PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Selection of the Type of Methane Conversion for Catalytic Reduction of Sulfur Dioxide

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Abstract—Catalytic reduction of sulfur dioxide with converted gas obtained by various methods of conversion of natural gas was studied to select the most active reducing agent for SO_2 .

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A lot of research efforts dedicated to sulfur recovery from sulfur dioxide using different (solid, gaseous) reducing agents have resulted in demonstrating the predominant practical importance of gaseous agents. Among them, the most economical agent is natural gas which is composed mainly of methane. However, the latter, because of its chemical inertness, needs conversion or thermal decomposition in order to exert a reducing action. This process requires high temperatures (1250–1200°C) [1–4] achievable via partial combustion of natural gas, thereby leading to dilution of the reducing gas with its combustion products and general complication of the process. In the presence of catalysts the reduction of sulfur dioxide with methane goes at 800–900°C [5, 6]; moreover, high temperatures increase side reactions generating COS, CS_2 , and H_2S whose conversion to sulfur in some cases requires three catalytic conversion stages. The above-said suggests the need in sulfur dioxide reduction with preconverted rather than raw natural gas.

The aim of this study was to optimize the conditions and parameters of sulfur dioxide reduction with gases containing hydrogen and carbon monoxide in different ratios, which were obtained by steam, steam-oxygen, oxygen, and carbon dioxide catalytic conversion of natural gas. The conversion conditions were chosen in the effect that the CO_2 , H_2O , and residual methane content in the converted gas be minimized and leave unaffected the reduction process (Table 1).

Table 1 shows that the composition of the natural gas conversion products is close to theoretical in all the cases

Table 1. Results of analysis of the products of methane conversion using different oxidants (average value) $T = 900^{\circ}$ C, P = 0.1 MPa, W = 500 h⁻¹, catalyst GIAP-16

Conversion process using	CH ₄ : oxidant ratio	Con					
indicated oxidant		CO ₂	СО	H ₂	CH ₄	N ₂ +Ar	$-CO: H_2$ ratio
Carbon dioxide	$CH_4: CO_2 = 1: 1.25$	4.95	46.45	47.70	0.10	0.80	1:1
Oxygen	$CH_4: O_2 = 1: 0.6$	3.10	30.50	65.25	0.35	0.80	1:2.1
Steam-oxygen mixture	$CH_4: H_2O: O_2 = 1:1:0.6$	2.10	28.70	68.10	0.15	0.95	1 : 2.5

except for the steam conversion products. In the latter case, the hydrogen content is slightly higher because of a secondary reaction of carbon monoxide with excess steam. Reduction of sulfur dioxide with converted gas of different compositions was carried out at 300–400°C, space velocity 1000 h⁻¹, and (CO + H₂) : SO₂ = 2.1 (vol/ vol); the catalyst particle size was 1–2 mm. As contacts served cobalt- and nickel-alumina catalysts, whose high catalytic activity in the process of interest was revealed earlier [7].

Table 2 lists the results of experiments on sulfur dioxide reduction with converted gas at different CO : H_2 ratios.

Data in Table 2 for the cobalt–alumina catalyst suggest that, with the CO : H_2 ratio varied within 1 : 1–1 : 4, the sulfur yield increases from 60.0 to 80.2% and from 62.7 to 82.5% at 300 and 350°C, respectively. Further increase in temperature (to 400°C) and variation of the CO : H_2 ratio over the same range results in decreased sulfur yield

due to larger amount of hydrogen sulfide and carbonyl sulfide among the reaction products.

The cobalt–alumina catalyst is most active at 300– 350°C and CO : $H_2 = 1 : 2.5-1 : 4.0$ (i.e., when the steam and steam–oxygen conversion products are used), under which conditions the sulfur yield reaches 80.9–82.5%. As to the nickel–alumina catalyst, at 350–400°C and CO : $H_2 = 1 : 2.5-1 : 4.0$ it is slightly less active. Increase in temperature above 300–350°C in the case of cobalt–alumina catalysts and above 400°C in the case of nickel-alumina catalyst adversely affects the yield of the target product.

Table 2 shows that, at CO : $H_2 = 1$: 1 (in the case of carbon dioxide conversion of natural gas), the highest yield of sulfur was achieved at 400°C with both catalysts. Because of a relatively high concentration of carbon monoxide in the reducing gas, the mixture of reduction products contains, along with hydrogen sulfide, a significant amount of carbonyl sulfide, and their conversion

			Sulfur distri	SO ₂ conversion.				
Catalyst	<i>T</i> , °C	$CO : H_2 ratio$	S	H_2S	COS	SO ₂	0/0	
Al ₂ O ₃ ·Co ₃ O ₄	300	1:1.0	60.0	4.8	4.2	31.0	69.0	
2 3 5 1		1:2.1	76.5	4.1	0.9	18.5	81.5	
		1:2.5	81.8	5.8	0.4	12.0	88.0	
		1:4.0	80.2	4.2	—	15.6	84.4	
	350	1:1.0	62.7	5.7	3.7	27.9	72.1	
		1:2.11	73.6	10.4	0.7	15.3	84.7	
		1:2.5	80.9	10.1	0.4	8.6	91.4	
		1:4.0	82.5	9.8	0.3	7.4	92.6	
	400	1:1.0	65.9	7.8	2.1	24.2	75.8	
		1:2.1	63.9	19.0	—	17.1	82.9	
		1:2.5	63.7	21.8	—	14.5	85.5	
		1:4.0	32.1	23.0	—	14.9	85.1	
Al ₂ O ₃ ·NiO	300	1:1.0	32.1	—	1.8	65.3	34.7	
		1:2.1	60.8	2.6	1.3	35.3	64.7	
		1:2.5	75.4	5.0	0.3	19.3	80.7	
		1:4.0	76.9	6.8	0.2	16.2	83.9	
	350	1:1.0	50.8	—	2.9	46.3	53.7	
		1:2.1	67.2	6.2	1.3	25.3	74.7	
		1:2.5	77.8	10.7	0.9	10.6	89.4	
		1:4.0	78.0	10.2	0.2	11.6	88.4	
	400	1:1.0	64.5	3.5	1.3	30.7	69.3	
		1:2.1	73.0	10.8	0.9	19.3	84.7	
		1:2.5	76.4	12.4	0.7	13.5	88.5	
		1 : 4.0	79.0	11.2	0.2	9.6	90.4	

Table 2. Reduction of sulfur dioxide with converted gas $W = 1000 \text{ h}^{-1}$, (CO + H₂) : SO₂ = 2.1, $c_{SO_2} = 20\%$

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Fig. 1. Sulfur yield *S*, %, vs. CO : H_2 ratio. Catalyst Co/Al₂O₃. Space velocity of the gas mixture, h⁻¹: (*1*) 500, (*2*) 1000, (*3*) 1500, and (*4*) 2000.

to sulfur requires two additional catalytic Claus stages.

Thus, the most appropriate reducing gas can be found in the products of steam conversion of natural gas, characterized by the CO : H_2 ratio of 1 : (3.5–4.0).

Further, the sulfur yield was examined in relation to the space velocity of the gas mixture at different CO : H_2 ratios (Fig. 1). It is seen from Fig. 1 that, with the space velocity increasing within 500–2000 h⁻¹, the yield of sulfur decreases, and with the CO : H_2 ratio increasing within 1 : 1–1 : 4, increases, so that the highest sulfur yield is achieved at the space velocity of 500–1000 h⁻¹ and CO : H_2 ratio of 1 : 4.

The experiments showed that the stationary state of the catalysts examined was achieved after certain residence period in reaction medium, depending on the composition of the sulfurous gas to be reduced and the temperature of the process. This phenomenon may be associated with formation of catalytically active phases from reactions of catalyst components with reacting substances.

To determine the state of the promoting component in the cobalt–alumina catalyst and to identify the most active phase of the contact, advanced physicochemical analysis techniques were employed: X-ray diffraction, DTA, and IR spectroscopy. The cobalt–alumina catalyst had the following characteristics: bulk, true, and apparent densities of 0.69, 3.1, and 1.7 g cm⁻³, respectively; porosity 5.6%.

The cobalt–alumina catalyst containing 10 wt\% Co_3O_4 (initial sample and sample after 400 h in reaction medium) was examined by derivatography, X-ray diffraction analysis, and IR spectroscopy. The results are presented



Fig. 2. Derivatograms of the cobalt-alumina catalyst samples. (*T*) Temperature, $^{\circ}$ C, and ($_{\tau}$) time, min. Catalyst: (a) initial and (b) spent in the SO₂-CO-H₂-N₂ medium.

in Figs. 2 and 3 and Table 3.

Figure 2a and 2b show the derivatograms of the initial cobalt–alumina catalyst and catalyst spent in the reaction medium, respectively. The DTA curve of the initial catalyst sample contains three endothermic peaks. Among them, the peak at 115°C may be associated both with decomposition of cobalt nitrate and loss of physically bound adsorbed water, and the peaks at 190 and 267°C, with the loss of crystallization water molecules. In the case of the spent catalyst samples, a DTA endothermic peak associated with loss of physically bound water is observed at 100–120°C. Further heating is also accompanied by a weight loss, as indicated by the corresponding TG curves. The weight loss at 200–480°C is evidently due to escape

Sample no.	Ia		IIa		Al ₂ O ₃		CoO		CoS		CoSO ₄	
	d, Å	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å	I/I ₀	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀	d, Å	<i>I</i> / <i>I</i> ₀
1	1.38	85	1.35	66	1.396	100						
2	1.51	48	1.49	36			1.50	100				
3	1.64	34	1.60 1.65	44 34					1.625		1.62 1.67	$10 \\ 24^{7}$
4	1.94	60	1.89	55					1.909	100		
5	1.96	69	1.99	76	1.975	72						
6	2.17	70	2.15	45			2.12	100				
7			2.33	28							2.35	20
8	2.42	48	2.44	50			2.45	67				
9			3.10	35							3.08	48
10			3.14	52					3.11			40
11			3.36	84							3.40	100

Table 3. X-ray diffraction data for the cobalt-alumina catalyst

^a I is initial catalyst, and II, catalyst spent in the SO₂-CO-H₂-N₂ medium.

of condensed sulfur from the catalyst surface.

The exothermic DTA peak observed at 530–540°C in the case of spent catalyst sample may be associated with cobalt sulfide oxidation in air atmosphere. The corresponding TG curve is indicative of a minor weight growth due to formation of cobalt sulfate which is stable at the temperature indicated. The resulting cobalt sulfate is decomposed at 320°C, as confirmed by an endothermic DTA peak (Fig. 2b).

Thus, the derivatographic data suggest the occurrence of cobalt sulfide in the spent catalyst sample.



Fig. 3. IR spectra of the cobalt-alumina catalyst. (*A*) Absorption, and (v) wavenumber, cm^{-1} . Catalyst: (*1*) initial and (*2*) spent in the SO₂-CO-H₂-N₂ medium.

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Figure 3 shows the IR absorption spectra of the dried and calcined initial cobalt–alumina catalyst sample (spectrum *I*) and of the catalyst sample spent under the conditions of sulfur dioxide reduction with converted gas (spectrum 2). In the case of the initial sample, unambiguous assignment of the absorption band at 440 cm⁻¹ (Fig. 3, spectrum *I*) is troublesome, because absorption in this



Fig. 4. Sulfur yield *S*, %, vs. catalyst operation time τ , h. *T* = 350°C, *W* = 1000 h⁻¹, (CO + H₂) : SO₂ = 2.1, c_{SO_2} = 20%. (*I*) Al₂O₃·CoO, (*2*) Al₂O₃·CoS, and (*3*) Al₂O₃·CoSO₄.

region be associated with the stretching vibrations of both Co-O and Al-O in y-Al₂O₃. A characteristic feature of the spent sample is that its absorption spectrum contains bands at 280 and 240 cm⁻¹, suggestive of the presence of cobalt sulfide.

The absorption bands observed in the spectrum of the spent sample at 1080, 1100, and 1260 cm⁻¹ can be assigned with high reliability to vibrations of the sulfate ion. It must be added that vibrations of the carbonate ion can also be manifested in this region, but the presence of the carbonate-carboxy moieties in the system is out of question because of the lack of comparatively highfrequency absorption bands at 1200–1700 cm⁻¹.

The absorption band of sulfates may occur at v =1070 cm⁻¹, and those of Al₂O and CoO, at 970 and 930 cm⁻¹, respectively. However, these bands cannot be differentiated because of a strong overlap with absorption of alumina proper (1000–1100 cm⁻¹).

A characteristic band of aluminum sulfate at 1300 cm⁻¹ is lacking in the spectrum recorded. This fact, coupled with the results of comparing the spectra of the catalyst with those of cobalt sulfate, allows the bands observed to be tentatively assigned to cobalt sulfates in the catalyst, whose absorption bands occur at 1100, 1030, and 970 cm⁻¹.

Along with the above-mentioned surface reactions leading to formation of sulfates and sulfides, the catalytic process can involve chemisorption of SO₂ via coordination with the metal ions by the donor-acceptor mechanism. This interaction may result in a shift of the absorption band of S=O to lower (1280 cm⁻¹) frequencies, as actually observed in the spectrum recorded (in the gaseous state $v_{S=0} = 1361 \text{ cm}^{-1}$).

The absorption bands at 3680 and 3550 cm⁻¹ are characteristic for bound hydroxy groups of alumina. These bands suggest that reduction of sulfur dioxide with converted gas involves partial chemisorption of the water molecules, thereby leading to formation of bound hydroxy groups which are subsequently involved in adsorption of other components of the reaction.

Therefore, the spectrum recording technique that was employed in this study allows accurate differentiation of the bands of sulfates, but the fact of proceeding on the surface of these catalysts of reactions giving sulfates (which concerns predominantly supported cobalt catalysts) is beyond any reasonable doubt.

The X-ray diffraction data for both the initial and

spent cobalt-alumina catalyst samples are in good agreement with the corresponding DTA and IR-spectroscopic findings (Table 3). In other words, the X-ray patterns recorded after the appropriate treatment procedures were performed are indicative of formation of new, in particular, cobalt sulfide, sulfate, and oxide, phases.

Thus, the results of the physicochemical examinations suggest that new phases (in particular, sulfide and sulfate) are generated on the surface of the cobalt-alumina catalyst during formation of the contacts. To identify the most active phase, experiments with individual CoS·Al₂O₃, CoSO₄·Al₂O₃, and Co₃O₄·Al₂O₃ as catalysts were carried out.

The optimum conditions for these experiments, as established earlier, were as follows: temperature 350°C, space velocity 1000 h⁻¹, (CO + H₂) : SO₂ = 2.1 (vol/vol), and SO₂ concentration in the initial gas 20 vol %. The results are shown in Fig. 4, which suggest that the most active compound among those tested is γ -Al₂O₃-supported Co₃O₄; its maximum activity is stabilized after 2 h in reaction medium.

Obviously, the most active ratio of the components (CoS, CoSO₄, CoO) is achieved faster in the case of cobalt oxide. Thus, in the spent catalyst sample cobalt occurs in three different forms: sulfide, sulfate, and oxide.

CONCLUSIONS

(1) The products of steam conversion of natural gas, characterized by the CO : H_2 ratio of 1 : 4, were found to be the most active reducing agents for SO₂.

(2) The cobalt-alumina catalyst displays high catalytic activity at 300-350°C, with the sulfur yield after the stage I reactor being 64-90% depending on space velocity (250-2000 h⁻¹).

(3) In spent cobalt-alumina catalyst sample, cobalt is represented by a mixture of cobalt oxide, sulfide, and sulfate.

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