

The Influence of a Quartz Surface on the Transformation of Molybdenite under the Action of Hydrogen Oxidation

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Abstract—The process of the transformation of powdered molybdenite (MoS_2) under the action of hydrogen oxidation is studied under the conditions of adding quartz pieces, different in shape and size. The investigation is carried out in flow-type conditions at an atmospheric pressure and 873 K. The time of contact with the gas phase, where the hydrogen oxidation takes place, is 38 s. The ratio of initial compounds is $P_{\text{H}_2} : P_{\text{air}} = 3 : 1$. It is shown that the presence of quartz pieces increases the degree of molybdenite desulfurization.

Earlier, it has been shown [1–4] that the gas phase chain reactions of hydrocarbon and hydrogen oxidation can cause the transformation of inorganic compounds and, in particular, can induce the formation of hydrogen sulfide if this chain reaction takes place in contact with metal sulfides. It was shown in [5–7] that these processes involve atoms and radicals and, particularly, that sulfur-containing paramagnetic species are formed in these complex coupled processes. It is also necessary to note that hydrogen sulfide is not formed under these conditions if only hydrogen or only hydrocarbon is in contact with metal sulfides metals.

However, a comparison of experimental data obtained in the study of the action of the same chain reactions on copper chalcopyrite and molybdenite shows some difference between these two processes. For example, a decrease in the reactor diameter, in which the gas phase chain reaction takes place, leads to an increase rather than to a decrease in the intensity of the process of molybdenite transformation, as was observed for copper chalcopyrite [3] and expected from the general laws of chain reactions [8].

This work deals with the influence of a quartz surface on the formation of sulfur-containing compounds and particularly hydrogen sulfide during the transformation of molybdenite (MoS_2) under the action of hydrogen oxidation.

Experiments were carried out in reactors made of quartz tubes of different diameters. The first reactor was a cylindrical quartz tube, 1.8 cm in diameter. A special quartz boat with molybdenite powder was placed into the tube. The second reactor was a U-shaped tube, 0.8 cm in diameter, and filled with molybdenite powder (Fig. 1). The reactors were placed into a temperature-controlled heater. Experiments were carried out under flow conditions at 873 K and atmospheric pressure. The initial mixture of hydrogen with air with the composition $P_{\text{H}_2} : P_{\text{air}} = 3 : 1$ passed through the reactors.

As a result, the gas phase where the hydrogen oxidation took place continuously contacted the solid inorganic compound. The rate of supply and the ratio of initial gas components were controlled with flow meters. The gas mixture was sampled directly from the first reactor using a quartz capillary (Fig. 1a) and from the gas outlet of the second reactor (Fig. 2b). The weight of the molybdenite sample was 2 g in all experiments. The contact time in the gas phase reaction was 38 s. Hydrogen sulfide and sulfur dioxide (SO_2) were analyzed by chromatography as described in [2, 5, 9].

The first set of experiments was carried out in the first reactor (1.8 cm in diameter, Fig. 1a). The quartz boat was placed into the reactor and filled with: (1) the molybdenite sample, (2) the molybdenite sample with rectangular quartz pieces buried in the powder to half-length, (3) the molybdenite sample with horizontal quartz cylinders buried in the powder to 2/3 of the length, and (4) the molybdenite sample with relatively small quartz pieces put onto the sample surface.

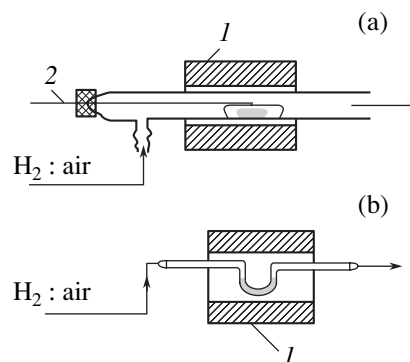


Fig. 1. Schematic of the reactor assembly: (a) cylindrical reactor ($d = 1.8$ cm) with a boat for the molybdenite sample, (b) a U-shape reactor ($d = 0.8$ cm) filled with molybdenite sample. (1) a heater with a temperature controller, (2) a capillary for gas sampling for chromatographic analysis.

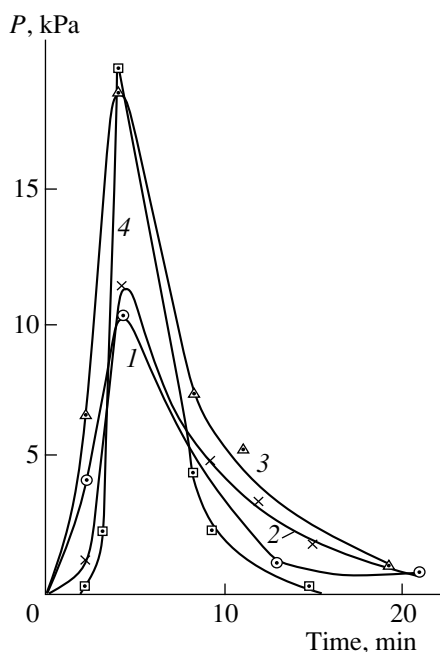


Fig. 2. Kinetics of hydrogen sulfide formation in the reactor (1.8 cm in diameter). $P_{H_2} : P_{air} = 3 : 1$. The boat with the following sample was placed into the reactor: (1) the molybdenite sample; (2) the molybdenite sample with rectangular quartz pieces buried in the powder to half-length, (3) the molybdenite sample with horizontal quartz cylinders buried in the powder to 2/3 of the length, and (4) the molybdenite sample with relatively small quartz pieces put onto the sample surface.

Figure 2 presents the curves showing a change in hydrogen sulfide amounts in the reacting gas during the process. The total amount of H_2S formed in the process and, correspondingly, the degree of desulfurization calculated using these curves are presented in the table. The results presented in Fig. 2 and the table show that the conversion is highest if cylindrical quartz pieces ($S_{quartz} = 2.26 \text{ cm}^2$) are partially buried into the powder sample (Fig. 2, curve 3). The percentage of desulfuriza-

tion increases in this case from 1.67% (Fig. 2, curve 1) to 3.1%.

This effect could have been associated with an increase in the total quartz surface area, which is equal to the area of the quartz reactor surface and the area of quartz pieces $S + S_{quartz}$, and with respective increase in the ratio of $S + S_{quartz}$ to the reactor volume. Indeed, when comparing data obtained in reactors with different diameters (see the table), we see the correlation between the extent of desulfurization and the ratio between the reactor surface area and its volume (S/V). However, in the experiments with cylindrical quartz pieces, the ratio of the quartz surface area to the reactor volume increases insignificantly (from 2.22 to 2.31), but the efficiency of the process almost doubles (Fig. 2, curves 1 and 3).

The degree of molybdenite desulfurization also increases when the rectangular pieces of quartz ($S_{quartz} = 1.25 \text{ cm}^2$) are placed onto the molybdenite sample and buried in the powder to half-length (Fig. 2, curve 2). The desulfurization degree increases from 1.67 to 2.2%, that is, by a factor of 1.3, but the ratio S/V increases by only 2.5%. The degree of molybdenite desulfurization also increases when relatively small pieces of quartz with the surface total area $S_{quartz} = 2.16 \text{ cm}^2$ are placed onto the sample surface. In this case, the maximal concentration of hydrogen sulfide is achieved (Fig. 2, curve 4). However, if these quartz pieces are not placed onto the molybdenite sample surface but mixed with molybdenite powder, the effect is small. The kinetic curve of hydrogen sulfide formation changes insignificantly compared to the curve obtained in the experiment with molybdenite without quartz.

If quartz pieces are mixed with molybdenite at a weight ratio of 1 : 1, the process of desulfurization follows another route: only SO_2 is formed in this case. This experimental result requires a detailed study.

It was shown in [10–12] that not only radical decay [10] but other processes with their participation take place on the reactor surface [11]. In [12], it was experimentally confirmed that active species (for example, hydrogen atoms) are very mobile on the surface and can

The degree of desulfurization of molybdenite in reactors with different diameters after the addition of different quartz pieces to molybdenite

Diameter of the reactor, cm	Weight of molybdenite sample, g	Surface area of the reactor S , cm^2	Volume of the reactor V , cm^3	S/V , cm^{-1}	Surface area of quartz pieces S_{quartz} , cm^2	$(S + S_{quartz})/V$, cm^{-1}	Degree of desulfurization, %
1.8	2	56.52	25.43	2.22	*	—	1.67
1.8	2	56.52	25.43	2.22	1.25	2.27	2.20
1.8	2	56.52	25.43	2.22	2.26	2.31	3.10
1.8	2	56.52	25.43	2.22	2.16	2.30	2.00
3.6	2	113.04	50.86	1.11	*	—	0.86
0.8	2	47.22	7.98	5.92	*	—	3.90

* Without the addition of quartz pieces.

easily migrate from one active site to another. Therefore, we assume that quartz pieces placed onto the molybdenite surface promote the heterogeneous formation of active sites leading to the further formation of hydrogen sulfide.

The experiments showed that for any method of introducing the quartz pieces of any shape and size to molybdenite in the U-shaped reactor (Fig.1b, $d = 0.8$ cm) filled completely with sample powder, only a small increase in the process intensity is observed. This is expectable because the area of the quartz reactor surface that contacts molybdenite is much larger than the area of quartz pieces.

Therefore, according to the experimental data and the data presented in [10–12], we suppose that the process of hydrogen sulfide formation under the action of the reaction of hydrogen oxidation on molybdenite is affected considerably by the quartz surface contacting the molybdenite sample directly, that is by heterogeneous factors.

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