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The Liquid-Phase Hydrogenation of 1-Alkenes over a Partially Hydrogenated Cobalt Boride Catalyst

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The rates of hydrogenation of 1-octene and 1-hexadecene over a partially hydrogenated cobalt boride catalyst, designated P-3Co, in ethanol have been measured as a function of hydrogen pressure, alkene concentration, and amount of catalyst. The data indicate that the alkene is strongly adsorbed and that, at high catalyst concentrations, the reaction is diffusion controlled. The catalyst is poisoned by *n*-butanethiol but is relatively unaffected by thiophene. It is lower in hydrogenation activity but better in resistance to poisoning than its nickel analog.

INTRODUCTION

A number of studies have been made of the hydrogenation activity of catalysts prepared by sodium borohydride reduction of nickel and cobalt salts (*1–6*). Although their catalytic activity appears to depend somewhat on the method of preparation, they are comparable in activity to Raney nickel catalysts. Additionally these catalysts exhibit a high tolerance to poisoning by sulfur- and phosphorus-containing compounds (*1, 7*). In a previous paper we reported on an investigation of the activity and hydrogenation kinetics of a partially hydrogenated nickel boride (P-3Ni) catalyst (*8*). This paper presents the results of a similar study on a partially hydrogenated cobalt boride (P-3Co) catalyst. The P-3Co has a lower hydrogenation activity than P-3Ni but a superior resistance to poisoning by sulfur-containing compounds.

EXPERIMENTAL

The reaction vessel was a three-necked flask of approximately 100-ml capacity, the main neck of which was attached to a conventional vacuum system. One side-neck was fitted with a burette for substrate addition and to the other side-neck was attached a rotatable arm containing the catalyst precursor, i.e., cobalt "catgen," $CoCl_2 \cdot 4NaBH_4$ (supplied by the Ventron Corp.). The catalyst was prepared *in situ* by introducing a sample of the "catgen" into oxygen-free ethanol maintained in a hydrogen atmosphere in the reaction vessel. The mixture was stirred until hydrogen evolution was complete. After the hydrolysis of the excess sodium borohydride, the hydrogen pressure was reduced and the substrate added. Hydrogen was then reintroduced to the system and the reaction mixture rapidly stirred. The uptake of hydrogen, under essentially constant volume conditions was followed manometrically, readings being taken at 30-sec intervals for the first 10 min of the reaction. The reaction was investigated at ambient temperature, i.e., 21 ± 3°C.

The substrates used were 1-octene and 1-hexadecene (99%), obtained from the Humphrey Chemical Company, and these were further purified by distillation and degassing. In the catalyst poisoning studies, the poison, either *n*-butanethiol or thiophene, was mixed with substrate prior to its admission to the reaction vessel. Analysis of the reaction products was carried out by gas chromatography using *n*-octane/Porasil C columns which were temperature programmed from 40 to 135°C at a rate of 2°C/min. The experimental procedure has been reported in greater detail earlier (*8*).

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RESULTS AND DISCUSSION

The kinetics of hydrogenation of 1-hexadecene and 1-octene on the P-3Co catalyst have been investigated. Some of the results are shown in Fig. 1. Over the pressure range investigated, the initial rate of hydrogenation has a first-order dependence on hydrogen pressure, whereas a zero-order dependence on alkene concentration is observed. This suggests that the alkene is very strongly adsorbed on the catalyst surface and confirmation of this comes from results of experiments in which the conditions are the same as those in the catalytic experiments but in the absence of added hydrogen; in these circumstances there is only a 66% recovery of reactants and products, e.g., 1–2% *n*-octane and 64–65% 1-octene. The variation of the initial hydrogenation rate with the amount of catalyst is also shown in Fig. 1; at low catalyst concentrations a linear dependence is observed but at higher concentrations a limiting rate is attained.

The kinetics of hydrogenation are similar to those reported for P-3Ni (*8*) but the alkene appears to be more strongly adsorbed on the P-3Co catalyst. Comparison of the activities of the two catalysts indicates that P-3Ni is approximately twice as active for equivalent amounts of catalyst. However with P-3Co there is significantly less isomerization of the alkene than with either P-3Ni or Raney nickel; the maximum amount of isomerization under hydrogenation conditions with P-3Co is 7% compared to 27% obtained with the P-3Ni catalyst.

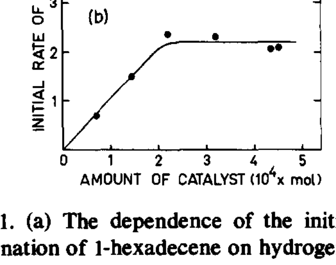

FIG. 1. (a) The dependence of the initial rate of hydrogenation of 1-hexadecene on hydrogen pressure [initial alkene concentration, 0.5 *M*] and alkene concentration [initial hydrogen pressure, 720 Torr]. In both investigations the amount of catalyst was 4.5 × 10^{-4} mol (as metal) and the solution volume 25 ml. (b) The dependence of the initial rate of hydrogenation of 1-hexadecene on the amount of catalyst [0.5 *M* alkene; 720 Torr hydrogen pressure; solution volume 25 ml].

The variation in hydrogenation activity with increasing amount of catalyst is indicative of a diffusion-controlled reaction at the higher catalyst concentrations. The difference in the limiting rate for P-3Co and P-3Ni (*8*) would appear to rule out transfer of hydrogen at the gas–liquid interface being rate determining and diffusion of hydrogen either in solution or at the solution–catalyst interface is the more probable slow step in the reaction. Watt and Walling (*9*) have shown that, for these diffusion conditions, the rate of hydrogenation (R) is given by

$$R = \frac{AWP_{H_2}}{1 + BW}, \qquad (1)$$

where W is the weight of catalyst, P_{H_2} is the pressure of hydrogen, and A and B are constants. The present results for P-3Co are consistent with Eq. (1). If the particle size and dispersion of P-3Ni and P-3Co are similar, then the difference in their limiting hydrogenation rates would indicate that it is diffusion at the solution–catalyst interface which is rate determining.

Some results for the poisoning of the hydrogenation reaction by sulfur-containing compounds are shown in Fig. 2. In the case of *n*-butanethiol poisoning one series of experiments was made in the region of the diffusion-controlled reaction (curve (a)) and another series in the region where there is a kinetic dependence on the amount of catalyst (curve (b)). In the latter, a linear reduction in hydrogenation activity with amount of poison is obtained; this is typical

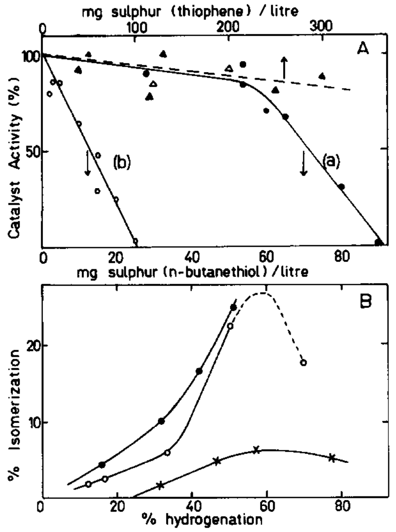

FIG. 2. (A) The effect of sulfur-containing catalyst poisons on the initial rate of hydrogenation of alkenes; ● (curve (a)), *n*-butanethiol poisoning of 1-hexadecene hydrogenation [0.5 *M* 1-hexadecene, 4.5×10^{-4} mol (as metal) of catalyst, 760 Torr hydrogen pressure]; ○ (curve (b)), *n*-butanethiol poisoning of 1-hexadecene hydrogenation [0.139 *M* 1-hexadecene, 1.08×10^{-4} mol (as metal) of catalyst, 720 Torr hydrogen pressure]; broken line refers to thiophene poisoning of 1-octene hydrogenation [720 Torr hydrogen pressure, 5×10^{-4} mol (as metal) of catalyst, ▲: 0.5 *M* 1-octene, △: 0.25 *M* 1-octene]. (B) The effect of thiophene on the isomerization of 1-octene on P-3Co; ×, unpoisoned; ○, 120 mg sulfur/liter; ●, 200 mg sulfur/liter. Initial conditions were 0.5 *M* 1-octene, 720 Torr hydrogen pressure, and 5×10^{-4} mol (as metal) of catalyst.

of the nonselective poisoning of metal catalysts (*10*). With the larger amount of catalyst, the poisoning curve can be rationalized with diffusion-control behavior. Because of the limitations of diffusion control, only part of the surface of the catalyst will be active at any one instant in time. The active surface will correspond to 2.2×10^{-4} mol of catalyst, Fig. 1. In obtaining poisoning curve (a) 4.5×10^{-4} mol of catalyst was used; hence 51% of surface could be poisoned without a significant change in the hydrogenation activity. In terms of the total amount of *n*-butanethiol added to completely poison the surface, i.e., 90 mg/liter S, the first 45 mg/liter S reduces the catalyst activity only by 10–15%, Fig. 2. The major poisoning effect is only evident after 58% of the surface is covered with *n*-butanethiol. It is also interesting to note there is a reasonable correspondence between curves (a) and (b) in regard to the amount of *n*-butanethiol required to eliminate the hydrogenation activity. The weights, and presumably the surface areas, of the catalyst in the two series of experiments are in the ratio of 4.1 : 1 while the amounts of *n*-butanethiol for complete poisoning are in the ratio of 3.5 : 1.

Compared to *n*-butanethiol, thiophene has a relatively minor poisoning effect on the hydrogenation activity of P-3Co. This contrasts with the earlier results for P-3Ni, where the effects of thiophene were ascribed to "pore-mouth"-type poisoning (*8*). It has been suggested (*11*) that thiophene adsorbs coplanar to the catalyst surface and the present results indicate that, for P-3Co, the alkene adsorption is much stronger than that due to the aromatic character of the poison. However, thiophene, as with P-3Ni, does appear to increase the isomerization activity of the catalyst, Fig. 2. The effects of the poison in this concentration range on hydrogenation activity are not significant and the results substantiate the viewpoint that hydrogenation and isomerization of alkenes occur on different reaction sites or by different reaction paths (*12*).

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