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NOTES

Oxidation of Cyclohexene Catalyzed by Cobalt Ion Supported on Carbon

INTRODUCTION

Many advances in the surface chemistry of carbon have been made recently (*1*), and some correlations have been observed between the catalytic activity of carbon and the amount of surface functional groups (*2*, *3*). Garten and Weiss (*4*) reported that there is an equilibrium between quinonoid and phenolic groups on the carbon surface, and that such groups have a catalytic effectiveness on the oxidation–reduction reaction. Catalytic activity of carbon on the oxidation of SO_2 (*5*) and HCl (*6*) have been investigated, and we reported (*7*) that the carbon can also catalyze the oxidation of an organic substance, for example, cyclohexene. In the present study, the catalytic activity of the supported catalyst of cobalt ion on carbon was examined. The effect of support was also investigated quantitatively by using various kinds of carbons with different amounts of surface oxides.

EXPERIMENTAL METHODS

Materials

Commercial cyclohexene was purified by passing over activated alumina in order to eliminate dissolved hydroperoxide, and its purity was estimated at above 99.5% by means of glpc. Two kinds of carbons with different surface area were used as supports: a carbon black (HAF) and an active carbon (AC). These carbons were modified by the methods of Boehm (*8*) and Studebaker *et al.* (*9*). The surface area and surface acidity (NaOH consumption) are listed in Table 1. Pretreatment of carbon is designated by an appended *n*, *o*, or *d* for oxidation by HNO_3, O_2, or methylation with CH_2N_2, respectively. Catalysts were prepared by impregnating carbons with an aqueous solution of a hexaminecobalt(III) chloride which was prepared according to J. Bjerrum (*10*). To 0.1 g of carbon, 0.1 mmole of $[Co(NH_3)_6]Cl_3$ in an aqueous solution was added at 60°C. After the adsorption was complete, the suspension was filtered and washed with a sufficient amount of distilled water.

Oxidation Procedure

The apparatus for oxygen absorption at a constant oxygen pressure (755 ± 2 mmHg) is shown in Fig. 1. A mercury manometer D detected the pressure drop due to the oxygen absorption, and actuated a relay which opened a solenoid valve S. Then the gas pressure in H increased, and the mercury level in B was elevated until the contact in D was detached. The rate of oxygen absorption was followed by recording the variation of the resistance of the platinum wire P. Reaction mixtures contained 20.0 ml of cyclohexene and 0.1 g of catalyst.

RESULTS

Initial absorption curves are represented in Fig. 2 for some catalysts used in this work. Included in this figure for comparison are curves for a heterogeneous salt (cobaltous sulfate), a carbon catalyst, and without catalyst. The rate of oxygen absorption for Co–carbon catalysts are larger than those for other heterogeneous catalysts. No remarkable induction period was observed for the present catalyst system. Total

TABLE 1
RATE OF OXYGEN UPTAKE AND SOME PROPERTIES OF SUPPORT

Carbon	Surface area (m^2/g)	Acidity (meq/g)	Rate (mmole/hr)	
			v_0	v_p
HAF	81	0.02	3.3	11
HAF-*n*3	82	0.06	6.0	10
HAF-*n*1	78	0.10	7.0	10
HAF-*n*4	71	0.15	9.2	10
HAF-*o*1	170	0.40	10.2	10
AC-*d*1	1120	0.15	8.4	—
AC	1230	0.33	11.4	9
AC-*n*4	980	1.05	12.7	9
AC-*n*3	—	1.11	13.7	10

amount of oxygen taken up was 146 mmole for 198 mmole (20 ml) of cyclohexene when one used Co–HAF catalyst. The conversion was 72%. The distribution of oxidized products was analyzed by glpc: Cyclohexenone (27%) and cyclohexenol (18%) were main products among volatile oxidation products. In nonvolatile materials (49%), a considerable amount of acid (15 meq) was detected by titrating with an alkali solution. This tendency was quite similar to the cases for cobalt catalysts previously reported (*11*, *12*).

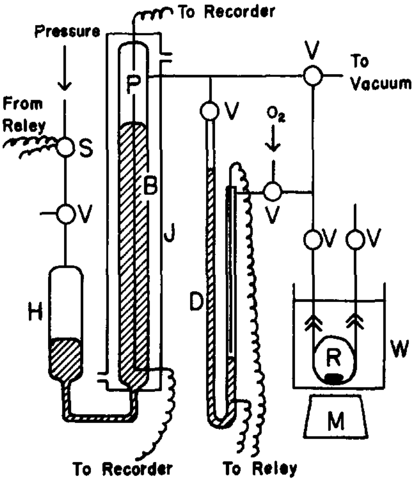


FIG. 1. Apparatus for measuring the rate of oxygen absorption: (S) Solenoid valve; (V) valve; (H) Hg reservoir; (P) Pt wire; (B) gas buret (150 ml); (J) water jacket (28.1°C); (D) detector; (R) reactor; (W) water bath (59.0°C); (M) magnetic stirrer.

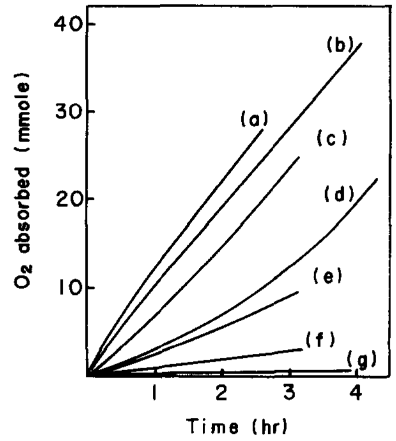


FIG. 2. Initial rate of oxygen absorption: (a) Co–AC*n*3; (b) Co–AC; (c) Co–HAF*n*3; (d) Co–HAF; (e) AC; (f) $CoSO_4{\cdot}7H_2O$; (g) uncatalyzed. Reaction condition: Co ion, 0.1 mmole; carbon 0.1 g; temperature, 59.0°C.

In order to examine the effect of support, we modified the surface of carbon and obtained carbons having different amounts of surface oxides. The NaOH consumption ranges from 0.02 to 0.40 meq/g for HAF series carbons, and from 0.15 to 1.11 meq/g for AC series carbons. The variation of the oxidation rate with time was illustrated in Fig. 3 for the catalysts from cobalt ion and these modified carbon supports. Figure 3 shows that the rate for Co–HAF series catalysts increased at an early stage, whereas

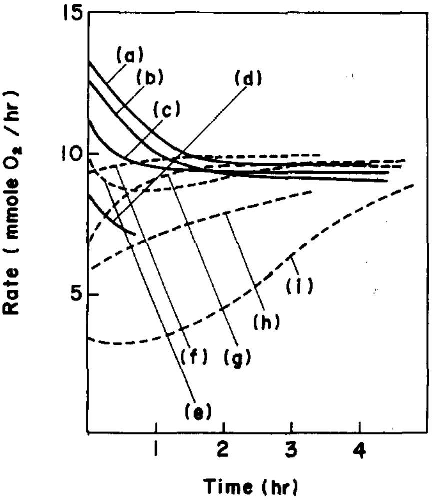


FIG. 3. Variation of the rate with time for various catalysts: (a) Co–AC*n*3; (b) Co–AC*n*4; (c) Co–AC; (d) Co–AC*d*1; (e) Co–HAF*o*1; (f) Co–HAF*n*4; (g) Co–HAF*n*1; (h) Co–HAF*n*3; (i) Co–HAF.

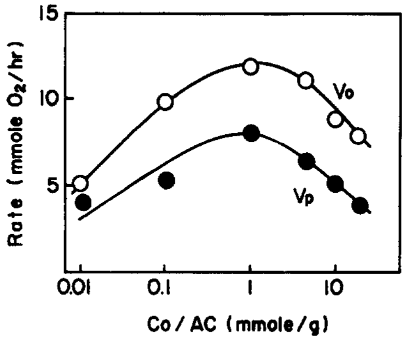


FIG. 4. Dependence of rate on the degree of adsorption of Co^{3+} ion on carbon. Carbon: AC, 45 mg.

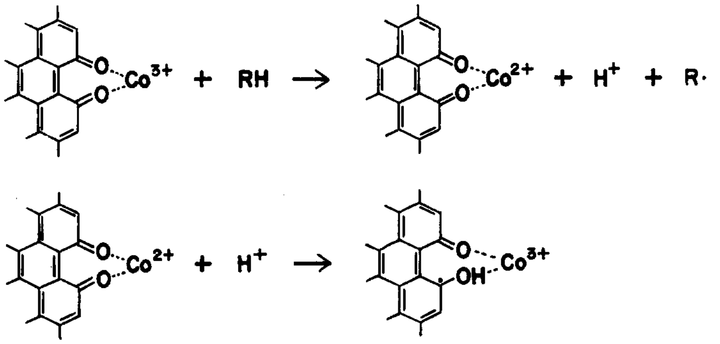
those for Co–AC series catalysts decreased with time. Then the rate for both series came to have nearly equal values at the plateau region. The rate at this region (v_p) was summarized in Table 1 together with the rate at the beginning of the reaction (v_0). The value v_0 was obtained by extrapolation to zero time, and it was used as an indication of the initial catalytic activity of the catalyst. It can be seen that there is a good correlation between v_0 and the acidity of the support.

Figure 4 shows the dependence of the rate on the degree of adsorption of cobalt ion on carbon. In these runs, AC was used as a support without pretreatment. The amount of AC was kept constant (45 mg), and the amount of cobalt ion was varied in the range from 0.45 to 900 μmole. The activity for the least Co/AC ratio was slightly higher than the activity of AC catalyst with no cobalt ion. Increase in catalytic activity occurs until the ratio, Co/AC, exceeds approximately 1 mmole/g, whereafter activity drops off again.

DISCUSSION

The detailed nature of the complex ion adsorbed on carbon has not been clarified, but our previous experiments (*3*) suggest that two or three ammonia molecules dissociate from a $[Co(NH_3)_6]^{3+}$ ion upon adsorption on carbon. The cobalt ion is bound to the acidic functional groups on carbon surface with one of these vacant coordination sites. If the area occupied per $[Co(NH_3)_6]^{3+}$ ion is taken as 31×10^{-20} m², the amount corresponding to the monolayer adsorption on AC is estimated to be 6.6 mmole/g AC, since the surface area of AC was determined to be 1230 m²/g. This value and the value at the optimum condition shown in Fig. 4 are of the same order. Therefore, the increase in the rate at a lower degree of adsorption can be simply interpretated by the increase of the amount of cobalt ions. The decrease beyond the maximum rate shows that cobalt ions adsorbed at the top layer are less active than those adsorbed directly on carbon. This fact suggests the important effect of the interaction of cobalt ion with the surface of carbon.

Additional evidence from Table 1 seems to support this conclusion: Carbons having many acidic sites are good carriers in the oxidation of cyclohexene at the beginning of the reaction. In an initial stage of the oxidation, it is generally accepted that one of the important chain initiating step for the formation of active radicals is the hydrogen extraction by catalyst. In our system, the quinone–hydroquinone character (*4*) of the surface acidic groups seems to play an important role in cobalt ion regeneration, for example, in the following manner. The



reduced carbon surface can be oxidized by molecular oxygen. Similar catalytic role of carbon surface has been postulated for the reduction of cobaltous ion by molecular hydrogen (*13*). The lower activity of the cobalt ion on the top layer may be attributed to the difficulty of such regeneration. In the plateau region, the dependence of the rate on the acidity of carbon is quite different from that at the beginning of the reaction as shown in Table 1. The direct interaction between cobalt ion and the acidic sites on carbon surface seems to be unimportant for the catalytic activity. The detailed mechanism in this region, however, remains to be elucidated.

In conclusion, the catalytic action of the cobalt–carbon catalysts for liquid-phase oxidation was demonstrated. This is a kind of solidified homogeneous catalyst, the advantage of which was emphasized by Acres (*14*, *15*). The effect of carbon carrier was also investigated quantitatively, and it was found that the catalytic activity at the beginning of the reaction depends on the surface acidity of the carrier. The cooperative action of cobalt ions and the acidic oxides on carbon was suggested.

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Isomerization of 1-Olefins Using 1,5-Cyclooctadienetungsten Tetracarbonyl

There are many catalysts for the isomerization of alk-1-enes to nonterminal olefins; however, some, if not all, of these reactions produce results and/or side effects which are often undesirable. For instance, some tend to promote polymerization and/or degradation of either the reactant or the product of the isomerization. Other of these processes suffer from low conversions. A few examples of these are illustrated here:

$$\text{4-methyl-1-pentene} \xrightarrow{\text{Fe carbonyls}} 74\%\ \text{2-methyl-2-pentene} + 13\%\ \text{2-methyl-1-pentene} + 13\%\ \text{4-methyl-2-pentene (Ref. } 1\text{);} \qquad (1)$$