EFFECT OF THE METHOD OF MAKING MODIFYING ADDITIONS ON THE PROPERTIES OF OXIDE CATALYSTS

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The way in which additives are distributed at the surface and in the body of a catalyst and the possibility of interaction between additives and the catalyst are matters of great interest for the understanding of the laws governing the action of additives on catalysts. It was considered probable that change in the method of introducing additives can result in a change in their distribution in the catalyst and have a substantial effect on the catalytic properties of the catalyst.

As a model reaction of the oxidation-reduction type we made use of the decomposition of hydrogen peroxide in presence of magnesium oxide [1]. It was found that, in the pure state, magnesium oxide has only moderate catalytic activity, and this facilitated the detection of positive effects attributable to additions. Stannic oxide was selected as additive; in the pure state this substance has a negligible catalytic effect. The rate of decomposition of hydrogen peroxide was determined gasometrically, the procedure being similar to that described previously [1].

Fig. 1 shows kinetic curves for the decomposition of hydrogen peroxide over pure magnesium oxide and over pure stannic oxide. It will be seen that the activity of the former is about 35-40 times as great as that of the latter. As stannic oxide is introduced into the magnesium oxide in small amounts (0.01-6.4%), the effect of the simple summation of the activities of the two oxides can be neglected.

For the introduction of stannic oxide into magnesium oxide, the following three methods were used:

1. Impregnation of prepared magnesium oxide with solutions of tetr phenyltin. Magnesium oxide is impregnated with chloroform solutions of tetr phenyltin at various concentrations, dried at 100-120°, and calcined for one hour at 600° in a quartz vessel in an atmosphere of air. Pyrolysis of tetrphenyltin gives phenyl radicals and atomic tin, which is oxidized by atmospheric oxygen to stannic oxide (Series 1).

2. Impregnation of prepared magnesium oxide with solutions of stannic chloride. Magnesium oxide is impregnated with aqueous stannic chloride solutions of various concentrations, and the stoichiometric amount of 20% sodium carbonate solution is added to the resulting paste. The catalyst samples prepared in this way are washed, dried, and calcined for four hours at 450° in a quartz vessel in an atmosphere of air (Series 2).

3. Coprecipitation of magnesium and tin salts with sodium carbonate solution, the basic carbonates formed being washed, dried, and calcined at 450° (Series 3).

The amount of stannic oxide introduced was determined by polarography and spectrum analysis.

For our study of the catalytic properties of the magnesium oxide samples containing additions of stannic oxide it was necessary to select a method of determining the relative activities of the samples. It was established that the course of the decomposition of hydrogen peroxide is satisfactorily described by a first-order equation. The value of
the rate constant served as a measure of the activity of the catalyst. Rate constants could be determined accurately within 5%.

Fig. 2. Kinetic curves for the decomposition of hydrogen peroxide plotted in accordance with the first-order law for the samples of Series 1. The decomposition reaction was carried out at 90°C. The figures on the curves denote stannic oxide contents (%).

Fig. 3a. Dependence of the activity of catalyst samples of Series 1 on stannic oxide content. The figures on the curves denote reaction temperatures.

Fig. 3b. Dependence of the specific activity of the same samples on stannic oxide content.

It is interesting that increase in stannic oxide content form 0.04% to 5.3% by weight did not alter the form of the kinetic law (a first-order equation), but affected only the value of the rate constant. This can be seen from the linear form of the curves in Fig. 2, which express the dependence of the logarithm of the amount of unchanged hydrogen peroxide on time.

Our study of the dependence of catalyst activity on stannic oxide content showed that the form of this relationship varies with the temperature of the reaction. This is illustrated in Fig. 3a for reaction temperatures ranging from 20°C to 90°C. Thus, at 90°C there is a maximum at an additive content of 0.08%, and at this point the activity is 4.1 times as great as that of pure magnesium oxide. At 75°C there is a maximum at the same stannic oxide content, but the effect of the addition is somewhat less than at 90°C.

When the reaction temperature is lowered further to 45°C, the maximum moves from 0.05% to 0.4%, and the activity relative to that of pure magnesium oxide is 2.1. Finally, at still lower temperatures (20°C and 5°C), the maximum disappears, and, beginning from the very smallest amounts of additive, the activity is less than that of pure magnesium oxide. As the temperature of the catalytic reaction is lowered, the curves for the dependence of the specific activity of the catalyst on additive content flatten out (Fig. 3b).

This behavior indicates that the value of the activation energy varies for the different catalyst samples (pure magnesium oxide and magnesium oxide containing stannic oxide). A summary of data on the activation energy and pre-exponential factor is given in Table 1. The probable error in the determination of activation energy is ±0.5 kcal/mole.

It follows from the data in Table 1 that a substantial change in the activation energy and in the logarithm of the pre-exponential factor is brought about by the first very small additions of stannic oxide. In the further range of additions from 0.40 to 3.30, the variations in activation energy and in the logarithm of the pre-exponential factor are approximately equal to the experimental error. At high stannic oxide contents both quantities are reduced somewhat.