ISSN 1070-4272, Russian Journal of Applied Chemistry, 2010, Vol. 83, No. 9, pp. 1548–1552. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © Yu.A. Aleksandrov, A.V. Belyaev, A.Yu. Sozin, M.F. Churbanov, 2010, published in Zhurnal Prikladnoi Khimii, 2010, Vol. 83, No. 9, pp. 1448–1452.

PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Hydrogen Sulfide Oxidation by Ozone on Sorbents-Catalysts

Yu. A. Aleksandrov[a], A. V. Belyaev[a], A. Yu. Sozin[b], and M. F. Churbanov[b]

[a] Lobachevsky State University, Nizhni Novgorod, Russia
[b] Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, Nizhni Novgorod, Russia

Received February 15, 2010

Abstract—Effect of the sorbents SK-2001, SK-2002, SK-1138, SK-498, SK-8, SK-174, SK-57, SK-458, SK-455, SK-19, and SK-72 based on a KhIPEK synthetic ceramics on the oxidation of hydrogen sulfide by ozone was studied. The sorbents that catalyze the reaction of hydrogen sulfide oxidation by ozone were determined.

DOI: 10.1134/S1070427210090089

Hydrogen sulfide is used or formed in a number of chemical industries and is one of the main products in such processes as biomass rotting and volcanic eruptions. Hydrogen sulfide is highly toxic. Therefore, purification of air to remove hydrogen sulfide is a topical task in a number of cases. A promising method for air purification to remove hydrogen sulfide is its oxidation with ozone.

It is known [1] that ozone is widely used for sanitary purification and deodorization of air. However, this process is insufficiently effective in the homogeneous mode of air purification to remove ecologically hazardous chemical compounds with low or extremely low maximum permissible concentrations (MPCs) in air and, in particular, hydrogen sulfide.

It is known that, in the gas phase, one molecule of ozone reacts with one molecule of hydrogen sulfide to give sulfur dioxide and water [2]. However, the relevant kinetic data are contradictory. Studies of this reaction in flow conditions demonstrated that its order with respect to ozone is 1.5 and that with respect to hydrogen sulfide is “zero” [3] or 0.5 [4]. It was found in [3] that the rate constant k [$M^{-1}/2\ s^{-1}$] of the reaction between ozone and hydrogen sulfide is described by the equation

$$\log k = 6.9 - 8300/2.3RT, \tag{1}$$

where $k(25°C) = 8.5 \pm 2\ M^{-1}/2\ s^{-1}$, R is the universal gas constant (1.987 $cal\,mol^{-1}\,K^{-1}$), and T is the absolute temperature (K).

It should be emphasized that the rate constant is small at room temperature. Therefore, it seems promising to oxidize hydrogen sulfide with ozone in the presence of sorbents that raise the reactant concentrations on their surface and thereby make higher the process rate.

The aim of the study was to examine whether the sorbents can be used to accelerate the reaction of hydrogen sulfide oxidation by ozone.

EXPERIMENTAL

Experiments were carried out with sorbents based on a KhIPEK synthetic ceramics (SC) [5, 6]. The KhIPEK sorbents are based on natural clays. Ceramic materials of acid and alkaline nature were used. The acid nature of a ceramic was provided by introduction of H_3PO_4 into the raw material. The composition of the stock for the acid ceramic was varied by changing the proportion of the introduced amount of natural clays with addition of an anticorrosive cement and wood flour. In calcination of the sorbents, the wood flour burns out and makes the sorbents porous. The alkaline nature of a ceramic was provided by introducing powdered aluminum, oxides of alkaline-earth metals into the stock and using a high-modulus liquid glass as a stock binder. In this study, some separate components of the stock were also used to study the behavior of ozone and oxidation of hydrogen sulfide.

The following sorbents were used: SK-2001, SK-2002, SK-1138, SK-498, SK-8, SK-174, SK-57, SK-

458, SK-455, SK-19, and SK-72. The characteristics of these sorbents are listed in Table 1.

Table 1. Characteristics of the sorbents used

Sorbent	S_{sp}, m^2 g^{-1}	Nature of a sorbent
SK-174	1.30	Acid
SK-458	0.20	The same
SK-72	0.60	″
SK-19	4.50	Alkaline
SK-8	1.60	Acid
SK-455	1.86	The same
SK-2001	0.60	″
SK-2002	16.00	″
SK-498	11.80	″
SK-1138	11.50	Alkaline
SK-57	1.10	The same

The behavior of ozone in the presence of an SC was examined as follows: the ozone concentration in the gas phase was measured at the outlet of a flow-through reactor when passing an ozone–oxygen mixture (OOM) with and without a sorbent. A flow-through tubular Pyrex-glass reactor with a length of 50 mm and diameter of 9.5 mm was charged with a fraction of sorbent grains with a diameter of 1.0–1.5 mm. The ozone concentration in the OOM was determined spectrophotometrically on an SF-46 spectrophotometer in a gas-flow cuvette 50 mm long and 12 mm in diameter. The measurements were made at a wavelength of 254 nm. The molar extinction coefficient of ozone was taken to be 3033 M^{-1} cm^{-1} [7]. The spectrophotometric cuvette was made of a fluoroplastic and had quartz windows. The OOM was delivered into the reactor at a rate of 100 ml min^{-1}, the experiments were carried out at a temperature of 20 ± 0.5°C. The ozone concentration in the gas phase at the reactor inlet was $(3.3 \pm 0.1)\times10^{-5}$ M. The installation for analysis of the ozone decomposition is shown schematically in Fig. 1. The ozone concentration in the gas phase at the reactor inlet was measured when the OOM passed through reactor *1* at closed valves *2* and *3* and open valve *4*. The ozone concentration in the gas phase at the reactor outlet was measured when the OOM was passed through the reactor at open valves *2* and *3* and closed valve *4*. First, the ozone concentration at the reactor inlet was measured. Then valve *4* was closed, valves *2* and *3* were open, and the ozone concentration in the gas phase was measured at the reactor outlet as a function of the time of OOM blowing-through. The time of the OOM contact with the sorbent was calculated as the ratio between the sorbent-free volume of the reactor and the OOM delivery rate. This ratio was 1.0 ± 0.1 s in all the experiments.

Hydrogen sulfide was oxidized with ozone in the same reactor as that used for analysis of the ozone decomposition. The kinetics of hydrogen sulfide oxidation by zone was studied with pulsed introduction

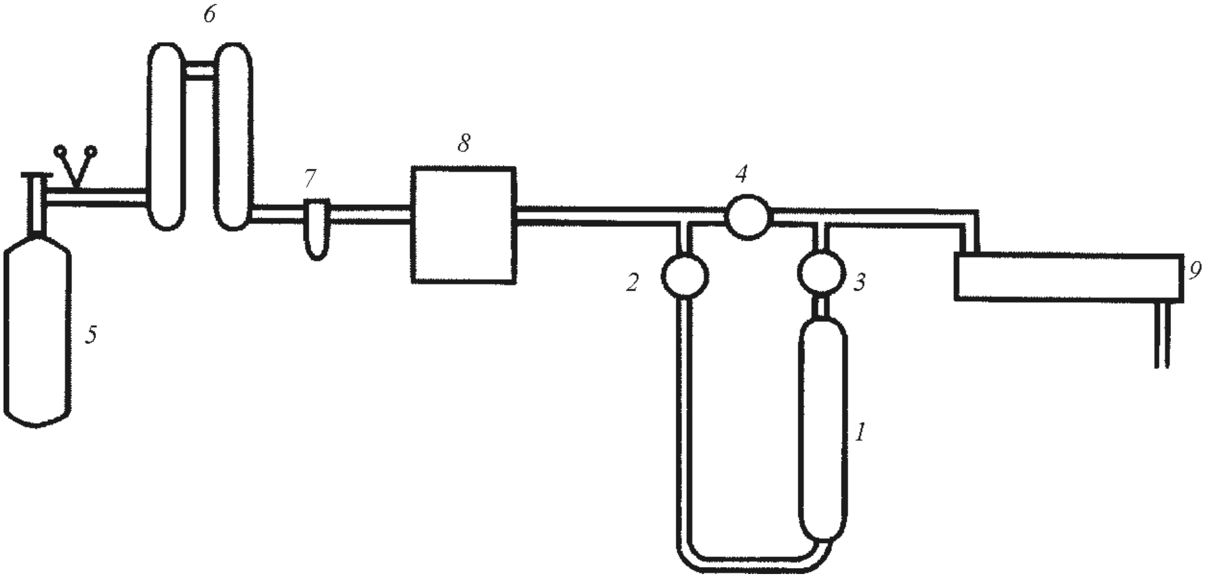

Fig. 1. Schematic of the installation for studying the kinetics of ozone decomposition on SCs. (*1*) Reactor, (*2*–*4*) fluoroplastic valves, (*5*) cylinder with oxygen, (*6*) drying columns with molecular sieves and phosphorus pentoxide, (*7*) gas flow controlling unit, (*8*) ozonizer, and (*9*) spectrophotometric cuvette.

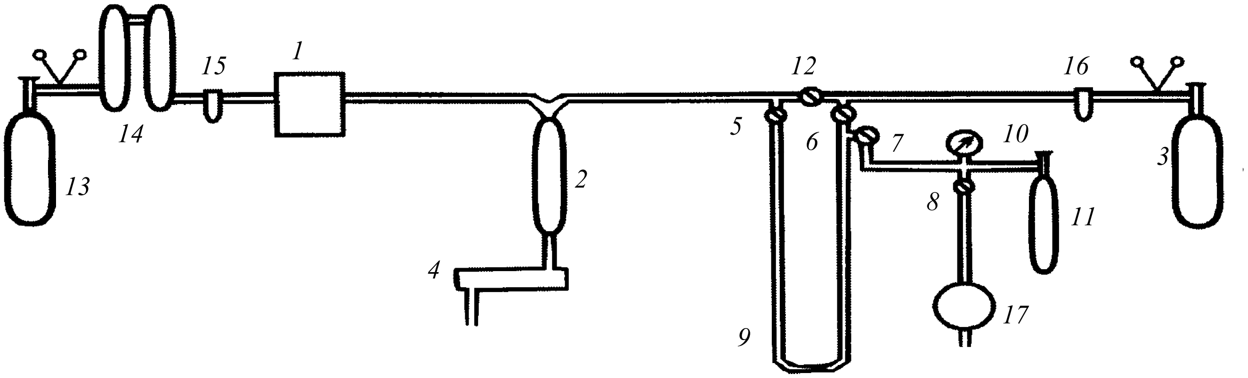

Fig. 2. Schematic of the installation for studying the oxidation of hydrogen sulfide. (*1*) Ozonizer, (*2*) reactor, (*3*) cylinder with dried air, (*4*) spectrophotometric cuvette, (*5–8, 12*) fluoroplastic valves, (*9*) feed chamber, (*10*) standard vacuum gage, (*11*) cylinder with a mixture of H_2S (0.25 vol %) with air, (*13*) cylinder with oxygen, (*14*) drying columns with molecular sieves and phosphorus pentoxide, (*15, 16*) gas flow controlling units, and (*17*) roughing pump.

of the reagent into the reactor. The installation used for this purpose is shown schematically in Fig. 2. The experiment was carried out as follows: an ozonized flow of oxygen at the outlet of ozonizer *1* was permanently mixed, before being fed into the reactor, with a flow of air from cylinder *3*, which carries hydrogen sulfide. After passing through the sorbent bed in reactor *2*, the mixture was delivered to spectrophotometric cuvette *4*, in which the ozone concentration was measured.

A prescribed amount of hydrogen sulfide was introduced into the air line as follows: air was evacuated at closed valves *5* and *6* and open valves *7* and *8* from feed chamber *9*, with the process monitored with a standard vacuum gage *10*. Further, a mixture of hydrogen sulfide and air from cylinder *11* was let in until the atmospheric pressure was attained. After that valves *7* and *8* were closed. Hydrogen sulfide was delivered into the reactor by opening valves *5* and *6* and closing valve *12*. Air from the bypass channel transferred hydrogen sulfide from feed chamber *9* to the reactor inlet, where it was mixed with the OOM.

The concentrations of hydrogen sulfide and ozone in the reaction mixture before the reactor were $(5.5 \pm 0.1)\times10^{-5}$ M. The delivery rates of the OOM and air carrying a “pulse” of hydrogen sulfide were 50 ml min^{-1}. The total rate of reactant delivery into the reactor was 100 ml min^{-1}. The temperature during the experiment was 20 ± 0.5°C. The time of contact between hydrogen sulfide and a sorbent was 1.0 ± 0.1 s in all the experiments. Hydrogen sulfide and its oxidation products, sulfur dioxide and trioxide, have the following molar extinction coefficients at a wavelength of 254 nm: 1.8 [8], 40 [9], and 4.2 $\text{M}^{-1}\,\text{cm}^{-1}$ [10], respectively. Because of the extinction coefficients are small, the additive contribution of hydrogen sulfide and products of its oxidation to the optical density of ozone can be neglected. The ozone concentration in a pulse at the outlet of the reactor with a sorbent was used to calculate the loss X (%) of ozone by the formula

$$X = \frac{D_0 - D}{D_0} \times 100, \qquad (2)$$

where D_0 and D are the optical densities of ozone in a “pulse” at the inlet and outlet of the tube with a sorbent.

Experiments aimed to study the behavior of ozone on SCs yielded typical kinetic curves describing the dependence of the optical density D of the OOM at the outlet of the reactor packed with a sorbent on the time τ of OOM blowing-through (Fig. 3).

The region delimited by curves *3* and *4* and line *1* corresponds to displacement of air by the ozone–oxygen mixture from a reactor with quartz crumb (material hardly causing any decomposition of ozone under the experimental conditions). The sharp decline and rise in the optical density of ozone in displacement of air from the reactor packed with quartz make it possible to use curves *3* and *4*, with the “boundary” diffusion and mixing neglected, in interpretation of kinetic curves obtained with sorbents.

The region delimited by curves *2* and *3* and line *1* reflects the fact that, in addition to the displacement of

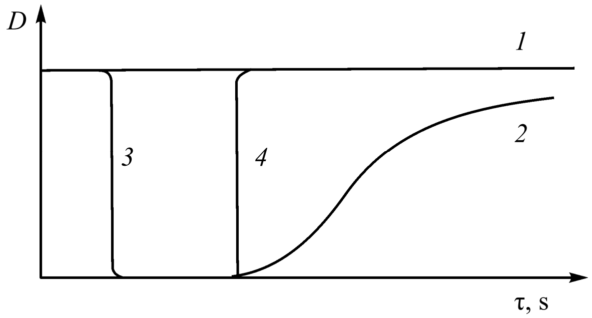

Fig. 3. Typical dependences of the optical density *D* of the OOM at (*1*) inlet and (*2–4*) outlet of the reactor with a sorbent on the time τ of OOM blowing-through.

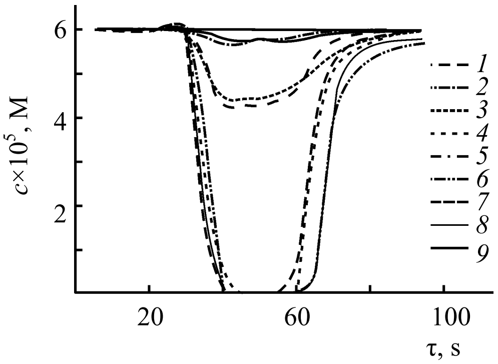

Fig. 4. Variation of the concentration c of ozone in the case when a hydrogen sulfide pulse passed through the reactor with (*1*) SK-2001, (*2*) SK-72, (*3*) SK-458, (*4*) SK-57, (*5*) quartz, (*6*) SK-498, (*7*) SK-174, and (*8*) SK-19. (τ) Time during which the mixture is passed through the reactor. (*9*) Ozone concentration at the inlet of the reactor.

air from the reactor, there occurs consumption of ozone as a result of its interaction with the sorbent.

The curves of ozone consumption on the sorbents SK-72, SK-2001, and SK-458 are identical to the curve of ozone consumption on quartz. This suggests that these materials have no significant influence on the consumption of ozone.

The consumption of ozone on the sorbents SK-498, SK-8, SK-174, SK-57, SK-455, and SK-19 is described by a kinetic curve similar to curve *2* in Fig. 3, which suggests that ozone interacts with these sorbents.

With the sorbents SK-2002 and SK-1138, no ozone was detected by the instrument during 5 min. This is indicative of a catalytic effect of the sorbent in ozone decomposition or a large surface area of the sorbent (Table 1) and, accordingly, a large number of reaction centers on the sorbent surface, which have not enough time to be noticeably consumed in the reaction with ozone in 5 min. The data on decomposition of ozone on SK-2002 and SK-1138 suggest that these sorbents can be regarded as promising materials for decomposition of ozone.

The heterogeneous oxidation of hydrogen sulfide by ozone was studied using SK-72, SK-2001, and SK-458 (comparatively inert toward ozone) and SK-57, SK-498, SK-174, and SK-19, "passivated" with ozone until its consumption in blowing-through the OOM through the rector with a sorbent ceased. When an ozone pulse mixed with the OOM is passed through the reactor under the experimental conditions, ozone is only consumed for the reaction with hydrogen sulfide. Figure 4 shows curves of how ozone is consumed when hydrogen sulfide is passed through an SC bed.

The calculated loss of ozone in a "pulse" at the outlet of the reactor with a sorbent is presented in Table 2. The loss of ozone from the mixture, calculated for a reaction mixture passed through a quartz crumb bed (X = 6%), was used to evaluate the efficiency of the sorbents in acceleration of the reaction of hydrogen sulfide by ozone. With the sorbents SK-2001, SK-498, SK-57, and SK-19, no ozone is observed at the instant when the OOM–H_2S mixture leaves the reactor. The acceleration of the oxidation of hydrogen sulfide by ozone in the presence

Table 2. Loss of ozone from a hydrogen sulfide pulse in its passing from a sorbent bed

Sorbent	Sorbent mass *m* in the reactor, g	Sorbent area *S* in the reactor, m^2	Loss of ozone, *X*, %
Quartz crumb	–	–	6±2
SK-2001	3.77	2.26	99±1
SK-498	2.60	30.68	99±1
SK-174	2.08	2.70	28±5
SK-57	0.95	1.05	99±1
SK-458	2.37	0.47	26±5
SK-19	1.02	4.59	99±1
SK-72	2.75	1.65	4±2

of SK-57 and SK-19 can be attributed to the alkaline nature of the sorbent, owing to which hydrogen sulfide is actively bound as an acid with the sorbent surface. In the presence of SK-498, the oxidation of hydrogen sulfide is possibly provided by its larger surface area, compared with the rest of the sorbents.

The results obtained indicate that SK-2001, SK-57, SK-19, and SK-498 are promising sorbents for accelerating the reaction of hydrogen sulfide oxidation by ozone.

CONCLUSIONS

(1) A procedure for evaluating the activity of sorbents as catalysts for oxidation of hydrogen sulfide by ozone and catalysts for ozone decomposition was developed.

(2) It was found that the sorbents SK-2001, SK-57, SK-19, and SK-498 catalyze the oxidation of hydrogen sulfide by ozone, and the sorbents SK-2002 and SK-1138 catalyze the decomposition of ozone.

REFERENCES

1. Lunin, V.V., Popovich, M.P., and Tkachenko, S.N., *Fizicheskaya khimiya ozona* (Physical Chemistry of Ozone), Moscow: Mosk. Gos. Univ., 1998.
2. Gregor, I.K. and Martin, R.L., *Aust. J. Chem*., 1961, vol. 14, no. 3, pp. 462–468.
3. Cadle, R.D. and Ledford, M., *Int. J. Air Water Pollut*., 1966, vol. 10, no. 11, pp. 25–30.
4. Hales, J.M., Wikes, J.O., and York, J.L., *Atmos. Environ*., 1969, vol. 3, no. 6, pp. 657–667.
5. RF Patent 2351573.
6. RF Patent 2331473.
7. Molina, L.T. and Molina, M.J., *J. Geophys.Res*., 1986, vol. 91, pp. 14501–14508.
8. Wu, C.Y.R. and Chen, F.Z., *J. Quant. Spectrosc. Radiat. Transfer*, 1998, vol. 60, pp. 17–23.
9. Bogumil, K., Orphal, J., Homann, T., Voigt, S., et al., *J. Photochem. Photobiol. A.: Photochem*., 2003, vol. 157, pp. 167–184.
10. Robinson, T.W., Schofield, D.P., and Kjaergaard, H.G., *J. Chem. Phys*., 2003, vol. 118, no. 16, pp. 7226–7232.