BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2101—2104 (1966)

Catalytic Activities of Metal Oxides in the Oxidation of Propylene

By Toyosaburo TAKEUCHI, Michiaki HONMA* and Hideo TAKEDA

Faculty of Literature and Science, Toyama University, Gofuku, Toyama

(Received December 9, 1965)

The catalytic oxidation of propylene by the flow method was carried out in order to investigate the correlation between the activity and the physical properties of the catalyst, using the oxides of zinc, copper, nickel, cobalt, iron, manganese, chromium, vanadium and titanium, all of which were supported with alumina. The analysis by means of gas chromatography indicated that the main products of the reaction were carbon dioxide and water. An abrupt increase in the rate of conversion against the temperature, denoted by C_T, was irrespective of the amount of oxide and was characteristic of each oxide. The C_T was expressed as a function of the % d character of the metal of the oxide, as well as a function of the heat of formation per gram-atom of oxygen in the oxide. The mechanism of the abrupt change in the rate of conversion was discussed in relation to the ability of oxygen to be removed from the oxide and the amount of propylene adsorbing on the oxide during the reaction.

The usefulness of metal oxides in the catalytic oxidation of hydrocarbons has been extensively investigated by many workers.[1-5] However, many problems still remain for the establishment of the correlation between the physical properties of metal oxide and the catalytic activity. Recently, Kwan and his co-workers[6] have presented a rule of the catalytic activity of metallic oxides by the use of the experimental results given by Popovskii and Boreskov,[7] who studied the catalytic oxidation of hydrogen. Their rule claims that the activity of the oxidation can be expressed by a function of the heat of formation per gram-atom of the oxygen of the oxide.

This study will deal with the oxidation of propylene on various metallic oxides in order to ascertain wheteher the rule can be applicable to the oxidation of hydrocarbon. The catalytic activities of the oxides will also be discussed from the standpoint of the electronic property of the metal atom of the oxides. The % d character of the metal of the oxide will be taken into consideration for this purpose. The metallic oxides used were titanium(IV) oxide, vanadium(V) oxide, chrome(III) oxide, manganese(IV) oxide, iron(III) oxide, nickel(II) oxide, copper(II) oxide and zinc oxide.

Experimental

The test of the catalytic activity was carried out by a flow method using air. The apparatus used is shown in Fig. 1, where A is the reaction tube, whose diameter and length are 12 mm. and 200 mm. respectively. P is a premixer, and C is a damper of air coming from the compresser, D. F is a flow meter of the soap film. M is an oil manometer, and T is a trap cooled by a mixture of ice and sodium chloride in order to remove the water vapor present in a mixture of propylene and air. The volume of the reaction tube,

---

* Present address: Nikki Chemical Co., 2-4 Ootemachi, Chiyodaku, Tokyo.

[1] G. Parravano and M. Boudart, "Advances in Catalysis," Academic Press, **7**, 50 (1955).

[2] E. R. S. Winter, ibid., **10**, 196 (1958).

[3] J. K. Dixon, "Catalysis," Reinhold Pub., **7**, 183 (1960).

[4] F. S. Stone, "Advances in Catalysis," **13**, 1 (1962).

[5] G. K. Boreskov, ibid., **15**, 286 (1964).

[6] I. Komuro, H. Yamamoto and T. Kwan, This Bulletin, **36**, 1532 (1963).

[7] V. V. Popovskii and G. K. Boreskov, *Probl. Kinetiki; Kataliza, Akad. Nauk. SSSR.*, **10**, 67 (1960).

including an oil manometer of the U-type portions was about 200 cc.

0.5 g. of the oxide was used; it was replaced afresh for each run of the test. The glass fiber was packed at both sides of the catalyst. The ratio of propylene to air was always kept at 0.04—0.05. The flow rate of the mixed gas in the reaction tube was in the range from 100 to 120 cc./min. The analysis of the reaction products was made by means of gas chromatography, using helium as the carrier. The intervals of every analysis were 30 or 60 min. The fluctuation in the amounts of products could be found over about a 30 min. period in the initial stage. The average was taken for the evaluation of the activity. It was calculated from the values measured for five hours, except for the initial hour.

The catalysts, except for those of titanium dioxide and vanadium pentoxide, were prepared from the nitrates. 30—50 mesh γ-alumina was used as the carrier. It was immersed into about a 2 N solution of each nitrate for about 48 hr. at room temperature; then the precipitate was separated from the solution and ignited at 550°C in a furnace. Vanadium pentoxide was prepared by immersing alumina in a solution of meta-ammonium vanadate, which had been dissolved in nitric acid. Titanium dioxide was prepared by immersing alumina into the solution of titanium, which had been dissolved in hydrofluoric acid; then the precipitate was separated from the solution and ignited at 550°C.

Five oxides, i. e., cupric oxide, vanadium pentoxide, zinc oxide and chromium trioxide, were tested without a carrier in order to investigate the influence of the carrier on the oxidation of propylene. The powder of about 50 mesh was selected by sifting it before use. The B. E. T. areas of the catalysts were determined by using nitrogen or methane at -196°C. Nitrogen was used for the supported catalysts, while methane was used for the unsupported catalysts.

Results

The products of the oxidation of propylene were, in most cases, carbon dioxide and water. The products of the oxidation in the presence of vanadium pentoxide gave a stimulant smell. The gas chromatogram of the products, however, gave only the patterns of carbon dioxide and water.

The activity was represented as a percentage of the amount converted, which was determined from the amount of carbon dioxide produced. The results are summarized in Figs. 2 and 3. In Fig. 3, the results on pure alumina are also shown for the purpose of comparison. The alumina used for this purpose was prepared by heating it in vacuo at 450°C. The figures indicate that the percentage of the conversion on the oxides of nickel, manganese, chromium, iron, cobalt and vanadium changes markedly in a certain temperature range. However, no such remarkable change could be found either on pure alumina or on the supported oxides of copper, zinc and titanium. The temperature of the remarkable change was independent of the amount of the catalyst. It can be said, therfore, that the temperature is characteristic of each oxide. The inclination of the line at a point of remarkable change for the pure oxides (unsupported catalysts), except vanadium oxide, is steeper than those for the oxides combined with alumina (a supported catalyst). We denote the temperature of the remarkable change as C_T. The figures indicate that the C_T of chromium oxide and that of vanadium oxide are lowered by the presence of the carrier, while, C_T of cupric oxide is raised. The influence of the carrier is very small in the case of zinc oxide.

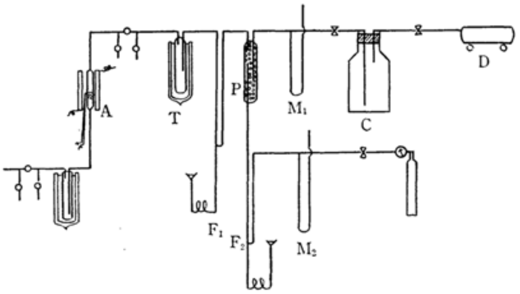

Fig. 1. Apparatus for oxidation of propylene.

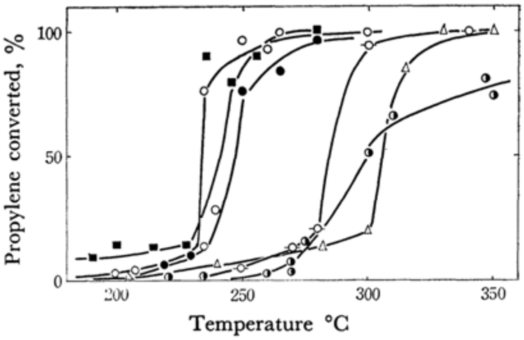

Fig. 2. Result of the oxidation of propylene.
■ NiO, ● MnO_2, ○ Cr_2O_3, -○- Fe_2O_3,
△ V_2O_5, ◑ Co_3O_4.

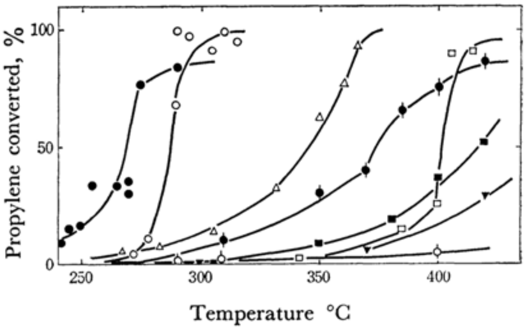

Fig. 3. Result of the oxidation of propylene.
○ unsupported Cr_2O_3, ● unsupported CuO,
△ unsupported V_2O_5, □ unsupported ZnO,
● CuO, ■ ZnO, ▼ TiO_2, ○ γ-Al_2O_3.

Figure 4 shows the correlation between C_T and ΔH, the heat of formation per gram-atom of the oxygen of the corresponding oxide. The figure shows that an approximate linear relation can be established for all the oxides except for the supported cupric oxide and chromium oxide. The rates of reaction were calculated by the following equation:

$$V = rFX/(1+r)S$$

where V is the rate of reaction, X is the percentage of the propylene converted, and F is the space velocity of gas. S and r are the surface area of the catalyst and the mole ratio of propylene to air, (O_2 in air)/(propylene), respectively.

Figure 5 shows the correlation between log V and the reciprocal of the reaction temperature. The correlations are represented by broken lines, suggesting that the activation energies below and above C_T differ from each other. However, no systematic correlation between the activation energy and ΔH could be found in either temperature range, as has previously reported by Morooka and Ozaki.[8]

Discussion

The change of catalytic activity in the presence of alumina may suggest that a change of structure of oxide occurs. An experimental confirmation of the structural change of each supported oxide could not be made, nevertheless, the oxide whose activity is changed may be considered to have the spinel structure from the standpoint of valency.

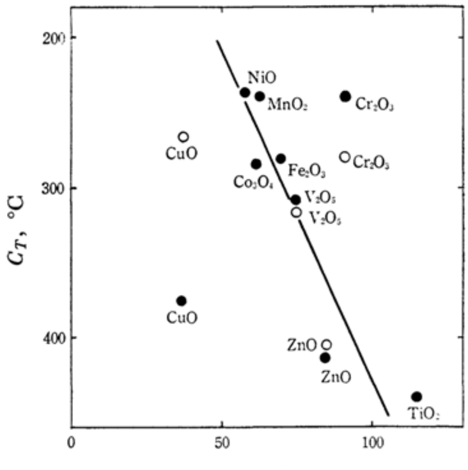

Fig. 4. Correlation between C_T and ΔH.
○ indicates unsupported oxide.

The rates of the reaction in the temperature range above C_T could not be known accurately. The temperature would rise due to the accumulation of heat by the explosive fast reaction which could be supposed to occur, though the thermometer of the reaction tube always showed a constant temperature. Whatever may be the accurate value of the reaction rate above C_T, the change in the activation energy below and above C_T may suggest a change in the mechanism of the reaction, as is clear from the results in Fig. 5.

Hofer et al.[9] investigated the oxidation of ethylene and carbon monoxide on cupric oxide, cobalt

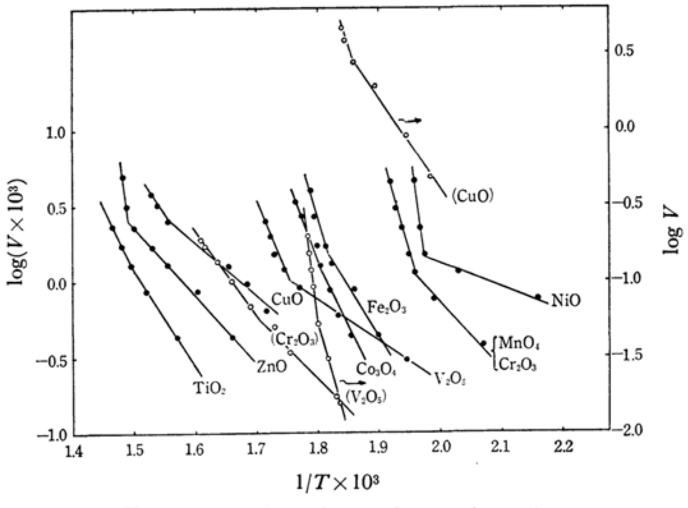

Fig. 5. Temperature dependence of rate of reaction.
The unit of the rate V is cc./min.m².
Bracket indicates unsupported oxide.

---

[8] Y. Morooka and A. Ozaki, *Shokubai*, **6**, 27 (1964).

[9] L. J. E. Hofer, P. Gussey and R. B. Anderson, *J. Catalysis*, **3**, 451 (1964).

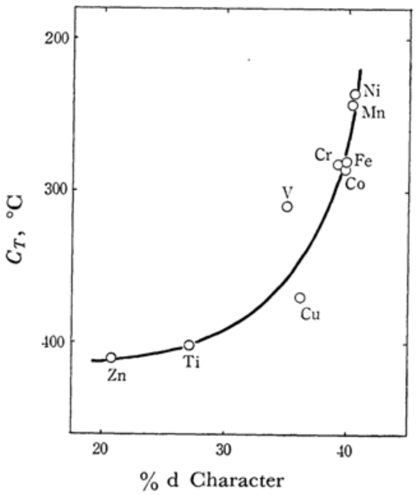

Fig. 6. Correlation between C_T and % d character of metal of oxide.

oxide and chromium oxide by means of gas chromatography; they reported the dependence of the amount of the product and that of the reactants adsorbed on the oxide upon the reaction temperature. Evidently from their data, a remarkable change in the amount of conversion takes place at the temperature where the amount of the reactants adsorbed on the oxide becomes nearly zero, though they put no scuh interpretation on thier results. An exception is found, however, in the reaction on copper oxide. They reported that the amounts of reactants adsorbed on the cupric oxide were nearly zero in the temperature range investigated. The extremely small value obtained from the measurement of adsorption on the copper oxide seems to result from the difficulty of accurate measurement of the amount of adsorption, because the surface of the copper oxide is particularly small, about 1/20 that of the other oxides. Considering from their results, the remarkable increase of the amount of conversed propylene may be due to the decrease of the adsorbed propylene to a certain concentration at the temperature of C_T. The ability of gas to be adsorbed on the metal oxides can be estimated from the heats of adsorption on them. Unfortunately, no information on the heats of adsorption of propylene on metal oxides has appeared in literatures so far. However, the heats of adsorption on oxides may be estimated, if we assume that the propylene is adsorbed on the metal atoms of the oxide, and that the cohesive binding between metal and oxygen occurs by the shift of the valence electron of 4p orbitals of the metal atom to oxygen, without affecting the d electron of the metal atom. By applying the valence bond theory of Pauling(10) to the metal oxides and the proposal by Beeck,(11) who found the correlation between the heat of adsorption and the % d character of metal, the correlation between the % d character of the metal atom of each oxide and C_T can be obtained. The results are shown in Fig. 6, where the % d character of all the metal atoms except for zinc are quoted from the list given by Pauling. The % d character of zinc was calculated by assuming 4.56 for its valence(12) and the resonance structure of $V(2)$ and $V(6)$, where V indicates the valence of the metal. The correlation in the figure seems to be more satisfactory than that between ΔH and C_T, because the deviation is smaller. The figure indicates that C_T increases with decreasing % d character. Since the heat of adsorption is connected with the ability of adsorption and since it decreases with increasing % d character of metal atom,(11) it can be said that the oxide of the lower C_T value has a smaller ability of adsorption of propylene than the oxide of the higher C_T value and that the surface of the catalyst would be covered more densely with oxygen than with propylene.

The reaction mechanism of the oxidation of hydrocarbon proposed by Bretton et al.(13) was the removal of hydrogen from the hydrocarbon at its first step. The same proposal has been made by Sachtler and De Boer(14) and by Adams and Jennings(15) for the oxidation of propylene. A satisfactory explanation of the difference in the mechanisms of the oxidation in the two temperature ranges below and above C_T is far from having been established at present. However, it can be concluded that the difference in C_T of various metal oxides may be due to the ability of oxygen to be removed from the oxide and that of propylene to be adsorbed on the metal atom of the oxide.

---

10) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947); *Proc. Roy. Soc.*, **A196**, 343 (1949).

11) O. Beeck, *Discussions Faraday Soc.*, **8**, 118 (1950).

12) L. Pauling, "The Nature of the Chemical Bond", Cornell U. P. and O. U. P., 3rd ed., Ithaca, N. Y. (1960), p. 396.

13) R. H. Bretton, S. U. Wan and B. F. Dodge, *Ind. Eng. Chem.*, **44**, 594 (1952).

14) W. H. N. Sachtler and N. H. De Boer, "Proc. 3rd Intern. Cong. Catalysis," North Holland Pub. Co. (1964), p. 252.

15) C. R. Adams and T. J. Jennings, *J. Catalysis,* **3**, 549 (1964).