Cobalt Boride as a Heterogeneous Catalyst

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Summary Cobalt boride is an active heterogeneous catalyst for reactions such as the decomposition of H_2O_2 (ΔE = 5 kcal./mole), the reduction of nitrate to ammonia by borohydride and of azobenzene to hydrazobenzene by hydrazine.

PREVIOUS work on the properties of transition-metal borides as heterogeneous catalysts has shown that cobalt boride (and perhaps the borides of Mn, Fe, Ni, and Cu) catalyses the liberation of H_2 from aqueous solutions of $NaBH_4$,[1] and that the borides of Co, Ni, Pd, Pt, and Rh are good catalysts for the liquid-phase hydrogenation of unsaturated organic compounds.[2] We have studied the catalytic activity of suspensions of cobalt (and in one case nickel and copper) boride with a wider range of reactions. The borides were prepared by treating 1 ml. portions of 1M-solutions of MCl_2 (M = Co, Ni, Cu) with an excess of $NaBH_4$; the supernatant liquid was then decanted off, and the precipitates were washed with water. Cobalt boride containing molybdenum or tungsten was prepared by adding 1 ml. of 0·5M-Na_2MoO_4 or Na_2WO_4 to the solution of $CoCl_2$ before the addition of $NaBH_4$.

First, the catalytic effect of cobalt boride on the decomposition of H_2O_2 was studied over the range of temperature 25–65° using 100 ml. of approx. 0·4M-H_2O_2 and cobalt prepared from 1 ml. of 1M-$CoCl_2$. The reactions all followed first-order kinetics and the activation energy was found to be 4·7 ± 0·5 kcal./mole. This should be compared with the values for the activation energies of the uncatalysed reaction (18 kcal./mole) and of the reactions catalysed by colloidal platinum (11·7 kcal./mole) and by catalase, which is the most active homogeneous catalyst known (5·4 kcal./mole).[3] Cobalt boride is clearly a very powerful catalyst for this reaction. Further experiments with other metal borides showed that the catalytic activity (percentage H_2O_2 decomposed after 5 min. given in parentheses) falls in the order cobalt boride (64%) > copper boride (31%) > nickel boride (6%), and that the catalytic activity of cobalt boride could be enhanced even further by the presence of molybdenum (>95%) or tungsten (100%).

Secondly, cobalt boride catalyses the reduction of nitrate to ammonia by aqueous solutions of $NaBH_4$; stoicheiometric yields of NH_3 are obtained when an excess of borohydride is used. The kinetics of the reaction were studied

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at 20° in the presence of an excess of borohydride. After an initial autocatalytic period the rate of reduction of nitrate to ammonia showed an approximately first-order dependence on the concentration of cobalt boride, while with a fixed concentration of cobalt boride the percentage of nitrate reduced after 10 min. was independent of the initial nitrate concentration. The reaction is fast; for example, the reduction of 10^{-3} moles of nitrate in approx. 20 ml. by borohydride in the presence of 10^{-3} moles of cobalt boride has a half-time of 2 min. This compares favourably with the rate of reduction of nitrate to ammonia by Devarda's alloy, which requires gentle heating to start the reaction and 30—60 min. for completion,[4,5] and suggests that cobalt boride might find a use in analytical chemistry for the determination of nitrate.

Thirdly, cobalt boride catalyses the decomposition of hydrazine to NH_3 (and other unidentified compounds), and the reduction by hydrazine of certain organic compounds, *e.g.* azobenzene to hydrazobenzene. Cobalt boride (20 mg.) was added to a solution of azobenzene (5 g.) in cold ethanol (50 ml.), and hydrazine hydrate (10 ml.) then slowly added. After 10 min., the mixture was warmed and the colourless solution was filtered. Recrystallisation gave a virtually quantitative yield of hydrazobenzene. Such fast and clean reactions may find application in preparative organic chemistry.

Most studies on heterogeneous catalysis have involved metals and semi-conducting metal oxides, while surprisingly little work has been done on the semi-conducting borides, carbides, and nitrides; our results show that cobalt boride, at least, is an unusually active catalyst for widely differing reductions.

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