1-Na-HAcO. This fact may be understood if the reaction rate is not determined simply by the amount of acid sites, but is correlated substantially with the acid strength of the catalysts. The correlation of the acid strength with the catalytic activity in some acid-catalyzed reactions was reported by Dzisko (*4*).

Among the various catalysts employed, alumina sulfate on silica gel, Al-S, has some particular features. Al-S is as high as or even higher than SA-1 in catalytic activity for dealkylation and xylene isomerization, while the former is lower than the latter for the cyclohexene isomerization. The γ_i' value of Al-S is a little smaller than that of SA-1, which suggests that Al-S may have stronger acid sites than SA-1, according to the tendency of γ_i' values among the SA-1-Na series where the stronger acid sites were successively poisoned with sodium ions. Moreover, Al-S, in fact, is liable to lose its catalystic activity by additional injection of the reactant pulse. If the cyclohexene isomerization reaction, which takes place at a temperature as low as 300°C, is assumed to be catalyzed even by weaker acid sites, the lower activity for this reaction of Al-S than that expected from Fig. 2 may be reasonably explained by its strong acidic nature, while its content is presumably small. Actually strong acid sites were detected on this catalyst by the preliminary measurement with the Hammett indicators.

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Dependence of the Catalytic Activity on Thickness of the Oxide Layer on Metal

One of the experimentally verifiable conclusions resulting from Volkenstein's electronic theory of catalysis is the effect of thickness of the oxide layer deposited on a metal on its catalytic activity and selectivity (*1, 2*). The theory postulates that the catalytic activity should change on passing from oxide layers of thickness smaller than the so-called "screening length" (10^{-5}–10^{-6} cm) to layers of greater thickness.

The character of this change is determined by a number of parameters involving both the catalyst (sign of the surface charge, position of the Fermi level) and a reaction which takes place (donor or acceptor rate-determining step).

The theoretical dependence of the reaction yield on the parameters given above is rather complex, the reaction yield decreasing or increasing monotonically with the thickness of oxide layer in some cases, or passing through an extremum for some systems of parameters. The aim of the present work has been to test experimentally whether a change of the thickness of a semiconducting oxide layer on a metal affects the rate of a catalytic reaction occurring on its surface. For this purpose the rate of decomposition of hydrogen peroxide (22%) on chromium covered with layers of chromium oxide of a thickness comparable with the screening length was measured. The various thicknesses of the Cr_2O_3 layers were obtained by oxidation of pure metal at different temperatures.

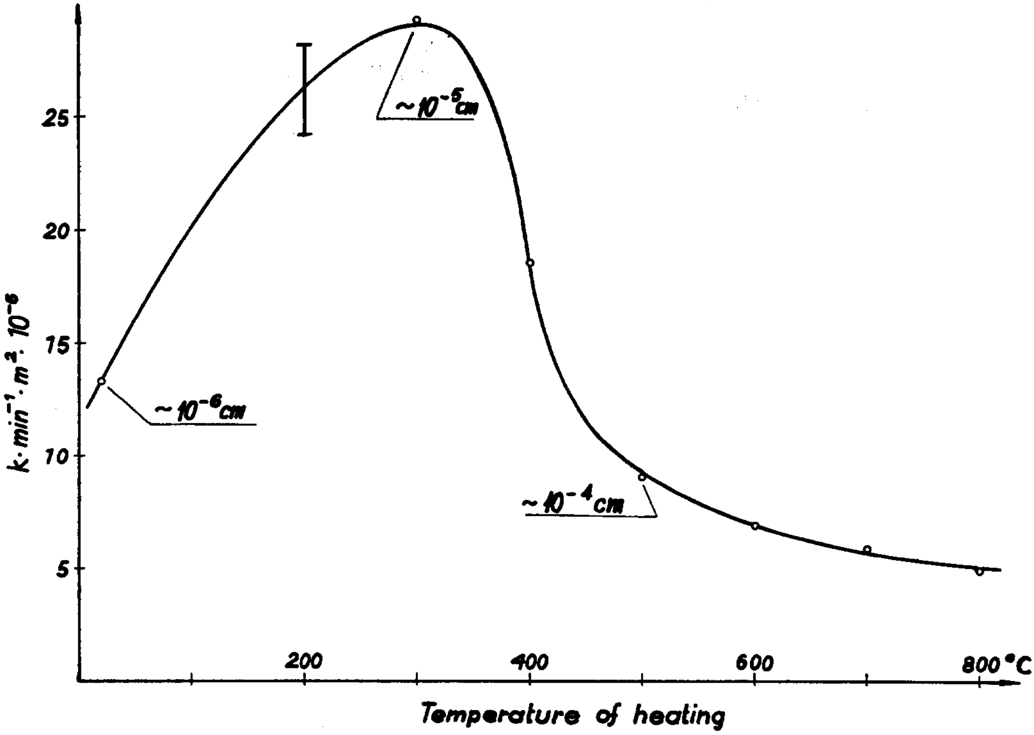

FIG. 1.

Grains of chromium (99.99%) 0.6–0.75 mm of diameter were oxidized for 5 min at temperatures of 200–800°C .They were then placed in the catalytic apparatus and the reaction was followed by measuring the volume of the oxygen evolved (*3*). The reaction temperature was 33.8°C. At this temperature no homogeneous decomposition took place. The concentration of hydrogen peroxide was so high as compared with the reaction yield that its changes during the reaction were negligible.

The samples oxidized at lower temperatures showed distinct interference colors and those oxidized at temperatures higher than 600°C were green (a color characteristic for Cr_2O_3). The thickness of the oxide layer was determined by measuring the content of oxygen in the samples and their surface area. For all the samples, with the exception of pure chromium, the dependence of the amount of oxygen evolved on the time of the reaction was linear. In the case of the reaction carried out on pure chromium a short induction period was observed, due probably to oxidation of the chromium surface by hydrogen peroxide occurring during the reaction.

Figure 1 shows some results of the experiments. The rate constant of the reaction is plotted here as a function of the temperature of oxidation which is taken as a measure of the layer thickness; the thickness of the oxide layers obtained at a given temperatures is also given for some preparations.

As seen from the figure the reaction rate increases initially, with increasing thickness of the Cr_2O_3 layer, up to a maximal value at a thickness corresponding to the screening length. Further increase of the oxide layer leads to a decrease of the activity which finally attains a constant value for the samples oxidized at higher temperatures (the green samples). The experiments are then in accord with the electronic theory of catalysis, which postulates a change of catalytic properties with increasing thickness of the oxide layer on a metal.

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