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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Catalytic Conversion of COS and CS_2 under an Excess of Sulfur Dioxide

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Abstract—Conversion of organosulfur components (COS and CS_2) in catalytic processing of a real reduced sulfurous gas was experimentally studied.

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At present, about 40 million tons of sulfur is annually produced in the world in purification of discharge gases by the Claus method in natural-gas- and oil-processing industries [1]. It is prognosticated [2] that, with the environment protection regulations becoming increasingly stringent and requiring higher ecological payments, the volume of accompanying sulfur used to manufacture fertilizers will grow via utilization of metallurgical sulfurous gases. The only working technology for processing of these gases into sulfur is reduction with hydrocarbons, followed by catalytic conversion by the Claus method [3]. Because of the specific features of reduced sulfurous gas, its catalytic conversion strongly differs from that in the classical Claus technique [1, 4]. This circumstance determines the topicality of its analysis with account of parameters of a gas being processed.

A characteristic feature of the reduced gas is the increased content of organosulfur compounds (CS_2 and COS) formed from carbon introduced with the reducing agent, which predetermines the priority role of their conversion, traditionally the most difficult stage in catalytic processing by the Claus method [1, 4]. At large contents of sulfur dioxide, characteristic of the reduced sulfurous gas [5], the commonly taken into account mechanism of COS and CS_2 hydrolysis [1, 3] experiences competition from the alternative channel of conversion by reactions of sulfur dioxide reduction:

$$CS_2 + SO_2 = CO_2 + 3/nS_n, \quad (1)$$

$$2COS + SO_2 = 2CO_2 + 3/nS_n, \quad (2)$$

whose contribution can be predominant under an excess of SO_2.

The aim of our study was to experimentally analyze specific features of the conversion of organosulfur components (COS and CS_2) in catalytic processing of a reduced sulfurous gas.

EXPERIMENTAL

We performed tests in the temperature range 220–600°C on a pilot installation with a flow rate of the gas mixture equal to 0.6–0.7 standard $m^3 h^{-1}$ at Gipronikel' Institute Limited Liability Company. We studied two promising vanadium-containing catalysts: titanium oxide catalyst AOK-78-57 with a specific surface area of 145 $m^2 g^{-1}$ (extrudates 4–5 mm in diameter), manufactured by Katalizator Limited Liability Company (Novosibirsk), and a new VA-2 catalyst on an alumina support, developed at the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, and manufactured by Novomichurinsk Catalyst Plant Private Company in the form of spherical grains 4–5 mm in diameter and active surface area of no less than 240 $m^2 g^{-1}$.

The tests were made in a vertical stainless steel reactor with external electric heating (catalyst-containing cartridge with an inner diameter of 53 mm and height of 175 mm) and a catalyst charge of 0.38 dm^3. The temperature was controlled and recorded in the course of the experiments with a DT-600 digital data-acquisition device [Data Taker Pty. Ltd. (Data Electronics)]. Metran 231-01 Chromel–Alumel thermoelectric transducers (thermocouples) with a sheath diameter of 3 mm were used as temperature sensors. One of the thermocouples, buried to 4/5 of the catalyst bed height, was also used to maintain the reactor temperature; the electric power for heating the reactor and gas heater was varied using TP 403 microproc-

Gas compositions before and after conversion on the VA-2 catalyst

Gas component	Content, vol %	
	initial	at the outlet
SO_2	20.9 ± 6.5	12.5 ± 8.0
CO	<0.001	0.00 ± 0.03
H_2	3.7 ± 2.4	4.0 ± 3.2
CO_2	14.6 ± 1.9	21.5 ± 5.0
H_2S	6.1 ± 3.0	8.3 ± 7.0
COS	2.0 ± 0.97	1.2 ± 0.8
CS_2	6.2 ± 2.6	2.9 ± 2.6
CH_4	3.7 ± 2.7	3.8 ± 2.6
N_2	43.8 ± 4.4	44.9 ± 6.1

essor heat-control units manufactured by Varta Research and Production Company (St. Petersburg).

The coefficient (degree) of conversion of components of the gas mixture, η_i, was found using the formula [6]:

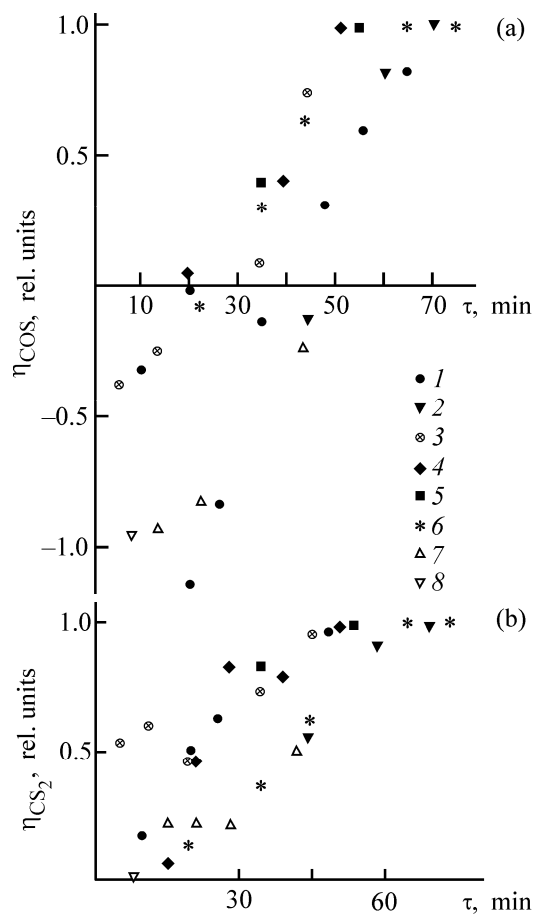

Fig. 1. Relative change in the conversion of (a) carbonyl sulfide, η_{COS}, and (b) carbon disulfide, η_{CS_2}, during tests for a time τ at different temperatures of the VA-2 catalyst. (*6–8*) Conversion on the AOK-78-57 catalyst. *T* (°C): (*1*, *6*) 310, (*2*) 340, (*3*, *4*) 380, (*5*) 450, and (*7*, *8*) 250.

$$\eta_i = 1 - \frac{c_i^{out} c_{N_2}^{in}}{c_i^{in} c_{N_2}^{out}}, \quad (3)$$

where c_i^{in} and c_i^{out} are the initial and final concentration of gas component i (i = H_2S, COS, SO_2), and $c_{N_2}^{in}$ and $c_{N_2}^{out}$, the initial and final concentrations of nitrogen in dried gas samples taken at, respectively, the inlet and outlet of the catalytic reactor.

The gas composition was monitored at four points of the pilot installation with an automated analytical complex based on a gas analyzer, EMG 20–1 time-of-flight mass spectrometer manufactured by METTEK Limited Liability Company (St. Petersburg), which can measure the volume concentrations of all the basic components of the gas: H_2S, SO_2, SO_3, COS, CS_2, CO, CO_2, H_2, CH_4, O_2, N_2, and Ar with a threshold sensitivity of 0.01–0.03%. The EMG 20-1 gas analyzer was calibrated against reference gas mixtures prepared at Scientific Instruments Open Joint-Stock Company and Monitoring Limited Liability Company (both from St. Petersburg).

In the course of the tests, a real sulfurous gas reduced in the homogeneous reactor of the pilot installation at a temperature of 1100°C in accordance with the promising technology for processing of metallurgical gases [7] was delivered to the inlet of the catalytic reactor (see table).

In all, the tests were made in 67 operation modes for the VA-2 catalyst and 57 modes for the AOK-78-57 catalysts. The modes differed in temperature at the same initial composition of the gas (see table) and volumetric flow rates W = 1500–1900 h^{-1}.

The results obtained in the pilot tests show that the high efficiency of conversion of organosulfur components on the catalysts under study is high. For example, this is indicated by comparison of the initial composition of the gas with that at the outlet of the catalytic reactor, found from a sample of measurements in 60 modes at a gas flow rate of 11 ± 1.1 standard dm^3 min^{-1} (W = 1600–1900 h^{-1}), also represented in the table.

It can be seen that more than a half, on average, of the organosulfur compounds (CS_2 and COS) is converted in catalytic processing of a reduced sulfurous gas. In the process, the content of carbon dioxide noticeably increases (nearly twice, on average), which points to the decisive contribution of reactions (1) and (2) of sulfur dioxide reduction to the overall conversion.

We observed a rapid variation of the activities of both the catalysts, which is manifested in that the conversion grows during the first hour after a catalyst is put into operation in the on-line mode. This effect is illustrated by Fig. 1, in which the conversion coefficients of sulfur-containing components, η_i, normalized to the maximum conversion of a given component, are arranged in order of increasing time τ elapsed from the beginning of a run. Different symbols in the figure show results of measurements in different runs, on different catalysts, and at different process temperatures.

The activity variation is manifested to the maximum extent in conversion of COS, whose relative conversion coefficient η_{COS} on the alumina catalyst VA-2 changes from –100% to 100% in 1 h (Fig. 1a). The conversion of sulfur dioxide and the overall conversion of sulfur-containing components varies qualitatively similar to η_{CS_2}. The conversion of hydrogen sulfide shows no dynamic effect.

A similar dynamic effect was observed on the titanium oxide catalyst AOK-78-57, on which the conversion of carbonyl sulfide varied under identical process conditions, e.g., at $T \approx 420$°C, from –80 to 76 rel % (Fig. 1).

The statistical scatter of values in the dynamic dependences of the conversion of both the organosulfur components, $\eta_i(\tau)$, is due to uncontrollable specific features of each run (duration of catalyst acidification) at its beginning. Nevertheless, the data scatter σ observed in different runs is noticeably smaller than the variance $\delta\eta_i(\tau)$: $3\sigma < \delta\eta_i(\tau)$, which demonstrates that the dynamic effect is revealed rather reliably.

The activities of the catalysts in CS_2 and COS conversion, determined after 1 h and more of uninterrupted operation, nearly coincide to within the experimental error, even though a tendency is observed for η_{CS_2} to somewhat exceed the conversion of carbonyl sulfide, η_{COS}, under the same conditions.

For illustration, Fig. 2 shows the average, over temperature intervals, conversions of carbonyl sulfide, η_{COS}, and carbon disulfide, η_{CS_2}, on the VA-2 catalyst as functions of temperature in the catalyst bed. The vertical portions correspond to the variances of the averages, and the horizontal portions (defined as variance) are proportional to the width ΔT of the averaging interval.

A possible reason for the appearance of the dynamic dependence of the activities of the catalysts

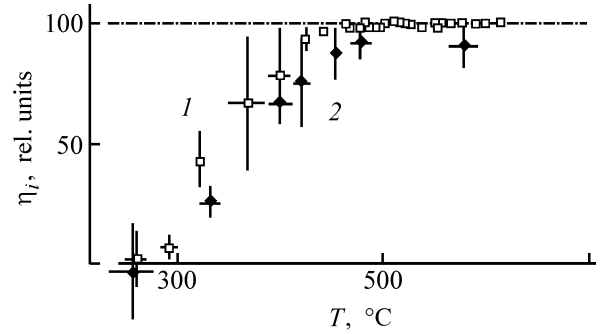

Fig. 2. Conversion η_i of (*1*) carbon disulfide and (*2*) carbonyl sulfide on the VA-2 catalyst vs. temperature T at a volumetric flow rate of 1600–1800 h^{-1}.

tested is their short-term poisoning via sulfation in the warm-up and startup of the installation with the oxygen-containing sulfurous gas. As follows from the results of our tests, the catalyst activity in conversion of organosulfur compounds, low at the beginning of a run, is completely restored during the first hour of on-line operation in the medium of a reduced gas, which contains reducing components (H_2, CO, and H_2S), but is free of oxygen. The differences in the degrees of initial sulfation of a catalyst in each startup predetermine the observed statistical scatter of the empirical values in the dynamic dependences $\eta_i(\tau)$.

As follows from the results of our experiments, CS_2 interacts with SO_2 at least in two stages, with carbonyl sulfide formed in the first of these. The only possible other intermediate in the first stage is, according to the stoichiometric balance of the overall reaction (1), sulfur oxide S_2O, as suggested by the two-stage scheme of the process [6]:

$$CS_2 + SO_2 = COS + [SO_2] = CO_2 + 1/8S_8. \quad (4)$$

In the initial period of operation of a catalyst after its sulfation, carbonyl sulfide is generated, which is manifested in large negative values of its conversion η_{COS} (Fig. 1a). Together with the simultaneously high conversion of carbon disulfide (Fig. 1b), this circumstance suggests that the second stage of carbonyl sulfide conversion is the rate-determining stage, the most sensitive to the catalyst sulfation.

An alternative explanation of the generation of carbonyl sulfide, e.g., that by interaction on the catalyst with sulfur vapor:

$$CO + 1/nS_n = COS, \quad (5)$$

would not do because of the insufficient initial concentration of carbon monoxide (see table). No con-

version of methane (also present in the starting gas), which could serve as a reactant for COS formation, was observed in our experiments within the experimental error limits.

According to the two-stage mechanism of carbon disulfide conversion by reaction (4), with the rate-determining second stage, the conversion of carbon disulfide should be more efficient than that of COS, and this, indeed, was observed in our experiments (Fig. 2). This makes it possible (at least as regards the processing of a reduced sulfurous gas) to reconsider the known paradigm [1, 4] of the more efficient conversion of COS. According to the results of this study, the conversion of organosulfur compounds under an excess of sulfur dioxide predominantly occurs via redox reactions with sulfur dioxide, of which the most efficient is that with CS_2.

The fact that the dynamic effect is observed on catalysts of different types (alumina catalyst VA-2 and titanium oxide catalyst AOK-78-57) means that the conversion of carbonyl sulfide is not directly related to the properties of the active surface, but occurs via adsorption of COS on active basic centers. By analogy with the hydrolysis process [8], the role of centers of this kind can be played by hydroxy groups, which are subject to sulfation in the presence of oxygen.

CONCLUSIONS

(1) If an excess of SiO_2 is present in the gas being processed, the conversion of organosulfur compounds predominantly occurs via their oxidation by sulfur dioxide. An intermediate formed in oxidation of carbon disulfide is carbonyl sulfide, whose further conversion is hindered by sulfation of the active centers of a catalyst. As a result, the conversion of carbon disulfide under an excess of SO_2 is more complete than that of carbonyl sulfide, which predetermines the principal characteristic feature of the catalytic processing of a reduced sulfurous gas.

(2) The experimental data obtained directly confirm for the first time the two-stage mechanism of carbon disulfide conversion by reaction (4) to give COS as an intermediate product of CS_2 conversion.

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