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Abstract

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ADSORPTION GAS RADIOGRAPHY AND ITS APPLICATION TO THE STUDY OF PROMOTED CATALYSTS FOR AMMONIA SYNTHESIS

Radiography has found wide application in various fields of science ([1–4]), but so far we know of no work using this vivid and direct method in catalysis.

This communication presents brief data from a radiographic study of an industrial catalyst for ammonia synthesis. The application of ordinary radiography in this case is hindered by the absence, among the chemical elements introduced as promoters or forming the catalyst, of convenient radioactive isotopes. Thus, Al^{29} is not readily available and has too short a half-life ($\tau_{1/2} = 6.5$ min.); K^{40}, with $\tau_{1/2} = 1.3 \cdot 10^9$ years, is likewise of little use. Given the duration of the process of preparing promoted catalysts, K^{42} is also inconvenient ($\tau_{1/2} = 12.4$ hours, $E_\beta = 1.1$ MeV). The study of Fe^{55} or Fe^{59}, consisting of electrons of internal conversion and γ-rays with an energy of 1.2 MeV, is difficult to apply for radiographic purposes, taking into account the considerable volumetric distortions of γ-radiation. Among the components of the ammonia synthesis reaction, N_2 has no isotopes suitable for radiographic measurements. Therefore we have developed a new method* of adsorption gas radiography. Its principle consists in obtaining radiograms by photographing the radiation from radioisotopes of elements taken in the form of simple substances or chemical compounds and adsorbed on the surface of the solid body under study. In the presence of multiple phases or of pores and zones with sharply different absorption properties, these features can be observed in the image.

The advantage of gas adsorption radiography is the possibility of studying the topography of elements that, in general, have no radioactive isotopes. In addition, it is possible to vary, over wide limits, the sizes and physicochemical properties of the molecules serving as the source of radiation, and to eliminate volume effects completely. The autoradiographed substance is introduced into the finished specimen either in isolated form or during a given process. The time required for introducing the isotopic label is reduced in comparison with ordinary radiography, which is especially important for the use of short-lived isotopes. Repeated experiments with one and the same sample, but with different

Fig. 1. Schematic diagram of the vacuum apparatus for adsorption gas radiography. 1 —vessels for $C^{14}O_2$; 2 —reactor for catalyst polished sections; 3

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radioactive sorbates, are readily carried out.

In catalysis, adsorption gas radiography is promising for studying the nature of the distribution of promoting additives, for investigating the topography of poisoning of catalytic and adsorption processes, the topography of catalytically active centers, etc.

The principal requirement of adsorption gas radiography in studying the distribution of promoters in a catalyst is the use of a radioactive gas that is sorbed preferentially on the promoting additive under investigation.

* The theory of the method will be described elsewhere.

In catalysts for ammonia synthesis, the principal promoter is potassium oxide introduced into the melt. The indicator gas for studying the distribution of the alkaline promoter may be any gas of acidic character. We used $C^{14}O_2$. The advantage of the selected radioactive isotope is the softness of the β-radiation of C^{14}; its disadvantage is the long half-life ($\tau_{1/2} = 5570$ years).

Experimental Part

To study the character of the distribution of the alkaline promoter in an ammonia catalyst, we used an industrial sample containing 2% K_2O and 5% Al_2O_3. The catalyst was studied in both the reduced and unreduced states. Preprepared polished sections were placed in the reaction vessel of a vacuum apparatus (Fig. 1), where chemisorption of CO_2 labeled with C^{14} was carried out on these samples.

From previously obtained data it is known that CO_2 is chemisorbed exclusively by regions of the alkaline promoter (^{7}) and is not desorbed in an atmosphere of nitrogen, argon, or hydrogen at room temperature (^{8}). Therefore all operations involving removal of the polished sections and exposure were carried out in an atmosphere of purified nitrogen. To protect the photographic plate from side interactions with the polished section during exposure, the latter was covered with a thin layer of collodion and placed in a desiccator. In view of the long half-life, the exposure time reached several days. It can be shortened by using special photographic plates*.

Fig. 1. Schematic diagram of the vacuum apparatus for adsorption gas radiography. **1** —vessels for $C^{14}O_2$; **2** —reactor for catalyst polished sections; **3**

The results obtained for unreduced Fe_3O_4 with additives are shown in Fig. 2.

Fig. 2a is an optical microphotograph in reflected light; Fig. 2b is a radiogram of the same sample; Fig. 2c is a radiogram of another sample at a similar magnification. In photographs 2b and 2c, the white regions correspond to alkali, and the dark ones to the surface of iron or aluminum oxide. The sharp difference between the optical and radiographic images of the same sample (Figs. 2a and 2b) and the nonuniformity of the distribution of the alkaline promoter over the catalyst grain are noteworthy. In the radiograms, zones where alkali is entirely absent and regions characterized by a considerable concentration of the alkaline additive are clearly visible. It is possible that potassium oxide, in the form of some compound of it, forms a separate phase.

Figure 3 shows a microphotograph (a) and a radiogram (b) of a reduced sample. It is easy to see that optical image 3a differs less from 3b than 2a from 2b. This indicates that during reduction a substantial change occurred in the topography of the distribution of alkali in the sample. The method of adsorption gas radiography can also be used to determine the distribution of Al_2O_3 and the structure of Fe.

In the literature there are a number of attempts to use surface processes for radiographic purposes. Thus, Rabinovich (^{5}) described the use of amyl iodide labeled with J^{131}, adsorbed from solutions, for the study of metal-

* For the time being, “spectrographic, type 1” photographic plates were used.

Fig. 2

Fig. 3

···metals and alloys. In this case, what occurred was not adsorption, but a surface chemical process propagating into the depth of the grain. Thompson et al. (^{6}) used for radiography compounds formed on the surface in the form of special thick layers during gas chemical reactions with a solid. The authors regarded adsorption as an undesirable side···

factor. In our case, the adsorption measurements additionally carried out make it possible to regard the adsorption of CO_2 as a surface process, without penetration into the volume of the grains; this is the basic condition for adsorption gas radiography, the main idea of which consists in using the features of physical and chemical adsorption with variations in filling both below a monolayer and in the region of multilayer adsorption and capillary condensation.

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Note: Figure translations are in progress. See original paper for figures.