Al}_2\text{O}_3$   | 0.03       | 46   | 48                        | 21.6                   |
|                                    | 0.13       | 70   | 130                       | 4.1                    |                                    | 0.08       | 70   | 98                        | 19.2                   |
|                                    | 0.18       | 90   | 166                       | 6.3                    |                                    | 0.20       | 88   | 140                       | 15.0                   |
|                                    | 0.22       | 100  | 187                       | 3.0                    |                                    | 0.15       | 96   | 167                       | 12.0                   |
| 3.0 % Cr/ $\text{Al}_2\text{O}_3$  | 0.02       | 30   | 56                        | 1.8                    | $\text{Cr}_2\text{O}_3$            | 0.05       | 30   | 2                         | 28.5                   |
|                                    | 0.10       | 70   | 132                       | 4.2                    |                                    | 0.14       | 70   | 15                        | 62                     |
|                                    | 0.14       | 86   | 162                       | 5.2                    |                                    | 0.18       | 80   | 16                        | 70                     |
|                                    | 0.20       | 95   | 178                       | 5.7                    |                                    | 0.26       | 91   | 19                        | 74                     |

causes the DMDS conversion level and product yield to increase (Table 4). In the presence of aluminochromium catalysts, the DMDS transformation rate is significantly higher than it is for aluminum oxide, to be dependent on the content of chromium therein (Fig. 2). After introducing 0.12 mass % of Cr in the  $\gamma$ - $\text{Al}_2\text{O}_3$  the DMDS conversion rate at 350 °C increases by about 2.6 times; with further increasing the chromium content this value increases being for 10 % Cr/ $\text{Al}_2\text{O}_3$  almost 17 times higher than the rate of conversion on pure aluminum oxide.

Increasing the catalyst activity with increasing the chromium content therein could be, to all appearance, connected with changing the surface acidity. In the initial aluminum oxide, there is a very small amount of strong Brønsted acidic centers ( $\text{PA}^a = 1270$  kJ/mol), Lewis acidic centers are present (mainly medium-strength centers and few strong centers). After introducing the chromium into aluminum oxide the surface of the catalyst exhibits stronger Brønsted acidic centers to appear ( $\text{PA}^a = 1200$ – $1245$  kJ/mol), whose content is an order of magnitude higher than the concentration of the strong Brønsted acidic centers on pure aluminum oxide surface. The addition of chromium oxide to  $\text{Al}_2\text{O}_3$  results in decreasing the concentration of strong Lewis acidic centers and in increasing the concentration of medium-strength centers.

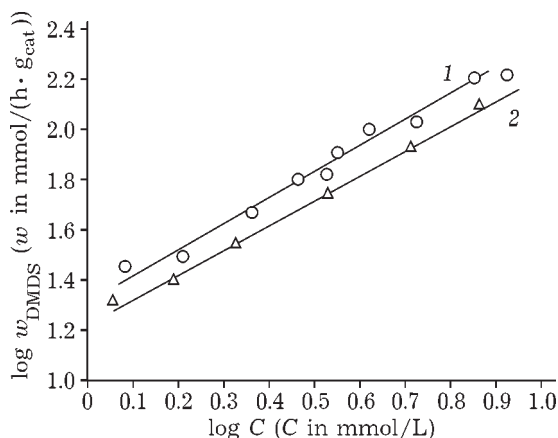


Fig. 3. Rate of dimethyl disulphide (DMDS) conversion depending on methanol (1) and DMDS (2) concentration on 1.5 % Cr/ $\text{Al}_2\text{O}_3$  catalyst.  $T = 350$  °C.

Changing the activity of chromium-containing catalysts could be also associated with the state of chromium. The authors of [11] demonstrated that when the chromium content in  $\text{Al}_2\text{O}_3$  is less than 2 mass %, the chromium is in a highly dispersed state being present in the form of a solid solution of  $\text{Cr}^{+6}$  and  $\text{Cr}^{+3}$ . In the case of higher chromium content, the element exists in the form of fine and coarse particles of  $\text{Cr}_2\text{O}_3$ . To all appearance, chromium cations act as additional Lewis acidic centers on the surface of aluminochromium catalysts, which promotes increasing the activity thereof in the reaction of DMS formation from DMDS and

TABLE 5

Productivity with respect to dimethyl sulphide (DMS) for the conversion of dimethyl disulphide (DMDS) in the mixture with methanol in the presence of aluminochromium catalysts ( $M = 2.3$ – $2.7$ ) [11]

| Content Cr on $\text{Al}_2\text{O}_3$ , mass % | $T$ , °C | $\tau$ , s | DMDS conversion level, % | Productivity, mmol DMS/(h · $g_{\text{cat}}$ ) |
|--|----------|------------|--------------------------|--|
| 0  | 350      | 1.51       | 72                       | 2.0  |
| 0.5  | 350      | 0.53       | 85                       | 11.4   |
| 1.0  | 350      | 0.25       | 88                       | 27.2   |
| 1.5  | 350      | 0.15       | 85                       | 43.0   |
| 3.0  | 350      | 0.13       | 80                       | 44.8   |
| 5.0  | 350      | 0.17       | 90                       | 35.0   |
| 10.0   | 350      | 0.17       | 96                       | 27.6   |
| 1.5  | 300      | 0.27       | 60                       | 12.0   |
| 1.5  | 325      | 0.35       | 87                       | 17.8   |
| 1.5  | 350      | 0.10       | 70                       | 56.2   |
| 1.5  | 380      | 0.19       | 96                       | 37.8   |

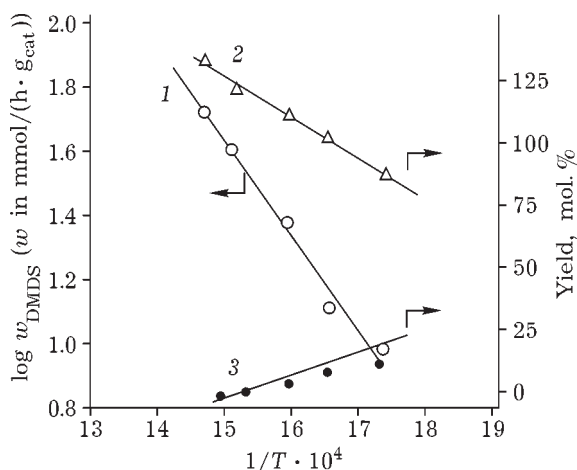


Fig. 4. Rate of dimethyl disulphide reaction with methanol ( $w_{\text{DMDS}}$ ) (1) and the yields of DMS (2) and MT (3) at different temperature values. Catalyst 1.5 % Cr/Al<sub>2</sub>O<sub>3</sub>.

methanol. A detailed study of the mechanism of the new reaction DMS formation from methanol and DMDS should be the subject of our further research.

The investigation of the reaction kinetics demonstrated that the presence of the 1.5 % Cr/Al<sub>2</sub>O<sub>3</sub> catalyst, under maintaining constant the concentration of one reactant and increasing the concentration of another reactant, the reaction rate exhibits an increase in direct proportion against the concentration of methanol and disulphide (Fig. 3). So, there is first kinetic reaction order observed both with respect to DMDS and with respect to methanol. With increasing the temperature, the reaction rate exhibits an increase, too, but at the same time there is an increase in the yield of MT observed (Fig. 4). The apparent activation energy is equal to (67±2) kJ/mol. The process occurs with a high efficiency (Table 5).

Basing on the results obtained one could conclude that the process of obtaining the DMS from methanol and DMDS should be carried out in the presence of catalysts containing 1.5–3.0 % of Cr/Al<sub>2</sub>O<sub>3</sub>, at the temperature of 350–400 °C,  $M \geq 2$ , and 100 % DMDS conversion level. Under these conditions, the DMS could be obtained with the selectivity higher than 95 %.

## CONCLUSIONS

In the presence of aluminosilicate and aluminochromium catalysts having strong acidic

centers on the surface, DMDS at 250–400 °C reacts with methanol to form DMS as the main product. The reaction takes place due to the interaction between one molecule of DMDS and two molecules of methanol. This is confirmed by the fact that the yield of DMS increases with increasing the methanol to DMDS molar ratio ( $M$ ) and when  $M \geq 2$  the DMS yield is equal to a two-fold DMDS conversion level. Therewith the concentration of methanol reacted with DMDS, and the concentration of DMS formed are equal. Zeolite HZSM-5 with a high content of silica exhibits a higher activity than the aluminosilicate and zeolite HNaY having lower acidity. The activity of zeolite HZSM-5 at 250 °C is increased after adding cobalt oxide thereto, however, such an effect is not observed at 350 °C. The activity of the zeolite does not increase also after adding chromium oxide thereto.

The aluminum oxide modified with chromium oxide exhibits a high activity in the course of DMS formation due to the reaction between methanol and DMDS; the activity increases with increasing the content of chromium in the catalyst. The catalysts containing 1.5–3 mass % of chromium exhibit are most efficient: the productivity with respect to DMS in the presence thereof is more than an order of magnitude greater than that inherent in aluminum oxide. From the kinetic data, it follows that the reaction on the Cr/Al<sub>2</sub>O<sub>3</sub> catalysts proceeds according to the first kinetic order with respect to both DMDS and methanol. The reaction rate increases with increasing the temperature, at a complete conversion of DMDS. The results obtained could be used in the course of developing a new method for recycling the DMDS released from the products of demercaptanizing the naturally occurring hydrocarbon mixtures by means of a selective catalytic DMS-DS transformation into the DMS valuable for practical use.

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