
**OXIDATION OF HYDROGEN SULFIDE OVER $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ CATALYST:
INFLUENCE OF SUPPORT TEXTURE AND Fe_2O_3 PRECURSOR**

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Activity and selectivity in hydrogen sulfide oxidation by oxygen on a $\text{Fe}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ catalyst was studied at 200°C and atmospheric pressure. Reaction products were sulfur and sulfur dioxide. Two factors influencing catalytic activity were studied: support porous structure and the type of Fe_2O_3 precursor. The porous structure of support influenced substantially catalytic activity; mesopores were more active than macropores. The catalysts prepared from $\text{Fe}(\text{NO}_3)_3$ and iron(III) acetylacetonate exhibited comparable activity, the lower activity was found for the catalyst prepared from $\text{Fe}_2(\text{SO}_4)_3$. The selectivity to sulfur formation was higher on catalysts containing greater amount of macropores and the value of it changed in the interval 0–85% depending on the type of catalyst.

The economy of chemical processes and the environment protection accelerate the effort to decrease the levels of pollutants in technical gases. One of the fields of interest now is the oxidative removing of hydrogen sulfide from natural gas, Claus tail gases, coal gas, biogas, etc., from percentage amounts to the ppm level.

It is very advantageous to keep the oxidation temperature above the melting point of sulfur because at such conditions the gaseous or liquid sulfur leaves the reactor and it is possible to work in a continuous regime. Efficiency and selectivity of such a process depend on the catalyst composition and its porous structure and they could be influenced by sulfur condensation in pores.

The $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ system is active and often studied catalyst for hydrogen sulfide oxidation^{1,2}. However, depending on the reaction conditions (temperature, water in the feed) it need not to be selective to sulfur formation^{2,3}. The Al_2O_3 support alone is very active at the beginning of the reaction but its activity decreases very quickly due to the formation of sulfates on its surface^{4,5}; sulfatation could be suppressed by Fe_2O_3 or Cr_2O_3 addition². Selectivity of this catalyst is decreased either by increasing temperature or by increasing of oxygen or water contents in the reaction mixture.

The activity and selectivity depend very deeply on the porous structure of the catalyst; important feature of porous media is pore radius. Steijns and Mars found²

that in the case of comparable dimensions of pores and sulfur molecules (0.5–1 nm) the adsorption of sulfur is very strong and hydrogen sulfide conversion is very high. They consider micropores to be dominant for the catalytic activity; on the other hand they state that meso and macropores* serve only as transport pores. Berben and Geus^{1,2} described the influence of Al₂O₃ support on the selectivity of oxidation for the Fe₂O₃/Cr₂O₃/Al₂O₃ system. The selectivity to sulfur was higher when α -alumina with low surface and wide pores was used while the lower selectivity was found for γ -alumina with high surface and narrow pores.

The present work is devoted to relation between porous structure of support and activity and selectivity of catalysts in hydrogen sulfide oxidation. The second aim of this work is to find any relations between the type of Fe₂O₃ precursor and activity of catalyst.

EXPERIMENTAL

Gases. Pure hydrogen sulfide (Merck-Schuchardt, 99.85%) and commercial nitrogen and air (both Technoplyn Praha) were used. The gases were dried on molecular sieves. Reaction mixture contained 1.7 vol. % H₂S, 1.7 vol. % O₂ and 96.6 vol. % N₂.

Catalysts. α -Alumina support denoted as N was supplied by Norton Chemicals (product number SA 3232) and contained 20% SiO₂. The samples of α -alumina denoted A0, A1, A2, A3, A4 and A5 were prepared from powdered boehmite (20–50 μ m, Pural SB, Condea Chemie, F.R.G.) by Valuš⁶ at various calcinating temperatures and pelleting pressures; the distribution of pore volume, V (cm³), with radius of pores, r (nm), have been gradually changed as it is shown in Fig. 1. All aluminas were crushed to the particle size fraction of 0.160–0.315 mm.

The preparation of catalyst consisted in impregnation of alumina by water solutions of Fe₂(SO₄)₃ and Fe(NO₃)₃ and ethanolic solution of iron(III) acetylacetonate; the catalysts contained 2 or 10% Fe₂O₃ in experiments where the influences of support texture or of precursor, respectively, were studied. Samples were dried and calcined in the stream of nitrogen at 400°C for 0.5 h. The surface areas of catalysts were measured by adsorption of nitrogen by the single-point dynamic method⁷. All catalysts were denoted as K(I), where I is the type of support.

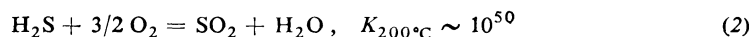
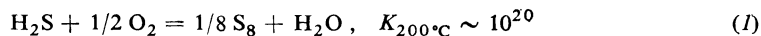
Apparatus and procedure. Tubular glass reactor (i.d. 2 mm) with fixed bed of catalyst was used. The feed rate of hydrogen sulfide was 0.77 ml min⁻¹ and the space time was 0.048 kg h mol⁻¹ and the reaction temperature was 200°C. The catalyst charge was activated at 400°C for 0.5 h and than the temperature of catalyst was kept at the temperature 200°C for 0.5 h. The content of H₂S and SO₂ in mixtures was determined by gas chromatography using a 2 m column filled with Chromosil 310 (Supelco) and a TC detector. The samples of reaction product and feed mixture were taken by sampling loop in thirty-minutes intervals.

Catalytic activity and selectivity. The conversion of hydrogen sulfide, x (H₂S), was obtained from the ratio of H₂S peak areas measured by integrator. The rate constants, k , were calculated from steady-state conversions providing that the oxidation is the first order reaction with respect to both H₂S and O₂.

* We distinguish three groups of pores in this work: micropores 0–30 nm, mesopores 30–500 nm and macropores larger than 500 nm.

The selectivity to sulfur was defined as ratio $S_{\text{SEL}} = [n^r(\text{H}_2\text{S}) - n(\text{SO}_2)] \cdot 100/n^r(\text{H}_2\text{S})$, where $n(\text{SO}_2)$ is number of moles SO₂ and $n^r(\text{H}_2\text{S})$ is number of moles H₂S reacted.

Thermodynamics of oxidation. The oxidation of H₂S at 200°C could be described by Eqs (1) and (2).



Very high equilibrium constants indicate the irreversible course of oxidation. The whole thermodynamical description of H₂S oxidation is rather more complex due to the presence of various sulfur molecules in the gas phase and due to the possibility of another reactions among reactants mentioned above. Gamson and Elkins⁸ have studied this equilibrium in detail and they found the equilibrium conversion of H₂S between 97–98% at 200°C.

RESULTS AND DISCUSSION

Condensation of sulfur. Assuming total conversions, the initial hydrogen sulfide concentration in the reaction mixture (1.7%) corresponds to the partial pressure of sulfur 0.23 kPa. The partial pressure of saturated sulfur vapour is 0.28 kPa at 200°C and so we can suppose that all sulfur should be in the gas phase. On the other hand, the presence of porous media in the reactor causes condensation of limited amount of sulfur in the narrowest pores. The initial deactivation of catalysts is obviously connected with deposition of sulfur in pores.

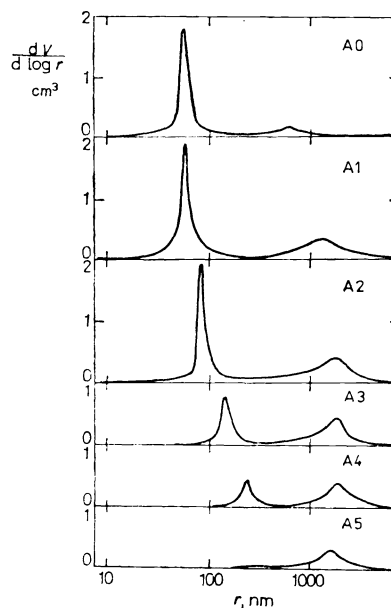


FIG. 1
Pore size distributions of alumina supports
A0 through A5

Initial deactivation is well seen in Fig. 2. The activity of all catalysts decreased continuously from the beginning of experiment and it was practically constant after 2 or 3 h; the representative steady-state activities were read out after 5 h. The catalyst K(N) exhibits the largest decrease of activity because it contains great amount of micropores. A significant fraction of surface area is blocked in the course of reaction (see Table I).

Steijns and Mars⁴ and Berben and Geus² described the same type of initial deactivation of Al_2O_3 and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts; the former authors found 1–6% of sulfur in catalysts after the reaction.

Selectivity of catalysts. Table I shows that the highest and the lowest selectivities exhibit catalysts K(N) and K(A0), while the selectivity of remaining catalysts is about 50%. It can be concluded that increased mesopore content in a catalyst diminishes its selectivity to sulfur formation. All other catalysts than K(A0) contain sufficient amount of macropores and that is why their selectivity is nonzero. The catalyst K(N) had the greatest amount of greatest pores and this is the reason of its highest selectivity. Conclusions presented are in accord with literature data² showing that very narrow pores decrease the selectivity to sulfur formation.

For the same conditions as in our work Berben and Geus² report 90% selectivity on the $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. Because they did not mention the porous structure of their catalyst in detail, the comparison with our catalysts is not possible.

Activity of catalysts. The oxidation reaction was studied at 200°C and atmospheric pressure on seven catalysts prepared by decomposition of iron(III) acetylacetonate on α -alumina supports mentioned above. All experimental data are collected in Table I.

The porous structure of catalysts K(A1) through K(A5) change continuously: the size and the volume of macropores is practically the same while the size and the volume of mesopores decreases and, at the same time, the surface area of catalysts decreases. Fig. 2 shows that the steady-state activities of catalysts decrease in the same order. For the sight it could seem that the fall of a steady-state activity of catalyst is only a consequence of surface area decrease (Fig. 3). However, the situation is not so clear and requires more detailed comparison of catalysts.

The catalysts K(A0) and K(A1) are very suitable for mutual comparison. Both samples have very close porous structure and they differ only in the volume and in the size of macropores and the surface area is nearly the same. The steady-state activity of sample K(A1) is three times higher than that of sample K(A0). The cause of activity increase obviously consists in better accessibility of catalytic centers in mesopores, let us say, in more effective transport of formed sulfur from mesopores. Simultaneously, it can be drawn from the presented data that mainly pores in radius about 50 nm are catalytically active. On the other hand, we could now expect, that catalyst K(N) will have significantly higher activity than K(A1) because

it contains approximately 50% pores smaller than 50 nm and the same amount of pores wider than 1 500 nm, i.e. enough of catalytically active pores and enough of transport pores; however, the steady-state activity of catalyst K(A1) is only

TABLE I
Texture and catalytical behaviour of catalysts

Catalyst	Texture of support ^a				S_{AR}^b $\text{m}^2 \text{g}^{-1}$	k $\text{m}^3 \text{kg}^{-1} \text{h}^{-1}$	S_{SEL}
	β	β_{MESO}	β_{MACRO}	S_{BET} $\text{m}^2 \text{g}^{-1}$			
K(N)	0.65	0.0	0.39	26	17	34.2	83
K(A0)	0.50	0.37	0.13	5.9	5.7	8.6	0
K(A1)	0.58	0.35	0.24	5.6	5.4	28.7	—
K(A2)	0.59	0.33	0.26	3.8	3.7	12.6	63
K(A3)	0.54	0.28	0.26	1.8	1.7	10.6	44
K(A4)	0.45	0.18	0.26	1.0	0.8	4.9	43
K(A5)	0.32	<0.02	0.32	0.4	<0.5	5.5	55

^a β is porosity; ^b surface area after the reaction.

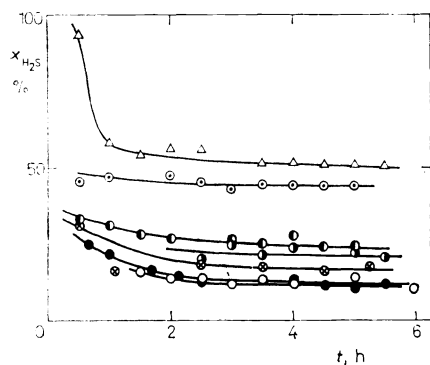


FIG. 2

Total conversion of hydrogen sulfide x (H₂S) versus time on stream t on catalysts K(I):
 Δ K(N); \otimes K(A0); \circ K(A1); \bullet K(A2);
 \ominus K(A3); \bullet K(A4); \circ K(A5)

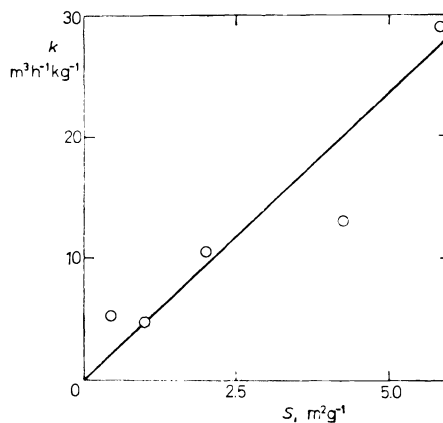


FIG. 3

Hydrogen sulfide oxidation rate constants versus surface areas on catalysts K(1) through K(5)

slightly lower than the activity of K(N). The content of 20% of SiO₂ in the sample K(N) probably causes this discrepancy.

The comparison of catalysts K(A2) and K(A3) is also illustrative. They possess similar porous structure differing only in the size of mesopores. The mesopores represent greater part of surface area of catalyst and that is why the sample K(A3) has about half surface area than sample K(A2) but its activity is only insignificantly lower.

The interesting result was obtained on the K(A5) sample. It does not contain any mesopores but the steady-state activity of it is still above 10%. The activity of catalyst is so represented fully by catalytical activity of macropores.

Mars et al.⁴ and Prettre et al.⁹ described also an increase of alumina activity with increasing surface area (decreasing size of pores); this is in accord with results presented here. However, they emphasize general meaning of micropores for a catalytic activity what need not be always true. On the basis of our experiments we can state that the micropores do not take part in a steady-state activity of our catalysts. The fall of activity in the initial period of reaction is caused by sulfur blocking of micropores; the surface area of catalysts after the reaction is really lower, for instance the surface area of sample K(N) fell from 26 to 17 m² g⁻¹ (see Table II). The comparison of catalyst texture before and after reaction showed no changes in meso and macrostructure of support.

The results presented above could be summarized by this way: The initial activity of oxidation catalyst Fe₂O₃/Al₂O₃ is the higher the higher is its surface area, i.e. the narrower pores it contains. Due to the capillary condensation, the small pores are filled by sulfur and do not contribute to the steady-state activity. The size of pores which are not filled by sulfur in steady-state and contribute to the catalyst activity is determined by the inlet concentration of hydrogen sulfide.

TABLE II
Activity and surface area of catalyst K(N) for various precursors of Fe₂O₃

Precursor of Fe ₂ O ₃	Conversion after 5 h, %	Surface area, m ² g ⁻¹	
		before reaction	after reaction
Fe(NO ₃) ₃	52	31·8	13·9
Fe(AcAc) ₃	53	30·6	16·0
Fe ₂ (SO ₄) ₃	18·5	17·8	6·5

Catalytical precursor. Three catalysts prepared by supporting of iron(III) salts on α -alumina (Norton) were tested to find the relation between the precursor of Fe₂O₃ and the activity of catalyst. The activities and the surface areas of these catalysts are presented in Table II.

The highest activities were exhibited by the samples prepared from iron(III) nitrate and acetylacetonate, because these compounds were totally decomposed to Fe₂O₃. On the other hand, the catalyst prepared from sulfate exhibited much lower activity; we assume that in this case only partially decomposition proceeded. The steady-state activity of support is negligible.

The comparison of surface areas of catalysts shows that the supporting of nitrate and acetylacetonate on alumina increases its surface while the supporting of sulfate decreases the surface nearly by one half. Partial decomposition of sulfate is probably the reason of low surface area of this catalyst. The surface area of all catalysts decreases twice or three times but the surface area of support remains 26 m² g⁻¹ without any change. The decrease of surface areas of supported catalysts is probably connected with filling of the smallest pores by condensed sulfur formed by hydrogen sulfide oxidation.

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