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## BRIEF COMMUNICATIONS

# Gas Composition Effect on the Klauss Process Efficiency

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**Abstract**—The effect of the initial gas composition on the efficiency of the catalytic reaction of the hydrogen sulfide oxidation by sulfur dioxide was studied experimentally.

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At present tens millions tons of sulfur are produced in the world annually at gas processing and petroleum refining plants according to the Klauss method based on the process of hydrogen sulfide catalytic oxidation by sulfur dioxide at 230–260°C [1]:

$$2H_2S + SO_2 = 2H_2O + 3/nS_n,\ n = 1–8 \quad (1)$$

In this case any estimate of the Klauss process efficiency (activity of catalysts) in sulfur recovery units (SRU) based on measuring final concentrations $[SO_2]$ and $[H_2S]$ in SRU tail gas [2, 3] should take into account a variation of composition (ratio of reagents) in a processed gas. This is especially important in processing gas with a low (less than 8 vol %) and variable initial concentration of hydrogen sulfide that is characteristic, for example, for the technology of coke-oven gas desulfuration used at "Magnitogorsk Iron and Steel Works" JSC [4].

## EXPERIMENTAL

The effect of original gas composition on the efficiency of Klauss reaction (1) was studied using the data of testing the process of conversion of sulfur-containing gases in a catalytic reactor, which forms a part of a pilot plant of the "Institute Gipronikel" Corporation [5]. The technique of the catalytic experiment on this pilot plant was described in detail earlier [6]. In this experiment we used an AO-MK-2 aluminum-oxide catalyst of the Klauss process produced by "Novomichurinsk catalytic factory" ZAO in the form of spherical granules of 4–5 mm in diameter with an active surface area no less than 240 $m^2\ g^{-1}$ [7].

The AO-MK-2 catalyst was tested in the temperature range of 219–279°C usual for industrial Klauss reactors. The gas consumption on the reactor inlet was 10–15 $ndm^3\ min^{-1}$, which corresponds to the volume rate of 1600–2000 $h^{-1}$ at the full load of the catalyst (0.38 $dm^3$). As the Klauss reactor is the third basic apparatus of the pilot plant, the composition of the gas containing sulfur and water vapors on the reactor inlet completely corresponds to the composition and variations of gas in industrial plants of sulfur extraction by the Klauss method according to the requirements of adequacy of tests [8]. Hydrogen sulfide initial concentrations $[H_2S]_0$ in the pilot tests of the AO-MK-2 catalyst were varied in the range of 0.8–37.4 vol %.

Gas composition on the inlet and outlet of the Klauss reactor of the pilot plant was measured by an automatic analytical complex based on an EMG 20-1 time-of-flight mass spectrometer as a gas analyzer allowing the determination of volume concentrations of all main gas components ($H_2S$, $SO_2$, $SO_3$, 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%. To calibrate the gas analyzer, we used the verification gas mixtures prepared by "Scientific devices" JSC and "Monitoring" Corporation (the both in St. Petersburg).

Typical characteristics of the dry gas composition observed in the pilot test on the Klauss reactor inlet are given in the table.

Conversion degree of hydrogen sulfide, as well as those of other sulfur-containing gas components $\eta_i$, were determined, as it is accepted in the industry [1, 2, 8, 9],

from measurements of the composition of dry gas samples on the Klauss reactor inlet and outlet by formula (2).

$$\eta_i = 1 - \frac{c_i^{out} c_{N_2}^{in}}{c_i^{in} c_{N_2}^{out}}, \quad (2)$$

Here $c_i^{in}$ and $c_i^{out}$ are initial and final concentrations of the $i$-th gas component ($i$ – $H_2S$, COS, $SO_2$), $c_{N2}^{in}$ and $c_{N2}^{out}$-initial and final nitrogen concentrations in dry gas samples taken on the inlet and outlet of the catalytic reactor, respectively.

The gas composition on the Klauss reactor inlet was taken into account as a ratio of components, which was determined according to Klauss ratio (3).

$$CR = \frac{[H_2S]^{in}}{[SO_2]^{in}} = [H_2S]_0/[SO_2]_0. \quad (3)$$

The average value of the Klauss ratio on the reactor inlet was $CR \equiv [H_2S]_0/[SO_2]_0 = 2.0$, and the maximal value $CR_{max}$ was 42.5 over the whole period of testing the AO-MK-2 catalyst.

The figure shows the empirical dependence of the observed hydrogen sulfide conversion degree on the initial composition of the processed gas, which was constructed by the results of the pilot experiments under Klauss conversion ordinary conditions. Separate values of the hydrogen sulfide conversion degree $\eta_{H_2S}$ calculated by formula (2) from the measured gas compositions are presented as a function of the initial gas composition defined by Klauss ratio CR (3). Points show real values of the hydrogen sulfide conversion degree found in the pilot tests of the AO-MK-2 catalyst and $\eta_{H_2S}$(CR) dependence of the hydrogen sulfide conversion degree on the factor of the composition calculated for the completed unique Klauss reaction (1) is depicted by a dashed line.

Gas composition on the Klauss reactor inlet

| Gas mixture component | Concentration, vol % |
|---|---|
| $SO_2$ | 7.4 ± 4.0 |
| CO | 1.2 ± 0.8 |
| $H_2$ | 3.4 ± 2.3 |
| $CO_2$ | 29.7 ± 4.9 |
| $H_2S$ | 6.6 ± 3.3 |
| COS | 0.03(0–1.2) |
| $CS_2$ | 0.06(0–0.9) |
| $CH_4$ | 3.8 ± 3.4 |
| $N_2$ | 47.5 ± 5.8 |

Vertical dash-dotted line denotes the ratio of components corresponding to the stoichiometry of Klauss reaction (1) CR = 2.

The comparison of the pilot test data in the figure with an ideal modeling curve for the conversion by reaction (1) confirms the fact that the degree of hydrogen sulfide conversion is independent of the initial gas composition in the region of considerable excess of sulfur dioxide (at CR < 1). It allows us to control the real activity of Klauss catalysts under conditions of a hydrogen sulfide shortage without taking into account its initial concentration.

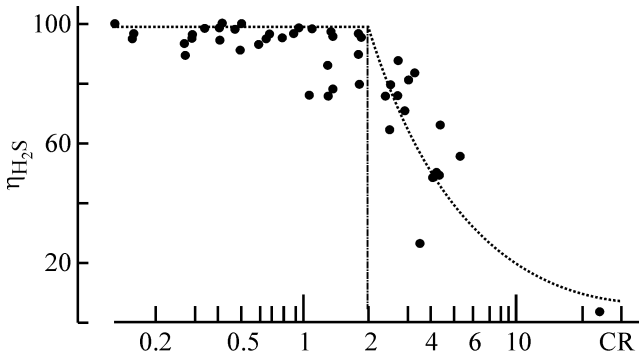
Obvious qualitative correspondence of the empirical data and the modeling curve (see the figure) allows us to simplify considerably the control over a catalyst in reactors operating at reduced Klauss ratios. It concerns, for example, catalytic reactors of the section of elemental sulfur production at Copper factory of Arctic branch of "Norilsk nickel" mountain-metallurgical company JSC at typical values of Klauss ratio: CR ≤ s1 [9].

Control of a catalytic activity can be based on the determination of the rate constant $K$ of the hydrogen sulfide conversion in kinetic equation (4) of the Klauss reaction.

$$-\frac{d[H_2S]}{dt} = K[H_2S][SO_2]^{0.5}, \quad (4)$$

Here $K$ values are determined in various ranges of the composition factor CR as follows.

At the initial ratios $CR \equiv [H_2S]_0/[SO_2]_0 = 2$ corresponding to the stoichiometry of Klauss reaction (1) the values of the kinetic constant $K$ in equation (4) can be determined from initial $c_0 \equiv [H_2S]_0$ and final $c \equiv [H_2S]$




Dependence of the hydrogen sulfide conversion degree $\eta_{H_2S}$ (%) on the Klauss ratio CR (relative units) in the initial gas according to the results of the pilot test of the AO-MK-2 catalyst at the volume rate $W \sim 1700$ h$^{-1}$ and temperature $T$ 230–250°C.

hydrogen sulfide concentrations in a purified gas attained during a catalytic contact time $t$ [10]:

$$K = (1 - c^{1/2}/ c_0^{1/2}) / (tc^{1/2}) = (c^{1/2}/ c_0^{1/2} - 1)/ (tc^{1/2}). \quad (5)$$

For the cases of processing gas under conditions of hydrogen sulfide shortage, i.e. at $[SO_2]_0 >> [H_2S]_0$ (that is characteristic for reduced sulfur dioxide [9]), the dependence on sulfur dioxide concentration is degenerated, and expression (4) is reduced to first-order equation (6).

$$K' = - \ln[H_2S][H_2S]_0/t, \quad (6)$$

Here the rate constant $K'$ is determined from the relative hydrogen sulfide overshoot $[H_2S]/[H_2S]_0$ at a contact time $t$.

The time dependence of the hydrogen sulfide conversion degree $\eta_{H_2S}$ ($t$)

$$\eta_{H_2S} = 1 - \exp(-K't) \quad (7)$$

corresponding to equation (6) does not depend on the initial concentration $[H_2S]_0$, which can essentially simplify the control in the industrial experiment and raise reliability of conclusions for considerable excesses of sulfur dioxide, i.e. at CR <1.

The results of the pilot tests have allowed us to compare characteristics of the AO-NKZ-2 catalyst activity with the characteristics of its industrial operation determined earlier. Thus, the substitution of the values of hydrogen sulfide conversion at 250°C $\eta_{H_2S} \approx 75\%$ (averages for the sample for Klauss ratios CR ≈ 1–4 in view of an error of CR determination), of the concentration on the pilot reactor inlet $[H_2S]_0 \approx 8$ vol %, and of empty (i.e. related to the whole catalyst volume) time $t^* \sim 1.2$ s in equation (5) gives the empty value of the reaction (1) rate constant: $K^* = 3.0$ atm$^{-1/2}$ s$^{-1}$. This value of the Klauss reaction rate constant practically coincides with the value $K^* \approx 2.8$ atm$^{-1/2}$ s$^{-1}$ determined similarly in [8] for the initial (from 11.04.2003 up to 20.04.2003) period of the AO-MK-2 catalyst operation in the Klauss reactor of "Magnitogorsk Iron and Steel Works" JSC.

## CONCLUSION

An examination of the data of pilot experiments shows that observed efficiency of the reaction of hydrogen sulfide oxidation by sulfur dioxide on aluminum-oxide catalysts essentially depends on a ratio of reagents that should be taken into account when controlling current activity of catalysts in industrial-scale Klauss plants.

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