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Abstract

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Application of the Emanation Method to the Study of Catalysts

Topochemical Decomposition of Carbonates and Hydroxides of Magnesium and Zinc

The catalytic activity of solids is most closely connected with defects in the structure of their crystal lattices. The number and character of these defects, which arise during the genesis of catalysts, are determined by the deep mechanism and microchemistry of the topochemical stages of preparation. These processes, closely connected with the displacements of individual atoms and groups in the lattice of a solid and on its surface, often escape the usual physical and chemical methods of investigation. It seemed promising to apply to their study the emanation method, proposed earlier by Kolowrat-Czervinski ([1]). In the works of Hahn, Starik, Zimens, and many others, the possibility was shown of detecting by means of this method hidden phase and chemical transformations of solids, as well as changes in the mobility of atoms in their lattice, specific surface area, and porosity ([2–5]).

Individual systems studied with the aid of the emanation method are of interest for catalysis; however, apparently, until now this method has not been used in catalytic investigations. We decided to fill this gap by using measurements of emanating ability to study the topochemical stages in the preparation of oxide catalysts and the transformations undergone by the latter during operation.

Of the three radium isotopes (Ra, ThX, AcX) that generate the isotopes of element 86 used in the emanation method, we employed Ra 226, in the form of a nitric-acid solution with a concentration of $3 \cdot 10^{-9}$ g/ml. The initial solution contained barium as a carrier. The concentration of barium nitrate in the solution was 0.1 g/ml.

For subsequent measurements of emanation (Rn), it proved convenient to introduce $6–7 \cdot 10^{-9}$ g Ra per 1 g of precipitated hydroxides or carbonates.

The procedure for measuring the released emanation and the preparatory operations was borrowed from the works of I. E. Starik and coworkers ([5]). The amount of emanation was measured with an SG-1M electrometer.

As special experiments showed, the topochemical processes studied by us can be interrupted at any moment in time, with subsequent return to the same point on the kinetic curve. Therefore, measurement of the emanation coefficient of samples of carbonates and hydroxides at various stages of transformation was carried out after stopping the process by cooling. The accumulation of radon and measurement on the electrometer were performed at room temperature.

Magnesium and zinc hydroxides were obtained by precipitation from concentrated solutions of nitrate salts with a concentrated solution of sodium hydroxide at a temperature of 40°. Precipitation was carried out with continuous stirring. After precipitation, the precipitates of magnesium and zinc hydroxides were thoroughly washed free of electrolyte impurities by repeated decantation. Magnesium carbonate was obtained by precipitation at room tempera-

···a slurry of a concentrated solution of magnesium nitrate with a concentrated solution of sodium carbonate saturated with carbon dioxide. The basic carbonate obtained was carbonated by passing a stream of dried carbon dioxide at a temperature of 150° to constant weight. The carbonic acid content in the preparation obtained in this way corresponded to the normal carbonate.

Zinc carbonate was prepared by precipitation, with stirring, from a concentrated solution of zinc nitrate cooled to 5° with a concentrated solution of sodium bicarbonate, previously saturated with carbon dioxide. In all cases, before precipitation, the above-mentioned solution of radium nitrate with accompanying barium nitrate was added to the solutions of the magnesium and zinc nitrates.

It was found that the hydroxides of magnesium and zinc occlude about 50% of the introduced radium, but more than 90% of the occluded amount is removed upon washing the precipitates, reducing the occlusion of radium to 2–5 wt.% of the initial amount. In this respect the carbonates differ favorably from the hydroxides, since, while occluding the same 50–60% of the introduced radium, they completely retain this amount upon washing.

Table 1

Values of the emanation coefficient in the transition from hydroxides and carbonates to oxides

Compound	$K_{\text{eman.}}$, %	Calcination temp., °C	Calcination time, h
Magnesium hydroxide → magnesium oxide	2–310–12	550	2

Compound	$K_{\text{eman.}}$, %	Calcination temp., °C	Calcination time, h
Basic magnesium carbonate → normal magnesium carbonate	8–91–2	150	4
Normal magnesium carbonate → magnesium oxide	1–22–5	450	2
Zinc hydroxide → zinc oxide	20–252–3	550	2
Normal zinc carbonate → zinc oxide	80–854–5	450	2

As a result, the occlusion of radium by the carbonates is approximately 10–20 times greater than by the hydroxides for the same amount of introduced radium. With such occlusion coefficients, taking into account the differences in the atomic weights of barium and magnesium, the content of $Ba(OH)_2$ in magnesium hydroxide was less than 0.4 at.%, and the content of $BaCO_3$ in magnesium carbonate was 4–8 at.%. The decomposition of the carbonates and hydroxides was carried out in a vacuum apparatus at a pressure of $5 \cdot 10^{-2}$ mm. Before decomposition the samples were conditioned to remove hygroscopic moisture. The degree of transformation was determined by weighing the samples. For a number of samples the specific surface area was determined by measuring the adsorption of *n*-heptane vapor according to B.E.T. In studying the dependence of the emanation coefficient on the calcination temperature of magnesium hydroxide, it was established, as in the work of Fricke and Feichtner (^{6}), that the maximum change in the emanation coefficient occurs at a temperature of 400°.

Table 1 gives the values of the emanation coefficient observed in the transition from hydroxides and carbonates to the corresponding oxides upon calcination. From the data obtained it may be concluded that the emanation coefficient changes considerably in these transitions.

The magnitude of the emanating ability also depends on the calcination temperature. For magnesium we determined the change in emanating ability during the successive transition in the series: magnesium hydroxide—basic carbonate—normal carbonate—magnesium oxide. The emanation coefficient is maximal for the basic carbonate and decreases on transition to the normal carbonate, which

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

may be a consequence of a decrease in the specific surface area of the latter (from 25 m^2/g to 10 m^2/g). For zinc, a similar series did not include the basic carbonate. The emanating ability of zinc hydroxide and carbonate decreases on transition to the oxide of the corresponding metal. The data given in Table 1 indicate a considerable influence of topochemical processes on the emanating ability···

capacity of the systems studied. Continuous measurement of the emanation coefficient during the topochemical process of decomposition of carbonates and hydroxides could characterize the subtle structural transformations occurring at various stages of the process. Measurements of the specific surface area of a series of hydroxide and carbonate samples at various stages of transformation make it possible to take into account the influence of surface area on emanating capacity.

The dependence of the emanating capacity and of the specific surface area on the percentage transformation of magnesium and zinc carbonates and hydroxides is presented graphically in Figs. 1–2.

Fig. 1. Dependence of the emanation coefficient *(2, 4)* and of the specific surface area *(1, 3)* on the extent of transformation of magnesium hydroxide and magnesium carbonate
Fig. 2. Dependence of the emanation coefficient *(1)* and of the specific surface area *(2)* on the extent of decomposition of zinc carbonate

As follows from Fig. 1, during dehydration of magnesium hydroxide at a temperature of 320° there is an increase in the emanation coefficient as the percentage transformation increases. At the same time, an increase in the specific surface area is also observed. The curves for the dependence of the emanation coefficient and of the specific surface area on the percentage transformation are parallel. At the end of the dehydration process (92% transformation), the emanation coefficient changes by a factor of 20, and the specific surface area by a factor of 5.

The dependences of the emanating capacity and of the magnitude of the specific surface area of magnesium carbonate (Fig. 1, 3 and 4) on the percentage of its decomposition at (T = 370^{ }) have an analogous character. In this case as well, there is a sharp increase in the emanation coefficient—by a factor of 9.3 at 80% decomposition of the carbonate. The specific surface area increases by a factor of 8.5.

A different picture can be observed in the decomposition of zinc carbonate and the dehydration of zinc hydroxide. As follows from Fig. 2, during the decomposition of zinc carbonate there is a decrease in the emanating capacity

Fig. 3. Dependence of emanating ability on the magnitude of the specific surface at the same degree of transformation for magnesium carbonate (2) and hydroxide (1), and zinc carbonate (3)

Figure 2: Fig. 3. Dependence of emanating ability on the magnitude of the specific surface at the same degree of transformation for magnesium carbonate (2) and hydroxide (1), and zinc carbonate (3)

with increasing extent of transformation, accompanied by an increase in the specific surface area. Thus, in this case the course of the curves characterizing the dependence of the emanation coefficient and of the specific surface area on the extent of transformation of the topochemical process is antibatic. A similar, but weaker, dependence is also observed for zinc hydroxide. In Fig. 3 the relationship between changes in emanating capacity and specific surface area in the course of the topochemical process is presented graphically for the three systems studied by us. As follows from this figure, the dependence of the emanation coefficient on the magnitude of the specific surface area in the process of dehydration of magnesium hydroxide is linear. The dependence of the emanation coefficient on the magnitude of the specific surface area during decomposition of magnesium carbonate has an analogous character.

The results of the measurements carried out on the change in emanating ability and in the magnitude of the specific surface showed the presence of substantial changes in the structure of magnesium and zinc hydroxides and carbonates in the course of the topochemical process of their decomposition.

The concurrent course of the curves characterizing the changes in the emanation coefficient and in the magnitude of the specific surface with the degree of transformation of the decomposition process of magnesium hydroxide and carbonate, as well as the linear dependence of the emanation coefficient on the magnitude of the specific surface, show that the principal factor determining the emanation coefficient during the topochemical processes studied is the change in specific surface.

Fig. 3. Dependence of the emanating ability on the magnitude of the specific surface at the same degree of transformation for magnesium carbonate (2) and magnesium hydroxide (1), and zinc carbonate (3).

The linear dependence between the change in the emanation coefficient and the magnitude of the specific surface in the course of the topochemical process, in all probability, indicates the formation of solid solutions of the carbonates of magnesium, barium, and radium obtained during their precipitation. This supposition is also supported by data on the similarity of the crystallochemical structure of magnesium and barium carbonates (7), and probably that of radium. As for the hydroxides of magnesium, barium, and radium, in view of the small content of the latter it is also possible that a solid solution is formed, or that they are distributed microheterogeneously among the grains of magnesium hydroxide. In the case of zinc carbonate and hydroxide, apparently, another type of capture of radium by the starting compounds occurs; one may suppose a sorption character of the capture of radium. Taking into account the very high emanation coefficient of radium, which in the form of carbonate or hydroxide is deposited on the surface of the initial solid phase during precipitation.

The decrease in the emanation coefficient with increasing specific surface during the topochemical decomposition of zinc compounds could be explained by the effect of penetration of radium into the depth of the solid phase, hindering the release of radon. A similar phenomenon was noted by Otto Hahn (2) for radium upon heating barium and lead nitrate salts. Thus, the unusual dependence—the decrease in emanating ability with increasing specific surface—in the present case may be caused by secondary effects of diffusion of radium into the zinc oxide being formed, or by envelopment of the radium and barium compounds by zinc oxide. It seems to us that further application of the emanation method to the study of topochemical stages in the preparation of catalysts may reveal a number of new regularities. In this connection, the new method developed by Iecho (8) is of interest.

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