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# Catalysis in Liquid-Phase Autoxidation

## III. Comparison of Metal Oxide Versus Polymeric Surfaces

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The rate of oxidation of tetralin in a solution of chlorobenzene was measured in the presence of metal oxide and supported metal oxide catalysts at 65 to 115°C at conditions identical to those previously employed with polymeric catalysts. At 90°C the specific activity of polymeric catalysts is higher than that of the metal oxide catalysts tested with the exception of copper oxide. Metal oxide catalysts also exhibited a lower apparent activation energy than poly(tetrafluoroethylene). Supporting the metal oxides on a high area substrate failed to increase their activity. The activity of the metal oxide catalysts for the decomposition of tetralin hydroperoxide in chlorobenzene under $N_2$ was also determined. Relative catalytic activity for the decomposition of tetralin hydroperoxide paralleled that observed for the oxidation of tetralin, and suggests that a major role of the catalyst is to accelerate radical production via the decomposition of tetralin hydroperoxide.

### I. INTRODUCTION

This laboratory has carried out an extended study of the catalytic effects of polymeric surfaces in liquid-phase autoxidation (*1*, *2*). It is well known that metal ions catalyze such reactions in a homogeneous, i.e., single-phase, reaction system (*3*). Less extensive studies have shown similar effects of insoluble metal oxides in a heterogeneous, i.e., two-phase, reaction system (*4-6*). Because of this known activity, it had been hoped that coating metal surfaces with polymeric materials would render these surfaces quiescent for autoxidative hydrocarbon reactions leading to deposit formation. Laboratory studies, however, indicated that rather than suppressing autoxidative deposit formation, polymeric coatings increased their rate of formation (*7*). Subsequent tests in larger scale equipment designed to closely simulate an actual autoxidative deposit formation environment in a high speed aircraft confirmed the results of these laboratory studies (*8*).

Because of the complexity of the autoxidative deposit formation process, these catalytic effects were further studied using the autoxidation of tetralin in an inert solvent as a model reaction (*1*, *2*). A number of polymeric surfaces were shown to be catalysts for the autoxidation of tetralin (*1*). Subsequently, it was shown that poly(tetrafluoroethylene) catalyzed the decomposition of tetraline hydroperoxide (*2*). A comparison with literature values suggested that the polymeric surfaces tested were approximately equivalent in activity to many metal oxide surfaces (*1*).

In a reaction system such as the heterogeneously catalyzed oxidation of tetralin, reactions take place both in the liquid phase and at the surface of the catalyst. Such a system is more complex, thus, than either a homogeneously catalyzed reaction in which the complexity of a two-phase reaction system is lacking, or the more common heterogeneously catalyzed reaction in which all the reactions take place on the surface of the catalyst. In addition, since autoxidative reactions involve a series of sequential reaction steps, the addition of a catalyst to the system poses a number of difficult questions such as (1) which step or steps are being influenced by the catalyst, (2) what is the nature of the influence, i.e., are reaction rates simply being speeded up or slowed down or are new products being formed indicating that new or altered reaction steps are occurring. Evidence already exists that catalyzed autoxidative systems are indeed complicated. For example, a complex effect of the amount of heterogeneous catalyst on the rate of oxidation of tetralin has been reported (*9*). At lower levels, the rate of oxidation increases with increasing catalyst concentration, however, ultimately a critical catalyst concentration is reached, above which the reaction is inhibited. An interpretation in terms of competitive adsorption on the catalyst surface was suggested (*9*). Similar effects have been observed in homogeneously catalyzed autoxidation reactions and it has been suggested that this complex behavior reflects a catalytic effect of the metal ions on both the initiating and terminating reactions (*10*).

Because of the obviously complex nature of the heterogeneously catalyzed oxidation of a hydrocarbon such as tetralin it was felt that only a direct comparison of the activities of metal oxides and polymeric catalysts would be meaningful. In the present study the catalytic activity of a number of metal oxide catalysts were determined at the identical conditions previously employed with the polymer catalysts so as to allow a direct comparison of catalytic activity to be made. Metal oxide catalysts were tested both as metal oxides and as metal oxides supported on an inert high area substrate. The activities of metal oxide catalysts for the decomposition of tetralin hydroperoxide under nitrogen was also studied.

## II. Experimental Methods

### *A. Apparatus and Procedure*

A conventional liquid-phase autoxidation apparatus was used (*11*). The rate of oxidation was measured at atmospheric pressure. The reactor was immersed in a temperature bath controlled to ±0.5°C. Mass transfer limitations were minimized by vibrating the reactor at a speed of 800 cpm. Experiments demonstrated that the rate of oxidation was independent of vibration speed at this level. In each run the reactant, i.e., tetralin or tetralin hydroperoxide, chlorobenzene, and a fresh charge of catalyst were added to the reactor and hooked into the reaction system; the reactants were degassed by repeated vacuum freeze–thaw cycles using liquid $N_2$. The reactor was then filled with $O_2$ for the tetralin oxidation experiments or $N_2$ for the tetralin hydroperoxide decomposition experiments, and immersed in the temperature-controlled bath. Aliquot samples for analysis during the run were removed via a syringe through a septum cap attached to a side arm on the reactor. The tetraline hydroperoxide content was determined chemically by the method of Wagner, Smith and Peters (*12*). Selected replicate runs indicated that the rate data obtained was reproducible. Tests indicated that neat chlorobenzene in the presence of catalysts at the conditions employed was inactive relative to the activity exhibited by tetralin in chlorobenzene.

### *B. Reagents*

Tetralin (Matheson, Coleman and Bell, practical grade) was purified by washing with concentrated sulfuric acid until the washings were colorless, followed by washing with distilled water to remove residual acidity and drying with anhydrous $MgSO_4$ (*9*). The resulting tetralin was then repeatedly distilled in a spinning band column until a fraction was obtained which showed no impurities by glpc analyses. Chemical analyses confirmed the tetralin was free of hydroperoxide (*12*). Tetralin hydroperoxide was prepared by the method of Woodward and Mesrobian (*13*) using purified tetralin and dry air. Product purity was verified by chemical titration. Glpc pure chlorobenzene (Matheson Coleman and Bell) was employed.

The neat metal oxide catalysts were prepared using reagent grade cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$; nickelous nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ and cupric nitrate $Cu(NO_3)_2 \cdot 3H_2O$ obtained from Baker and Adamson Products, Allied Chemical Corp., Morristown, NJ. Carefully weighted quantities of the nitrate salts were dried overnight at 105°C and then calcined in air for 4 hr at 470°C. The residue was broken up and screened to a 60/80 mesh size. Weight changes resulting from the calcination step and metal analyses of the prepared catalysts confirm the stoichiometry of the expected oxides, i.e., $Co_3O_4$, NiO and CuO (*14*). Surface areas (BET) were: NiO, 9.55 $m^2/g$; $Co_3O_4$, 3.47 $m^2/g$; CuO, 0.15 $m^2/g$. A sample of the neat NiO catalyst was further sintered by calcining in air for 2 hr at 800°C. Its surface area (BET) was 3.08 $m^2/g$.

The metal oxide catalysts supported on silica contained 10 wt% metal and were prepared as described previously (*15*), with the exception that the catalysts were calcined in air for 4 hr at 470°C, rather than being reduced in hydrogen. The silica used was Cabosil HS-5 (300 $m^2/$ surface area). The calcined catalysts were pressed at 3000 psi into wafers and then crushed and screened to a size between 60 and 80 mesh. The metal oxide areas of these supported catalysts are not known. The metal surface areas of the corresponding catalysts (which were reduced in hydrogen at 370°C rather than calcined in air at 470°C) as determined by $H_2$ chemisorption were: Ni, 13.6 $m^2/g$; Co, 5.6 $m^2/g$; Cu, 3.3 $m^2/g$ (*15*).

The polymer catalysts were prepared as 60/80 mesh powders as described previously (*1*). The poly(tetrafluoroethylene) was obtained from E. I. duPont Nemours & Co., Wilmington, DE. Its BET surface area was 0.69 $m^2/g$. The polypropylene was obtained from the Enjay Chemical Company, Linden, NJ. Its BET surface area was 0.21 $m^2/g$.

## III. RESULTS AND DISCUSSION

A series of metal oxide catalysts including cobalt, nickel and copper were prepared, both as neat metal oxides and as metal oxides supported on an inert, high area substrate. Details of the catalyst preparations are shown in the experimental section. The catalytic activity of the metal oxide catalysts was first measured for the oxidation of tetralin in chlorobenzene at 65 to 115°C. Conditions employed were identical to those previously used in the evaluation of the activity of various polymeric catalysts (*1*). Typical results are shown in Figs. 1, 2 and 3. The maximum oxidation rates obtained with these catalysts are shown in the Arrhenius plots in Figs. 4 and 5. The maximum oxidation rate corresponded to the initial oxidation rate for all catalysts except the copper oxide catalyst. A summary of the kinetic parameters obtained with these catalysts

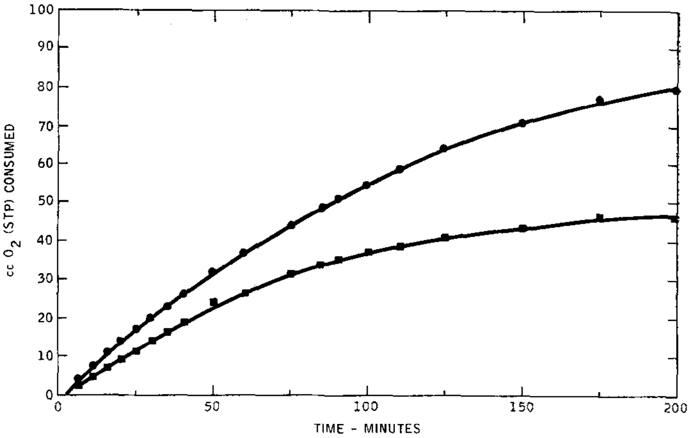

FIG. 1. Oxidation of tetralin at 90°C: (●) cobalt oxide; (■) cobalt oxide on silica. Other conditions: 2 $cm^3$ of tetralin, 2 $cm^3$ of chlorobenzene, 0.30 g of catalyst and 1 atm pressure.

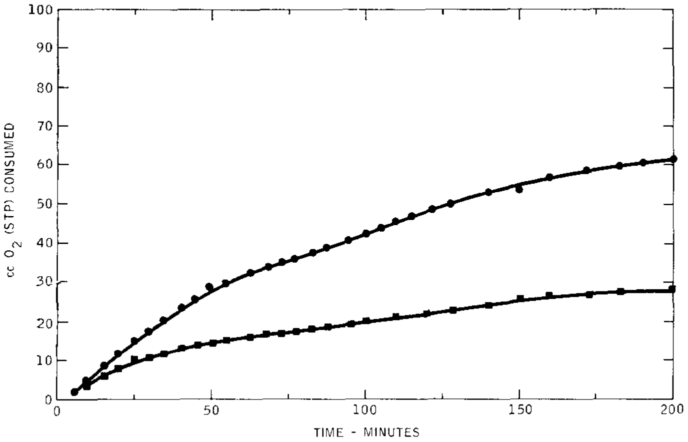

FIG. 2. Oxidation of tetralin at 90°C: (●) nickel oxide; (■) nickel oxide on silica. Other conditions: 2 $cm^3$ of tetralin, 2 $cm^3$ of chlorobenzene, 0.30 g of catalyst and 1 atm pressure.

is shown in Table 1. The specific catalyst activities (g-moles of $O_2$ per hr per $cm^3$ tetralin per $m^2$ of catalyst) were obtained by dividing the catalyst activity (g-moles of $O_2$ per hr per ml tetralin per g of catalyst) by the catalyst surface areas reported in the experimental section. The high area silica used as a substrate was also tested and found to be inactive. The surface area of the active metal oxide supported on the inert silica substrate is not known so that the specific activity of these catalysts cannot be calculated. Results are also shown for a nickel oxide catalyst which had its surface area reduced by a factor of three by sintering at high temperatures. For comparison purposes, results obtained previously (*1*) with two polymeric catalysts are also shown in Table 1.

A comparison of catalyst activities per unit weight of catalyst at 90°C and otherwise identical conditions indicates that the polymeric catalysts are approximately equal in activity to the metal oxide catalysts tested. On a specific activity basis the polymeric catalysts are more active than the metal oxide catalysts, with the exception of copper oxide. These results confirm the suggestion previously advanced based on calculations from the literature, that polymeric catalysts are comparable in activity to many active metal oxides for autoxidative reactions (*1*).

The copper oxide was clearly the most

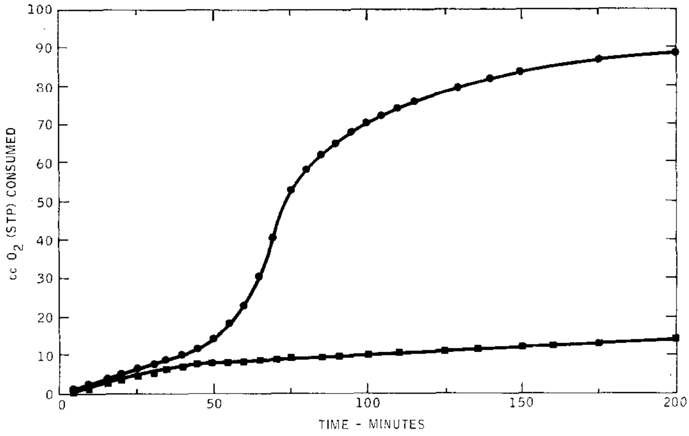

FIG. 3. Oxidation of tetralin at 90°C: (●) copper oxide; (■) copper oxide on silica. Other conditions: 2 $cm^3$ of tetralin, 2 $cm^3$ of chlorobenzene, 0.30 g of catalyst and 1 atm pressure.

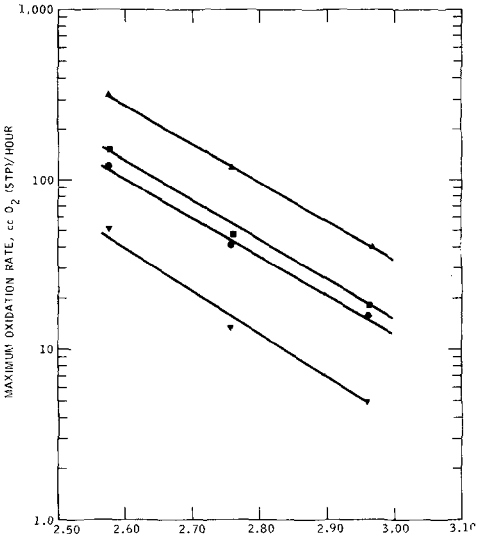

FIG. 4. The effect of temperature on the rate of oxidation of tetralin: (■) cobalt oxide; (●) nickel oxide; (▼) sintered nickel oxide; (▲) copper oxide. Other conditions: 2 $cm^3$ of tetralin, 2 $cm^3$ of chlorobenzene, 0.30 g of catalyst and 1 atm pressure.

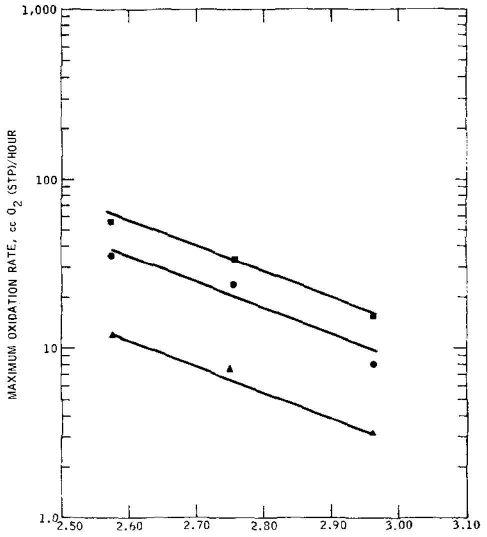

FIG. 5. The effect of temperature on the rate of oxidation of tetralin: (■) cobalt oxide on silica; (●) nickel oxide on silica; (▲) copper oxide on silica. Other conditions: 2 $cm^3$ of tetralin, 2 $cm^3$ of chlorobenzene, 0.30 g of catalyst and 1 atm pressure.

active catalyst of the metal oxides tested, both in terms of activity on a unit weight and a unit area basis (specific activity). The deleterious nature of copper surfaces in autoxidative reactions has been reported a number of times (*16*, *17*). The specific activity of the nickel oxide catalyst remained the same even though its surface area was varied by a factor of three via sintering, suggesting that high metal oxide areas are advantageous. In commercial practice, high catalyst areas are generally

TABLE 1

SUMMARY OF KINETIC PARAMETERS FOR THE CATALYZED OXIDATION OF TETRALIN

| Catalyst | Catalyst activity at 90°C (g-moles $O_2$ per hr per $cm^3$ of tetralin per g catalyst)[a] | Specific activity at 90°C (g-moles $O^2$ per hr per $cm^3$ per $m^2$ of catalyst)[b] | Apparent activation energy (kcal/mole) |
|---|---|---|---|
| Cobalt oxide | $3.50 \times 10^{-3}$ | $10.1 \times 10^{-4}$ | 10.5 |
| Nickel oxide | $2.98 \times 10^{-3}$ | $3.12 \times 10^{-4}$ | 10.7 |
| Sintered nickel oxide | $1.03 \times 10^{-3}$ | $3.34 \times 10^{-4}$ | 11.2 |
| Copper oxide | $8.78 \times 10^{-3}$ | $585 \times 10^{-4}$ | 10.5 |
| Cobalt oxide on silica | $2.46 \times 10^{-3}$ | — | 7.1 |
| Nickel oxide on silica | $1.79 \times 10^{-3}$ | — | 7.0 |
| Copper oxide on silica | $5.95 \times 10^{-4}$ | — | 7.1 |
| Silica | Inactive | — | — |
| Poly(tetrafluoroethylene) | $1.49 \times 10^{-3}$ | $21.6 \times 10^{-4}$ | 17.0 |
| Polypropylene | $4.47 \times 10^{-3}$ | $213 \times 10^{-4}$ | — |

[a] Based on maximum rate of oxidation. Other conditions: 2 $cm^3$ tetralin in 2 $cm^3$ chlorobenzene, 0.30 g of catalyst and 1 atm pressure. For all catalysts, with the exception of copper oxide, the maximum rate occurred at initial conditions, and thus these rates correspond to initial reaction rates.

[b] Catalyst activity per unit area of active catalyst surface obtained by dividing activity per unit weight by the catalyst surface area.

achieved by supporting the active material on a high area substrate. However, in the present work supporting the metal oxides on a high area inert substrate, in general, lowered their activity. An estimate of the magnitude of active metal oxide areas on these supported catalysts can be made via the known metal surface areas which would be obtained if the catalysts were reduced with hydrogen (*15*). In general, these supported metal areas are higher than the areas of the corresponding metal oxide catalysts. In contrast, the activity of the supported catalysts is lower, particularly that of the supported copper oxide catalyst which is markedly less active than the copper oxide catalyst.

Because of the complexity of the heterogeneously catalyzed reaction system, apparent activation energies were calculated from the measured rates of oxidation and comparisons made from these gross values. It has been reported that the poly(tetrofluoroethylene) and metal oxide catalyzed reactions are zero order in oxygen pressure (*2*, *9*). Because of this zero order dependence, changes in oxygen concentration with temperature at constant total pressure will not influence the apparent activation energy. However, these complex activation energies still represent the overall effect of a number of reaction steps, and possibly adsorption or desorption steps and thus must be compared with reservation.

Apparent activation energies of 10 to 11 kcal/mole were obtained for the metal oxide catalysts, which agrees closely with previous results obtained with neat metal oxide catalysts (*9*). Apparent activation energies for the supported metal oxide materials were slightly lower, (i.e., 7 kcal/mole) perhaps reflecting an effect of mass transport limitations with these high total surface area materials. In contrast, the apparent activation for the poly(tetrafluoroethylene) catalyst was higher (i.e., 17 kcal/mole) and more typical of that reported for the homogeneously catalyzed oxidation of tetralin (*13*, *18*). Because of this higher apparent activation energy, the poly(tetrafluoroethylene) catalyst will become even more active relative to the neat and supported metal oxide catalysts as the temperature is increased.

The catalytic activity of the metal oxide catalysts for the decomposition of tetralin hydroperoxide in inert chlorobenzene under nitrogen at 90°C was also measured. Again conditions identical to those used in the polymer catalyst studies were employed (*2*). The relative activity (on a catalyst weight basis) of the catalysts is shown in Table 2. An examination of the relative activity of the metal oxides for the catalytic decomposition of tetralin hydroperox-

TABLE 2

RELATIVE ACTIVITY FOR THE CATALYZED DECOMPOSITION OF TETRALIN HYDROPEROXIDE

| Catalyst | First order rate constant for the decomposition of the hydroperoxide at 90°C (min$^{-1}$)[a] | Relative hydroperoxide decomposition activity per unit wt of catalyst at 90°C[b] | Relative activity for the oxidation of tetralin per unit wt of catalyst at 90°C[c] |
|---|---|---|---|
| Cobalt oxide | $6.82 \times 10^{-3}$ | 1.00 (base) | 1.00 (base) |
| Nickel oxide | $4.91 \times 10^{-3}$ | 0.7 | 0.8 |
| Copper oxide | $1.08 \times 10^{-2}$ | 1.6 | 2.5 |
| Cobalt oxide on silica | $6.10 \times 10^{-3}$ | 0.9 | 0.7 |
| Nickel oxide on silica | $3.14 \times 10^{-3}$ | 0.5 | 0.5 |
| Copper oxide on silica | $1.43 \times 10^{-3}$ | 0.2 | 0.2 |
| Poly(tetrafluoroethylene) | $3.30 \times 10^{-3}$ | 0.5 | 0.4 |

[a] Conditions: 0.20 g of tetralin hydroperxoide in 4 cm$^3$ of chlorobenzene with 0.30 g of catalyst under 1 atm nitrogen.

[b] Calculated from the first-order rate constant obtained at the conditions shown in *a*.

[c] Calculated from the data shown in Table 1, at the conditions shown in *a* of Table 1.

ide indicates that the activity of the catalysts for this reaction parallels that of the catalyst for the oxidation of tetralin. It was suggested previously that the principal role of the poly(tetrafluoroethylene) surface in the oxidation of tetralin is to accelerate radical production via the catalyzed decomposition of the intermediate tetralin hydroperoxide. These results also suggest that the principal function of the metal oxide catalysts in the oxidation of tetralin is to accelerate the decomposition of the intermediate hydroperoxide. Similar observations have been made in regard to the role of metal ions in the metal catalyzed autoxidation of alkanes and alkylbenzenes in a homogeneous reaction system (*19*).

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