Synthesis of Methylmercaptan from Methanol and Hydrogen Sulfide at Elevated Pressure on an Industrial Catalyst

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Abstract—The catalytic reaction of methanol with hydrogen sulfide at a total pressure of 0.1–1.8 MPa was investigated. The main product at different values of total pressure in the system was methylmercaptan, and the by-products were dimethyl sulfide, dimethyl ether, carbon oxides. An increase in the contact time increased the yields of methylmercaptan and dimethyl sulfide, whereas the yields of dimethyl ether and gases changed slightly. The selectivity for methylmercaptan was approximately constant up to a ~95% conversion of methanol. The elevation in temperature increased the reaction rate but barely affected the product formation selectivity. The rate of methanol conversion increases linearly with the hydrogen sulfide concentration and depends on the methanol concentration raised to a power of 0.4–0.5; water retards the process. The selectivity for methylmercaptan decreases, and that for dimethyl sulfide and dimethyl ether increases at an H₂S to methanol molar ratio below 1.4 : 1, regardless of the value of total pressure. The reaction rate increases with the total pressure raised to a power 0.4–0.5; however, the selectivities for methylmercaptan and by-products remain unchanged.

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Methylmercaptan (methanethiol, MeSH) is an industrially important chemical used for the production of valuable thio compounds, in particular, methionine (a drug and feed additive). At present, MeSH is synthesized from methanol and hydrogen sulfide, primarily, over potassium- and tungsten-modified alumina as a catalyst. The catalyst mainly favors the formation of MeSH, but by-processes yielding dimethyl ether (DME), dimethyl sulfide (DMS), and carbon oxides also proceed. The reaction conditions temperature, concentration of the reactants, and their feed space velocity influence the performance of the MeSH synthesis process [1-5]. The process is carried out in the temperature range of 320-420°C at either atmospheric or elevated pressure. Reported in the literature [1, 2, 4, 5] are only the results of methanol reaction with hydrogen sulfide at atmospheric pressure. Surveying the industrial-scale production of mercaptans, Forquy and Arretz [3] noted that the process of methylmercaptan synthesis from methanol and H_2S is carried out at P = 0.7-1.2 MPa for engineering reasons. They reported a plot of the temperature dependence of methanol conversion at P = 0.1and 0.3 MPa and two values of space velocity of methanol. Analyzing these limited data, one may conclude that the methanol conversion at P = 0.3 MPa is somewhat higher than that at P = 0.1 MPa. Information concerning the influence of pressure on the direction of catalytic transformation of methanol in the presence of H_2S , on the product formation rates, and on the selectivity of the process is lacking.

In this work, we experimentally investigated the behavior of the methanol reaction with hydrogen sulfide at an elevated pressure in the presence of the industrial catalyst IKT-31-1.

EXPERIMENTAL¹

Hydrogen sulfide (99.5% purity) was obtained by the reaction of hydrogen with sulfur on an AlNiMo catalyst; organic substances used in the work were commercial chemicals of chemically pure and reagent grades. The experiments were carried out in a flow reactor with a fixed IKT-31-1 catalyst bed. A mixture of H₂S and helium was sent through a pressure regulator to a temperature-controlled saturator filled with methanol. Then, the saturated gas arrived to a catalytic reactor heated with a low thermal-inertia furnace and further to a chromatograph. The temperature of the system was $T = 170^{\circ}$ C. The initial mixture and the products were periodically sampled in 15-min intervals with a six-way cock. Their analysis was carried out on a "Tsvet-500" chromatograph with a katharometer (a column of

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SYNTHESIS OF METHYLMERCAPTAN

D MDa	7 a	V (7			Yield,	mol %		
<i>F</i> , IVIF a	1, 5	Λ, 70	MeSH	DMS	DME	CH ₄	CO ₂	СО
0.10	1.2	50	46	0.7	2.0	0.01	0.2	0.02
	2.9	75	69	1.5	1.8	0.10	0.4	0.10
	9.0	91	84	2.2	0.9	0.50	0.6	0.30
0.18	0.6	47	44	0.6	0.8	0.01	0.1	0.02
	1.1	76	72	1.2	0.5	0.02	0.2	0.01
	1.4	89	85	1.8	0.2	0.02	0.3	0.02
0.62	0.4	45	43	0.2	0.7	0.01	0.1	0.02
	0.8	70	66	0.7	0.6	0.01	0.2	0.01
	1.3	78	74	1.1	0.5	0.01	0.2	0.01
1.00	0.2	40	38	0.2	0.7	0.02	0.2	0.30
	0.3	59	56	0.7	0.6	0.10	0.4	0.50
	1.2	81	77	1.2	0.2	0.20	0.3	0.90
1.22	0.3	51	45	0.4	2.2	0.02	0.3	0.10
	0.5	68	61	1.0	2.4	0.02	0.3	0.40
	0.8	94	85	1.9	2.6	0.10	0.3	0.30
1.53	0.3	57	52	0.7	2.1	0.02	0.2	0.02
	0.6	76	70	1.4	2.0	0.01	0.4	0.03
	0.9	90	82	1.9	1.9	0.10	0.5	0.02
1.80	0.2	53	48	0.4	1.9	0.01	0.3	0.01
	0.3	68	63	0.7	1.8	0.02	0.2	0.02
	0.6	91	83	1.4	1.6	0.02	0.3	0.50

Table 1. Influence of the contact time on the methanol conversion and product yields at different total pressures. $T = 360^{\circ}$ C, $[MeOH]_0 = 4.5-4.7$ vol %, M = 1.7-1.8

 $2 \text{ m} \times 3 \text{ mm}$ in size packed with Porapak Q+R(1 : 1) phase). The analysis error was ± 5 rel. %.

From the analysis results, we calculated the methanol conversion (X,%), product yields as the number of moles of the product formed from one mole of methanol (Y, mol %), and selectivity (S, %) defined as the ratio of the product yield in percent of the theoretical yield to the methanol conversion. The methanol conversion rate (w, mmol/h(g cat)) was determined at a definite degree of conversion of methanol. The estimated contact time is equal to the ratio of the catalyst volume (cm³) to the rate of gas flow (cm³/s) at atmospheric pressure and room temperature.

RESULTS AND DISCUSSION

The experiments were conducted at $T = 325-380^{\circ}$ C and a total pressure of 0.10–1.80 MPa; the starting methanol and hydrogen sulfide concentration in the initial gas mixture varied within 1.3–14.7 and 2.0–25.0 vol %, respectively; and the H₂S : methanol molar ratio (*M*) was 0.5–14.7.

The products under the given conditions were methylmercaptan, water, dimethyl sulfide, dimethyl ether, methane, and carbon oxides. In all experiments, the yield of water was equal to the degree of methanol conversion within the limits of experimental accuracy, and the conversion of H_2S was equal to that of methanol minus the doubled yield of dimethyl ether.



Fig. 1. Influence of the contact time on (1) methanol conversion and the yields of (2) MeSH, (3) DMS, and (4) DME at $T = 360^{\circ}$ C, P = 1.0 MPa, [MeOH]₀ = 4.7 vol %, M = 1.7, and $d_{\text{cat. grain}} = 0.25-0.5$ mm.

On the catalyst with an average grain size of 0.25-0.5 mm, the reaction rate did not change with a decrease in the catalyst grain size, i.e., the process was

kinetically controlled. At constant temperature, total pressure, and reactant concentration, the methanol conversion grew, approaching 100% with an increase in the contact time. The yield of MeSH increased to a certain value with the contact time and then changed little; the yield of dimethyl sulfide increased somewhat in this case and that of dimethyl ether did not change or it decreased. Methane and carbon oxides were formed with low yields (0.01–0.6 mol %), and their yields slightly changed with an increase in the contact time (Table 1, Fig. 1). With varying methanol conversion up to $X \le 95\%$, the MeSH selectivity remained practically unchanged, the selectivity for DMS somewhat increased, and that for DME decreased (Fig. 2). The same trends were observed at different values of total pressure including atmospheric. It is likely that, as in the case of atmospheric pressure [6,7], the products are formed as a result of parallel-consecutive processes: methanol dehydration leads to DME formation, and the reaction of H₂S with methanol or DME yields MeSH, which converts further to DMS.



Partial degradation of DME and methanol leads to the release of carbon oxides and methane; methane can also result from MeSH and DMS degradation.

To elucidate the influence of the reaction conditions on the performance characteristics of the process, we determined the contact time corresponding to 60% methanol conversion from the kinetic curves at T =360°C and calculated the methanol conversion rate and product formation selectivity. Tables 2 and 3 list the data on the influence of the initial methanol ([MeOH]₀) and hydrogen sulfide ([H₂S]₀) concentrations on the performance of the process. As it is seen, an increase of the initial reactant concentrations leads to a growth in the rate of methanol conversion. We also observed an increase in the reaction rate with an increase in the current concentration of methanol (C_{Me}) or H₂S ($C_{\text{H}_2\text{S}}$). For example, the reaction rate increased proportionally to C_{Me} raised to a power of 0.4–0.5 on the catalyst with a grain size of $d_{\text{grain}} = 0.25-0.5$ mm at P = 1.0 MPa and [H₂S] of ~7.6 or ~20 vol %; the same results were also obtained at P = 0.1 MPa (Fig. 3).



Fig. 2. Selectivity for (1) MeSH, (2) DMS, and (3) DME at different degrees of methanol conversion: $T = 360^{\circ}$ C, P = 1.0 MPa, [MeOH]₀ = 4.7 vol %, M = 1.7, and $d_{\text{cat. grain}} = 0.25-0.5$ mm.



Fig. 3. Log–log plot of the rate of methanol conversion (*w*, mmol/h(g(Cat)) at $T = 360^{\circ}$ C versus the current methanol concentration (C_{Me}). Pressure is 1.0 (*1*–3) and 0.1 MPa (4); [H₂S]₀ = 20.1 (*1*) and 7.5–7.8 vol % (2–4); $d_{cat. grain} = 0.25-0.5$ (*1*, 2, 4) and 4–6 mm (3).

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[MeOH] ₀ ,	М	<i>w</i> ,	Selectivity, %			
vol %	171	mmol/h(g Cat)	MeSH	DMS	DME	
$d_{\text{grain}} = 0.25 - 0.5 \text{ mm}, P = 1.0 \text{ MPa}, [\text{H}_2\text{S}]_0 = 20.4 \text{ vol }\%$						
1.3	14.7	9.0	98	2.3	0	
3.0	7.2	15.7	98	1.3	0	
4.5	4.2	17.5	98	1.6	0	
7.7	2.8	23.2	97	1.7	0	
$d_{\text{grain}} = 0.23$	5–0.5 n	nm, <i>P</i> = 1.0 MPa	a, [H ₂ S]	₀ = 7.6 v	ol %	
1.8	4.2	8.9	95	2.0	3.0	
4.6	1.7	12.4	95	2.7	2.0	
7.0	1.1	15.0	88	2.3	8.7	
9.9	0.7	17.0	82	3.0	13.0	
$d_{\text{grain}} = 4-6 \text{ mm}, P = 1.0 \text{ MPa}, [\text{H}_2\text{S}]_0 = 7.8 \text{ vol} \%$					%	
1.9	4.2	3.5	96	2.5	0	
4.7	1.7	5.6	95	4.0	0	
7.2	1.1	6.8	91	7.0	0	
$d_{\text{grain}} = 0.23$	5–0.5 n	hm, P = 0.1 MPa	a, [H ₂ S]	₀ = 7.5 v	ol %	
5.0	1.5	2.0	84	2.5	12	
7.1	1.1	2.4	80	4.0	15	
12.5	0.6	3.0	72	5.0	23	
14.7	0.5	3.2	64	6.0	28	

Table 2. Influence of the initial methanol concentration on the reaction rate and the product selectivity. $T = 360^{\circ}$ C

Table 3.	Influ	ience	of th	ne starting	H_2S	concer	ıtra	tior	n on 1	the
reaction	rate	and	the	product	selec	tivity.	Т	=	360	°C,
[MeOH]	= 4.	5-4.7	vol	%		•				

[H ₂ S] ₀ , vol %	М	<i>w</i> ,	Se	lectivity, %			
		mmol/h(g Cat)	MeSH	DMS	DME		
	$d_{ m grai}$	$_{\rm n} = 0.25 - 0.5 {\rm mm}$, P = 1.0	MPa			
2.4	0.7	3.2	89	8.7	2.3		
6.9	1.4	8.6	95	2.7	2.0		
9.1	1.7	12.4	95	2.7	2.0		
25.0	4.1	22.0	98	1.6	0		
	d_{i}	$_{\text{grain}} = 4-6 \text{ mm}, P$	= 1.0 M	Pa			
2.5	0.5	2.7	93	5.2	0		
7.8	1.7	5.7	95	4.0	0		
20.7	4.5	12.0	98	1.3	0		
$d_{\text{grain}} = 0.25 - 0.5 \text{ mm}, P = 0.1 \text{ MPa}$							
4.3	1.0	1.6	72	8.1	18.0		
5.6	0.9	1.8	72	5.7	21.0		
9.6	1.7	3.0	92	3.0	5.0		
12.3	2.1	4.0	94	2.0	4.0		
24.3	4.1	8.1	95	2.4	2.1		
$d_{\text{grain}} = 4-6 \text{ mm}, P = 0.1 \text{ MPa}$							
2.0	0.6	0.7	86	6.7	6.7		
6.5	1.3	1.6	94	2.2	2.8		
8.6	1.7	2.2	97	1.3	1.0		

Table 4. The reaction of methanol with H_2S at different pressures. $T = 360^{\circ}C$, [MeOH]₀ = 4.5–4.7 vol %, M = 1.7-1.8

P MPa	w, mmol/h(g Cat)	Selectivity, %				
1, wii a	at $X = 60\%$	MeSH	DMS	DME		
0.10	3.0	94	2.0	4.0		
0.18	5.3	94	2.3	3.0		
0.33	6.8	95	2.4	3.0		
0.40	7.5	95	2.0	3.0		
0.51	8.6	95	1.3	3.0		
0.62	9.4	95	1.7	2.7		
1.00	12.4	95	2.7	2.0		
1.22	14.0	88	2.7	8.0		
1.53	16.8	90	3.3	6.5		
1.81	18.1	90	2.1	6.6		

From the data presented in Table 2, it follows that, at $[H_2S]_0 = 7.6$ vol % in the reaction mixture, the selectivity for MeSH decreased from 95 to 82% with the increase in methanol content; the selectivity for DMS increased insignificantly and that for DME slightly grew; at larger $[H_2S]_0$ (20.4 vol %), a change in the methanol concentration did not affect the MeSH and DMS selectivity and DME was not produced. At P =0.1 or 1.0 MPa and constant [MeOH]₀, an increase in the current H₂S concentration in the reaction mixture increases almost proportionally to the reaction rate (Fig. 4). An increase of the H₂S content enhances the selectivity for MeSH and decreases that for DMS and DME (Table 3). A variation of methanol and H₂S concentrations had practically no effect on the selectivity for gases, which remained at the level of 0.02-0.5%. The addition of water to methanol retarded the process; the rate of methanol conversion decreased linearly with an increase in the water content (Fig. 5a), with the selectivity for all products being constant.

The reaction of methanol with H_2S was investigated at constant initial concentrations of the reactants but at different total pressures. It was found that an increase in the total pressure resulted in an increase of methanol



Fig. 4. Log–log plot of the rate of methanol conversion (*w*, mmol/h(g Cat)) at $T = 360^{\circ}$ C versus the current hydrogen sulfide concentration ($C_{\text{H}_2\text{S}}$). Pressure is 1.0 (*1*, 2) and 0.1 MPa (3, 4); $d_{\text{cat. grain}} = 0.25$ –0.5 (*1*, 3) and 4–6 mm (2, 4).

conversion rate following the power law with an index of 0.4–0.5 (Fig. 5b), wherein the selectivity for MeSH somewhat decreased, that for DMS remained approximately constant, and the DME selectivity somewhat increased (Table 4). The gas formation rate was practically unaffected by variation in the pressure of the system.

When the catalyst used had coarse $(d_{\text{grain}} = 4-6 \text{ mm})$ grains, the trends in the methanol conversion rate with varying reactant concentrations and total pressure in the system were close to those found for the crushed catalyst $(d_{\text{grain}} = 0.25-0.5 \text{ mm})$ (Tables 1, 2, Figs. 3–5), although the process on the coarse-grained catalyst proceeds in the inner-diffusion region, as shown experimentally. The degree of usage of the catalyst surface (η) at



Fig. 5. Log-log plots of the rate of methanol conversion (*w*, mmol/h(g Cat)) at $T = 360^{\circ}$ C, [MeOH]₀ = 4.5-4.7 vol %, M = 1.7-1.8 versus (a) the current water concentration ($C_{\rm H_2O}$) and (b) the total pressure; $d_{\rm cat.\ grain} = 0.25-0.5$ (1, 2) and 4–6 mm (3).





1.0 MPa, $[MeOH]_0 = 4.6-4.9 \text{ vol }\%$, M = 1.6, $d_{cat. grain} = 0.25-0.5 \text{ mm}$.

different depths of methanol conversion was determined as the ratio of observed rates of methanol conversion on the large and small grain catalysts with the assumption that the entire inner surface of small-grain catalyst is available for the initials. The results are given in Table 5. It is seen that at different depths of methanol conversion, similar trends are observed but the degree

		P = 0.1 MPa		P = 1.0 MPa		
<i>X</i> , %	X, % w, mmol/h(g Cat)		n	w, mmol/h	(g Cat)	n
	$d_{\rm grain} = 0.25 - 0.5 {\rm mm}$	$d_{\text{grain}} = 4-6 \text{ mm}$	1	$d_{\rm grain} = 0.25 - 0.5 \rm mm$	$d_{\text{grain}} = 4-6 \text{ mm}$	11
40	4.2	1.9	0.45	20.0	7.6	0.38
50	4.1	1.8	0.44	19.2	6.3	0.33
60	3.0	1.6	0.53	13.4	5.7	0.42
70	2.5	1.3	0.52	9.7	4.7	0.48
80	1.6	1.0	0.62	6.8	3.5	0.51
90	0.8	0.6	0.75	3.8	2.5	0.66

Table 5. Degree of utilization of surface area (η) of an intact catalyst grain at different methanol conversions, $T = 360^{\circ}$ C, [MeOH]₀ = 4.6–4.7 vol %, M = 1.7-1.8

Table 6. Influence of temperature on the rate of methanol conversion and the product selectivity. P = 1.0 MPa; [MeOH]₀ = 4.6–4.9 vol %, M = 1.6, $d_{\text{grain}} = 0.25$ –0.5 mm

T°C	w, mmol/h(g Cat)	S	electivity, %			
1, C	at $X = 60\%$	MeSH	DMS	DME		
325	4.3	95	2.0	2.3		
340	4.8	95	1.3	2.7		
360	12.4	95	2.7	2.0		
375	16.3	97	1.3	1.7		
380	17.0	97	2.7	0.3		

of utilization of surface area at an elevated pressure is somewhat lower than at atmospheric pressure.

In the kinetic region when the total pressure and the reactant concentrations were maintained constant, elevation in temperature facilitates the reaction between methanol and H₂S, with the selectivity for all products remaining practically unchanged (Table 6). The value of the apparent activation energy determined from the plot of the logarithmic reaction rate against the inverse temperature at $X_{\text{Me}} = 60\%$ (Fig. 6) was 80 ± 10 kJ/mol.

In summary, it follows from the experimental data that at a constant temperature, the rate of the reaction between methanol and H_2S increases almost linearly with the H_2S concentration and, to a smaller extent, with the methanol concentration. Elevation of the total pressure of the system and the reaction temperature leads to a growth in the reaction rate but barely affects the product selectivity. At a low H_2S : methanol ratio, the selectivity for MeSH decreases and that for DMS and DME increases. It is advisable to conduct the synthesis of methanethiol from methanol and H_2S at an H_2S : methanol molar ratio of at least 1.4 : 1 and at an elevated pressure.

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