

Decomposition of isopropyl alcohol on sulfidic catalysts

I. Dehydrogenation and dehydration of isopropyl alcohol on natural chalcopyrite

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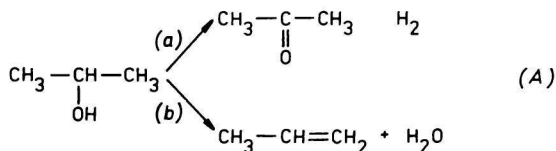
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The decomposition of isopropyl alcohol on natural chalcopyrite CuFeS_2 was investigated in the temperature interval 474—673 K by the use of the microcatalytic pulse method. The dependence of conversion of isopropyl alcohol, selectivity of dehydrogenation, and selectivity of dehydration on temperature exhibits a discontinuity at 613 K. The authors deduce that the acceleration of dehydrogenation and inhibition of dehydration may be due to a change in catalytic properties of chalcopyrite caused by liberation of sulfur from its structure.

Импульсным микрокаталитическим методом в интервале температур 474—673 К было изучено разложение изопропилового спирта на природном халькопирите CuFeS_2 . О зависимости конверсии изопропилового спирта, селективности дегидрирования и селективности дегидратирования от температуры свидетельствует скачок при 613 К. Авторы считают, что ускорение дегидрирования и подавление дегидратирования вызваны изменением каталитических свойств халькопирита вследствие выделения серы из его структуры.

In the present catalytic practice, the sulfidic catalysts are predominantly used in the processes of hydrogenation, hydrodesulfurization, and hydrodenitrification [1, 2]. The catalysts of the synthetic type are applied in all these cases. However, the natural sulfides represent a new group of potential catalysts of heterogeneous reactions. A convenient model reaction for studying these catalysts is the catalytic transformation of lower alcohols because it enables us to test the activity and selectivity of catalyst and to compare them with the values obtained by using common catalysts of the oxidic type [3].

The decomposition of isopropyl alcohol belongs among the most investigated reactions, especially, if they take place on the oxides of the transition metals or alkaline earth metals. The sulfidic catalysts have been studied in a lesser extent. According to literature [3], the decomposition on sulfidic catalysts obeys either dehydrogenation mechanism (a) or dehydration mechanism (b) and if need be both these mechanisms (a + b). The kind of decomposition is dependent on the type of the used catalyst.



This study is concerned with the decomposition of isopropyl alcohol on a catalyst of natural provenance, *i.e.* chalcopyrite CuFeS_2 . According to literature [1, 3, 4], the behaviour of isopropyl alcohol on sulfidic catalysts on the base of copper and iron has not been hitherto described.

Experimental

Apparatus

We used an apparatus working in the regime of the microcatalytic pulse method [5–8]. Its scheme is outlined in Fig. 1. The system consists of two principal parts: a microreactor (described in paper [9]) with accessories and an equipment for chromatographic analysis of products. The chromatographic analysis of the reaction mixture was carried out under these conditions: column (packing: "Porapak Q, 50–80 mesh", length 2500 mm, inside diameter 4 mm, temperature 413 K), carrier gas — argon (volume rate of flow $50 \text{ cm}^3 \text{ min}^{-1}$), detector-catharometer (temperature 413 K, filament current 70 mA). Besides isopropyl alcohol, we identified hydrogen, acetone, water, and propylene on our chromatograms. Other products were not observed.

Catalysts

Natural chalcopyrite CuFeS_2 from the locality Slovinky containing 30.65 % Cu was used. The chalcopyrite structure was identified by using X-ray diffractometry (ASTM card 9–423 [10]). The catalyst was activated for 1 h in a stream of argon ($10 \text{ cm}^3 \text{ min}^{-1}$) at 573 K. Under these conditions, the mass loss of catalyst was 1.8%. This loss corresponds to the sulfur liberated from the chalcopyrite structure.

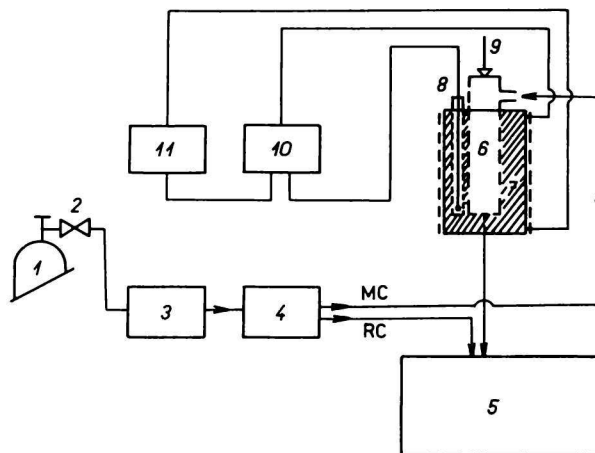


Fig. 1. Scheme of microcatalytic pulse apparatus.

1. Gas supply; 2. reduction valve; 3. purification of carrier gas; 4. distributor of carrier gas, MC-branch into measuring cell of catharometer, RC-branch into reference cell of catharometer; 5. gas chromatograph (Chrom 41, LP, Prague); 6. microreactor; 7. resistance furnace; 8. thermocouple (FeKo); 9. dosage of isopropyl alcohol; 10. temperature regulator (TRS 121, range 0—723 K, ZPA Jinonice); 11. autotransformer (2.5 A, Křížik, Prague).

Reactants

Argon was used as internal reaction medium and simultaneously as carrier gas for chromatographic analysis of the decomposition products of isopropyl alcohol. It was continuously purified by flowing through a system of columns filled with the industrial palladium catalyst (Cherox 40-00) and molecular sieve 5A. Isopropyl alcohol and acetone were anal. grade chemicals (Lachema, Brno) and their purity was checked chromatographically. Hydrogen and propylene were calibration mixtures (Matheson Gas Products, Oevel, Belgium) and we used them without previous purification.

Working regime

The results presented in this paper were obtained under these conditions: size of catalyst grains 0.5—0.8 mm, mass of catalyst 3 g, magnitude of the pulse of isopropyl alcohol 3 μ l, reproducibility of dosage $\pm 4\%$. The results concerning the temperature dependence of conversion and selectivity are average values of three measurements.

Processing of results

The evaluation of chromatograms was carried out by the method of internal normalization [11]. The total conversion of isopropyl alcohol X , selectivity of dehydrogenation $X(-H)$,

and selectivity of dehydration $X(-w)$ were calculated according to the following relationships

$$X = \frac{x_H + x_a + x_w + x_p}{x_H + x_a + x_w + x_p + x_i} 100 \quad (1)$$

$$X(-H) = \frac{x_H + x_a}{x_H + x_a + x_w + x_p} 100 \quad (2)$$

$$X(-w) = \frac{x_w + x_p}{x_H + x_a + x_w + x_p} 100 \quad (3)$$

where x_H , x_a , x_w , x_p , and x_i are mole fractions of hydrogen (H), acetone (a), water (w), propylene (p), and nonconsumed isopropyl alcohol (i), respectively. These values were calculated on the basis of the data obtained by chromatographic analysis of the reaction mixture getting out of the microreactor.

Results and discussion

The experimental results are presented in Fig. 2. The overall conversion of isopropyl alcohol X increases with temperature up to 613 K. Above this temperature, it remains constant at first and afterwards it starts to rise again (Fig. 2a). A more detailed information about the character of isopropyl alcohol decomposition is given by the temperature dependence of the selectivity of dehydrogenation $X(-H)$ and the selectivity of dehydration $X(-w)$ represented in Fig. 2b. The dehydrogenation and dehydration of isopropyl alcohol have monotonous course up to the temperature of 613 K. Above this temperature, the progress of reaction (A) by dehydrogenation mechanism (a) is preferred whereas the dehydration (b) is simultaneously hindered.

In interpretation of the course of relationships in Fig. 2, we started from the semiconductor character of chalcopyrite the properties of which change with temperature. It is known that CuFeS_2 disengages sulfur from its structure at higher temperatures [12]. It has been ascertained that this process is irreversible and begins at temperatures of about 473 K [13]. Because of the disengagement of sulfur, anionic vacancies arise in the surface of CuFeS_2 . These vacancies have positive effective charges and function as donors [14]. The liberation of sulfur brings about an increase in conductivity of the catalyst. According to the electronic theory of catalysis, an increase in conductivity of the catalysts elevating the decomposition of alcohols results in acceleration of dehydrogenation and retardation of dehydration [15, 16]. Our results are to be interpreted in agreement with this idea.

The decomposition of isopropyl alcohol proceeds according to the scheme (A). The overall process can be divided into the following steps: a) adsorption of isopropyl alcohol, b) surface reaction, and c) desorption of products.

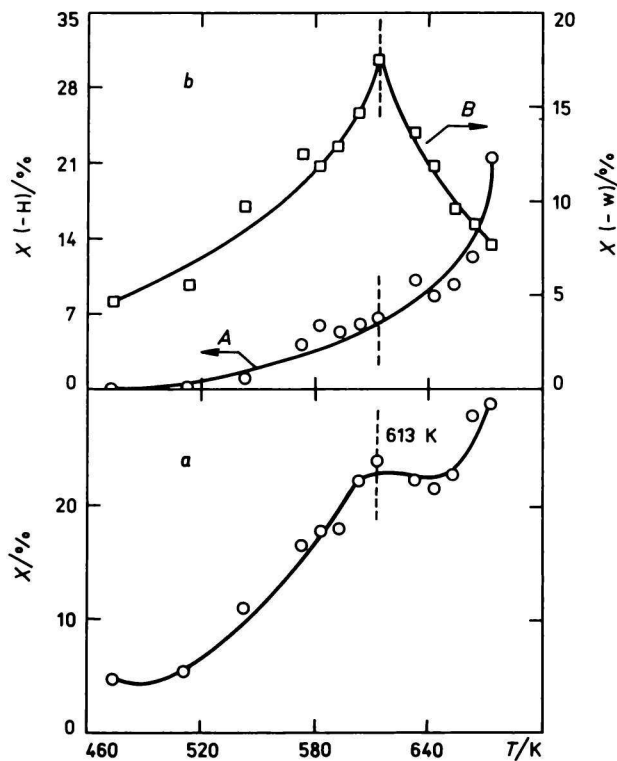


Fig. 2. Variation of overall conversion of isopropyl alcohol X with reaction temperature T (a); variation of selectivity of dehydrogenation $X(-H)$ and selectivity of dehydration $X(-w)$ with reaction temperature T (b).

A — dehydrogenation; B — dehydration.

a) According to *Wolkenstein* [15, 16], the character of decomposition of isopropyl alcohol is determined by the kind of the bond which is split by adsorption. A cleavage of the O—H bond brings about the formation of hydrogen and acetone (dehydrogenation). The adsorption takes place on the surface of catalyst which has free electric charge. As for chalcopyrite, its surface is a place with considerable concentration of free charge of different type, e.g. the anionic vacancies which further the formation of dehydrogenation products, as well as a place containing admixtures, especially SiO_2 which is a typical representative of dehydration catalyst in relation with the decomposition of alcohols [3].

b) The surface reaction takes place on different active centres by both mechanisms. The dehydrogenation comes forward with increasing temperature, which is a consequence of the mentioned increase in conductivity of CuFeS_2 . It is known

from literature that a more conspicuous disengagement of sulfur appears just over 613 K [12]. It may also be that the liberated sulfur mechanically blocks the reaction surface of the admixtures built in the catalyst and thus is responsible for the retardation of dehydration.

The relationships represented in Fig. 2b enable us to take up an attitude towards the rate-determining step of the reaction. The decrease in products of dehydration at temperatures above 613 K reveals that conditions for preferred adsorption of dehydration products arise on the surface of the catalyst. We assume that the surface of chalcopyrite enriched with anionic vacancies impedes the desorption of propylene which is strongly adsorbed just in the places with positive effective electric charge.

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