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Regularity in the Catalytic Properties of Metal Oxides in Hydrocarbon Oxidation

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The catalytic properties of various oxides were determined in the oxidation of isobutene, acetylene, ethylene, and propane and were correlated with the heat of formation of the catalyst oxides divided by the number of oxygen atoms in the oxide molecule (ΔH_O). It was observed there is a distinctive relation between catalytic activity and ΔH_O; the lower the ΔH_O of the catalyst, the higher its activity. For isobutene and acetylene oxidations, the reaction order in hydrocarbon increased and that in oxygen decreased with increasing ΔH_O, whereas for ethylene and propane both orders in oxygen and hydrocarbon were insensitive to ΔH_O.

Some experiments on competitive oxidation of hydrocarbons were undertaken, and it was concluded that the hydrocarbon reacts via the adsorbed state. The sequence of adsorption strength was determined as iso-$C_4H_8 > C_2H_2 > C_3H_6 > C_2H_4 > C_3H_8$, which is the reverse of the reaction order sequence.

INTRODUCTION

In recent studies on the catalytic properties of metals and metal oxides, correlations between catalytic activity and the physical properties of catalysts have been examined by several groups of workers (*1*, *2*). Special attention has been paid to the correlation between the catalytic activity and the heat of formation of catalysts (*3*, *4*, *5*).

In a preceding report by the authors (*6*), dealing with the catalytic oxidation of propylene, both the catalytic activity of metal oxides and the reaction order in propylene were correlated with the heat of formation of the catalyst oxides divided by the number of oxygen atoms in the oxide molecule (ΔH_O). It was shown that the larger the ΔH_O, the less active the catalyst and the higher the order in propylene. Considering that the ΔH_O signifies the bond strength between metal atom and adsorbed oxygen, those results were interpreted as indicating that the degree of surface coverage of oxygen increased whereas that of hydrocarbon decreased with increasing ΔH_O value of catalyst.

In the present paper, the catalytic properties of metal oxides were similarly examined in the oxidation of isobutene, acetylene, ethylene, and propane. Some experiments were directed to competitive oxidation of mixed hydrocarbons to examine whether the oxidation proceeds via an adsorbed state and to find the relative adsorption affinity of hydrocarbons to catalysts.

EXPERIMENTAL

All of the data were obtained using a flow system at atmospheric pressure. The reactant gas composition for catalytic activity measurement was a mixture of 50 vol % oxygen, 48 vol % nitrogen, and 2 vol % hydrocarbon. The reaction order was determined by varying the partial pressure of oxygen or hydrocarbon in the vicinity of this composition.

The catalysts were obtained from the same batch as reported in the preceding

TABLE 1

KINETIC PARAMETER OBTAINED IN ISOBUTENE OXIDATION

Catalysts	Reaction orders in isobutene	Reaction orders in oxygen	Temperature range (°C)	E (kcal/mole)	log A (A in mole/m^2 sec)	log V_{300} (V in mole/m^2 sec)
Pt	−0.41	1.05	92 ~ 118	22.6	5.58	−3.05
Pd	−0.22	0.78	132 ~ 153	33.4	10.14	−2.60
Co_3O_4	−0.09	0.75	220 ~ 262	38.4	8.35	−6.30
NiO	0.15	0.55	263 ~ 305	24.8	2.02	−7.45
MnO_2	−0.25	0.54	193 ~ 238	36.4	5.88	−6.01
Fe_2O_3	0.21	0.60	270 ~ 312	37.3	6.56	−7.66
Cr_2O_3	0.25	0.47	242 ~ 270	30.9	5.15	−6.64
CeO_2	1.00	0.00	207 ~ 250	23.8	2.71	−7.37
ThO_2	—	—	273 ~ 312	14.8	−2.72	−8.37

paper (*6*). The reactor was packed with 10 ml of catalyst and the total flow rate was fixed at 100 ml STP/min (25°C) for all experiments. The procedures for determining reaction orders and catalytic activity were the same as previously reported (*6*).

RESULTS

1. *Reaction Orders and Catalytic Activity*

In all cases carbon dioxide was the sole product of oxidation of isobutene, acetylene, ethylene, and propane, irrespective of the catalyst employed.

Values for both reaction orders, apparent activation energy, and pre-exponential factor observed for each of the four hydrocarbons are summarized in Tables 1–4. As shown in Tables 1 and 2, both reaction orders in oxygen and in hydrocarbon, for the oxidation of isobutene and acetylene, depend markedly upon the type of catalyst. In no case was the order in oxygen negative, while the order in hydrocarbon was occasionally negative, indicating the retardation of reaction rate by the hydrocarbon concerned. This retardation was particularly remarkable over Pt and Pd. These features are essentially the same as reported in the preceding paper on propylene oxidation.

On the other hand, both reaction orders for the oxidation of ethylene and propane depended slightly upon the type of catalyst. The oxidation of propane was, in every case, virtually first order in propane and independent of oxygen.

Thus the reaction order sequence for the hydrocarbons studied, including propylene, is assessed over a catalyst as follows: $C_3H_8 > C_2H_4 > C_3H_6 > C_2H_2 >$ iso-C_4H_8.

The apparent activation energy and pre-exponential factor show a compensation effect, as exemplified in Fig. 1 for acetylene. The effect is similarly observed for the result of propylene oxidation reported earlier, whereas the corresponding lines for iso-

TABLE 2

KINETIC PARAMETER OBTAINED IN ACETYLENE OXIDATION

Catalysts	Reaction orders in acetylene	Reaction orders in oxygen	Temperature range (°C)	E (kcal/mole)	log A (A in mole/m^2 sec)	log V_{220} (V in mole/m^2 sec)
Pt	−0.61	1.37	138 ~ 177	12.4	1.26	−4.47
Pd	−0.68	0.79	187 ~ 227	28.2	7.94	−5.11
CuO	0.08	0.49	176 ~ 206	26.1	6.83	−5.12
Co_3O_4	−0.28	0.71	186 ~ 207	41.4	13.8	−5.12
NiO	−0.07	0.61	217 ~ 257	27.6	6.25	−6.52
MnO_2	0.16	0.45	165 ~ 203	27.1	7.35	−5.10
Fe_2O_3	0.42	0.24	196 ~ 218	37.3	10.4	−5.78
Cr_2O_3	0.58	0.09	205 ~ 245	28.0	6.82	−6.14
CeO_2	0.91	0.00	176 ~ 216	17.4	1.86	−6.19

TABLE 3

KINETIC PARAMETER OBTAINED IN ETHYLENE OXIDATION

Catalysts	Reaction orders in ethylene	Reaction orders in oxygen	Temperature range (°C)	E (kcal/mole)	log A (A in mole/m² sec)	log V_{300} (V in mole/m² sec)
Pd	—	—	174 ~ 195	26.6	5.95	−4.23
CuO	0.39	0.27	238 ~ 282	24.5	4.12	−6.86
Co_3O_4	0.14	0.21	200 ~ 251	30.5	7.32	−5.93
NiO	0.38	0.39	268 ~ 316	26.3	4.05	−7.63
MnO_2	0.52	0.34	229 ~ 279	19.6	2.91	−6.21
Fe_2O_3	0.58	0.47	280 ~ 320	29.3	5.04	−7.77
Cr_2O_3	0.50	0.30	240 ~ 292	27.7	5.13	−7.07
CeO_2	0.67	0.32	342 ~ 395	24.4	1.45	−9.48

TABLE 4

KINETIC PARAMETER OBTAINED IN PROPANE OXIDATION

Catalysts	Reaction orders in propane	Reaction orders in oxygen	Temperature range (°C)	E (kcal/mole)	log A (A in mole/m² sec)	log V_{300} (V in mole/m² sec)
Pt	0.83	−0.09	220 ~ 260	17.0	1.39	−5.09
Pd	1.3	−1.6	337 ~ 368	36.3	6.89	−6.99
CuO	0.54	0.16	309 ~ 363	28.7	3.83	−7.13
Co_3O_4	0.94	0.30	275 ~ 341	24.5	2.58	−6.76
NiO	0.89	0.40	350 ~ 416	26.2	1.68	−8.33
MnO_2	1.01	0.00	294 ~ 358	28.3	3.80	−7.01
Fe_2O_3	0.68	0.22	395 ~ 425	35.9	4.87	−8.83
Cr_2O_3	0.78	0.17	283 ~ 341	21.9	1.47	−6.88
CeO_2	0.67	0.25	383 ~ 450	27.8	1.41	−9.21
ThO_2	—	—	373 ~ 418	36.8	4.65	−9.26

butene, ethylene, and propane are less satisfactory. Details of this effect will be published elsewhere.

In order to evaluate the catalytic activity on a common basis, the reaction rate at 300°C, V_{300}, was estimated by using the above activation energy and is shown in the last columns of Tables 1, 3, and 4. In the case of acetylene, since the rate data were taken at temperatures lower than 300°C due to its high reactivity, the catalytic activity was evaluated by the reaction rate at 220°C, V_{220}, and is shown in Table 2. The values of V_{300} or V_{220} indicate the reactivity difference among the hydrocarbons tested, the reactivity sequence of hydrocarbons is assessed as

$$C_2H_2 \gg \text{iso-}C_4H_8 > C_3H_6 > C_2H_4 \gg C_3H_8$$

with most catalysts, except Pt and Pd, on which considerable retardation by the hydrocarbon was observed.

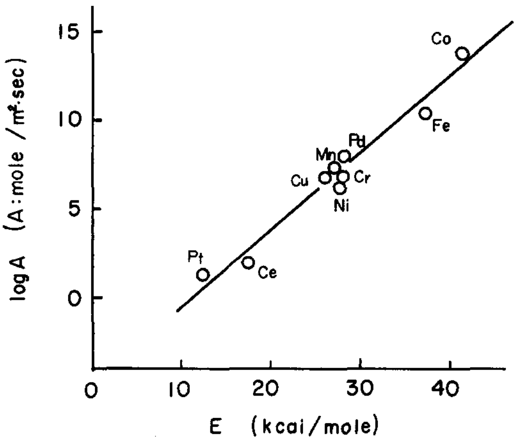


FIG. 1. Compensation effect for the oxidation of acetylene.

2. Competitive Oxidation

It is generally accepted that the reaction order of a surface-catalyzed reaction is strongly affected by the degree of coverage by reactant. The variety of orders found in this reaction might be the result of the difference in adsorption strength. Therefore, it would be of interest to investigate the affinity of hydrocarbon to the catalyst oxide under the reaction condition. However, the conventional static adsorption seems inadequate to this purpose, because the catalyst oxide could be reduced under the condition being employed. The competitive oxidation method (*7*, *8*) seems to be more favorable.

The experiments were carried out under the gas composition shown in the following table:

Hydrocarbon tested	Hydrocarbon added	O_2	N_2
2%	0% to 3%	50%	balance

The concentration of one of the hydrocarbons was fixed at 2 vol %, while that of the other was varied from 0 to 3 vol %. The total flow rate was adjusted at a fixed value by a corresponding decrease in nitrogen flow. The conversions of two hydrocarbons were determined in each run. As a typical example, the results of competitive oxidation of propylene and isobutene on Co_3O_4 at 260°C are shown in Fig. 2. In the separate oxidation run, the conversion of propylene was 32%, being higher than the 19% observed for isobutene as shown on the vertical axis of Fig. 2. However, replacing nitrogen by isobutene in the system of propylene oxidation produced a considerable decrease in the conversion of propylene. When isobutene was added up to a concentration equal to propylene, the reaction of propylene was completely inhibited. On the contrary, addition of propylene to the system of isobutene oxidation produced no decrease in the conversion of isobutene.

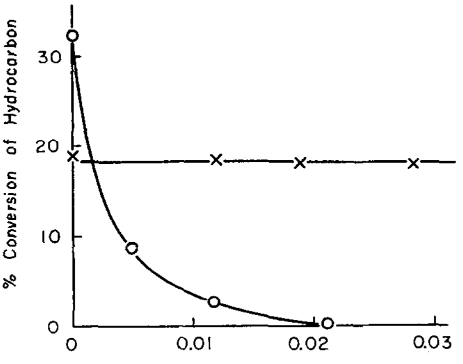


FIG. 2. Competitive oxidation of propylene and isobutene over Co_3O_4 at 260°C: —O—, effect of isobutene on the conversion of propylene; —X—, effect of propylene on the conversion of isobutene.

Three catalysts, Co_3O_4, Fe_2O_3, and CeO_2 were employed for these series of experiments. They were selected in view of the reaction order in hydrocarbon. Co_3O_4 belongs to the group of catalysts of lowest order, Fe_2O_3 to the medium, and CeO_2 to the highest. The variation of propylene conversion resulting from the added hydrocarbons was determined over Co_3O_4 around 260°C and is shown in Fig. 3. In the case of propylene addition to propylene, the incremental partial pressure of propylene is plotted on the horizontal axis. Figure 3 shows that the inhibitive effect of hydrocarbons on the propylene oxidation decreases in the order

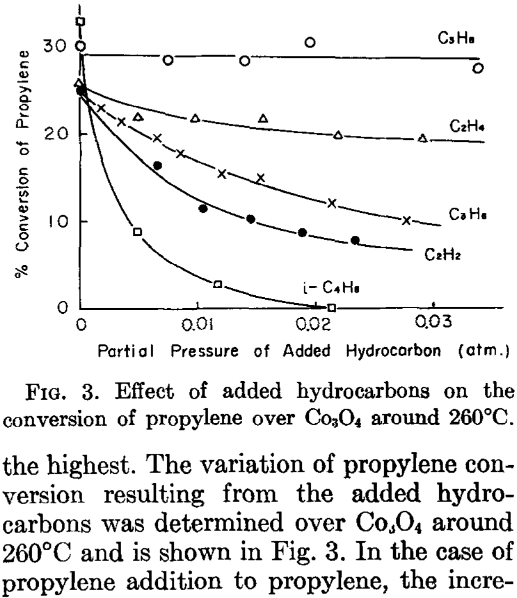


FIG. 3. Effect of added hydrocarbons on the conversion of propylene over Co_3O_4 around 260°C.

$$\text{iso-}C_4H_8 > C_2H_2 > C_3H_6 > C_2H_4 > C_3H_8$$

However, it might be possible that the effect of acetylene was underestimated because its high reactivity should reduce its partial pressure in the catalyst bed much faster than the other hydrocarbons. In this connection the effect of acetylene addition on the oxidation of isobutene was similarly examined. Although acetylene was more reactive than isobutene over any oxide catalysts including Co_3O_4 as already pointed out, addition of an equal amount of isobutene, i.e., 0.02 atm, resulted in complete inhibition of the reaction of acetylene. This inhibitive effect of isobutene was much more pronounced than that of acetylene itself.

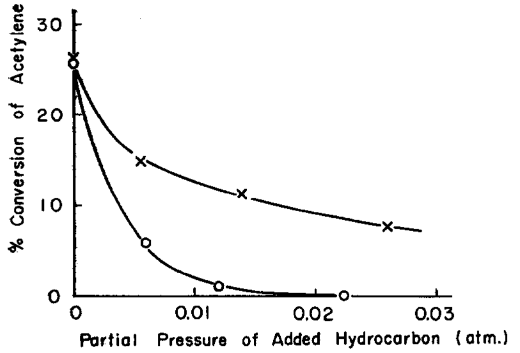


FIG. 4. Effect of added hydrocarbons on the conversion of acetylene over Co_3O_4 at 228°C: —O—, effect of isobutene; —X—, effect of acetylene.

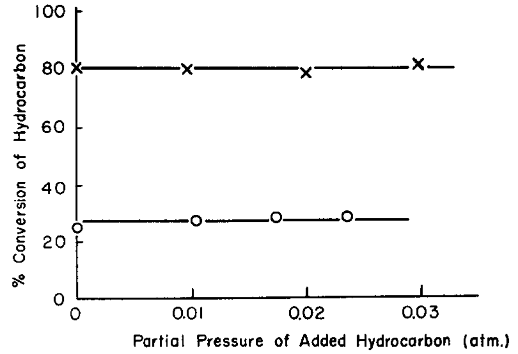


FIG. 5. Competitive oxidation of propylene and acetylene over CeO_2 at 343°C; —O—, effect of acetylene on the conversion of propylene; —X—, effect of propylene on the conversion of acetylene.

The data with the Fe_2O_3 catalyst are shown in Table 5, where the propylene oxidation with an equal amount of added hydrocarbon is compared with the respective separate oxidation. The features of the inhibitive effects of hydrocarbons indicated in this table are similar to those over the Co_3O_4 catalyst. Isobutene was the heaviest inhibitor so that propylene could not be oxidized in the presence of an equal amount of isobutene. Acetylene was moderately poisonous, while propane was completely nonpoisonous to the propylene oxidation. Such an inhibitive effect of added hydrocarbons was not observed over the CeO_2 catalyst as exemplified in Fig. 5.

TABLE 5

COMPETITIVE OXIDATION OVER Fe_2O_3

Pair of hydrocarbons	Temperature (°C)	Hydrocarbon	Conversion in separate oxidation (%)	Conversion in competitive oxidation (%)	Decrease of conversion (%)
C_3H_6–C_3H_8	393	C_3H_6	76.0	76.0	0
		C_3H_8	19.6	0	100
C_3H_6–C_2H_2	345	C_3H_6	20.8	10.7	48.5
		C_2H_2	76.2	61.8	18.9
C_3H_6–iso-C_4H_8	343	C_3H_6	17.8	0	100
		iso-C_4H_8	26.0	25.9	0

DISCUSSION

1. *Interpretation of Reaction Order on the Basis of Competitive Oxidation*

As described above, when two types of hydrocarbons were oxidized competitively on Co_3O_4 or Fe_2O_3, the reaction rate of one or both of them decreased as compared with the case of separate oxidation. Similar phenomena have been observed in other catalytic reactions. For example, when a mixture of ethylene and acetylene is hydrogenated competitively on palladium catalyst, ethylene is hardly hydrogenated until almost all coexisting acetylene is consumed (*9*). The phenomenon was interpreted as an inhibition of the hydrogenation of ethylene by the strong and exclusive adsorption of coexisting acetylene. In the case of oxidation, the competitive reaction of ethylene and carbon monoxide over various metal oxides was studied by Hofer *et al.* (*10*). Belousow *et al.* (*8*) determined the relative order of the strength of chemisorption for isobutene, propylene, ethylene, and propane on a silver catalyst by the method of competitive oxidation, by means of a pulse flow technique using oxygen as carrier gas.

While the inhibitive effect in the competitive reaction is reasonably explained by the difference of adsorption strength between two kinds of reactants, an alternative interpretation may be derived from the result shown in Fig. 2. That is, the decrease in propylene conversion might result, not from the decrease in surface concentration of propylene, but that of oxygen due to the higher reactivity of isobutene or stronger adsorption of isobutene. However, in view of the fact that isobutene inhibited the reaction of acetylene (cf. Fig. 4), which was proved to be more reactive than isobutene, the above interpretation can be ruled out. The most reasonable interpretation of the result shown in Fig. 2 is that propylene could not be adsorbed because of strong adsorption of isobutene. This seems to hold true in the other pair of hydrocarbons. The reacting hydrocarbon may be first adsorbed on the catalyst before the interaction with oxygen, instead of a direct attack to adsorbed oxygen.

On the basis of the above discussion, the inhibitive effect sequence of hydrocarbons (cf. Fig. 3)

$$\text{iso-}C_4H_8 > C_2H_2 > C_3H_6 > C_2H_4 > C_3H_8$$

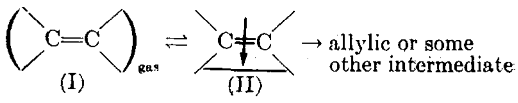
may be regarded as the order of the adsorption strength. This order would also be valid for the case of Fe_2O_3 catalyst, as shown in Table 5. On the other hand, the reaction order sequence of hydrocarbons

$$C_3H_8 > C_2H_4 > C_3H_6 > C_2H_2 > \text{iso-}C_4H_8$$

is completely the reverse of the above order. Therefore, it would be concluded that the higher the reaction order in hydrocarbon, the weaker the adsorption.

An electron-donating nature of propylene adsorption has been suggested by Enikeev *et al.* (*11*) over CuO, NiO, and V_2O_5 on the basis of measurement of work function change on adsorption.

While an allylic intermediate complex has been proposed for the oxidation of propylene or butene over bismuth molybdate by Adams and Jennings (*12*) and by Sachtler (*13*), and over cuprous oxide by Voge *et al.* (*14*), this intermediate was suggested to be formed after the rate-determining abstraction of hydrogen or dissociative adsorption of olefin (*15*, *16*). In the present case, the observed zero or near to zero order kinetics in hydrocarbon suggests that the adsorbed hydrocarbon is in equilibrium with gas phase. In this respect, the scheme is different from that suggested for bismuth molybdate catalyst. Thus, the adsorbed state of the hydrocarbon discussed here, though being not incompatible with the dehydrogenation mechanism, may not be identical with the allylic intermediate. The reaction of hydrocarbon may proceed as follows:



The adsorbed state revealed by the competitive oxidation may correspond to the state (II), which is rapidly equilibrated with gas phase.

2. The Relation between Reaction Orders and the Heat of Formation of Oxide

Both the reaction orders in hydrocarbon and in oxygen found in the oxidation of isobutene and acetylene were plotted against the heat of formation of catalyst oxide divided by the number of oxygen atoms, ΔH_O, as shown in Figs. 6 to 9. It is evident from those figures that the reaction orders in both reactants depend upon ΔH_O of the catalyst. The higher the value of ΔH_O the higher the reaction order in hydrocarbon and the lower the reaction order in oxygen.

For example, in the case of acetylene, the reaction kinetics over Pd or Pt catalyst shows a considerably negative order, i.e., -0.6 to -0.7 in hydrocarbon and virtually first order in oxygen. The kinetics over CuO,

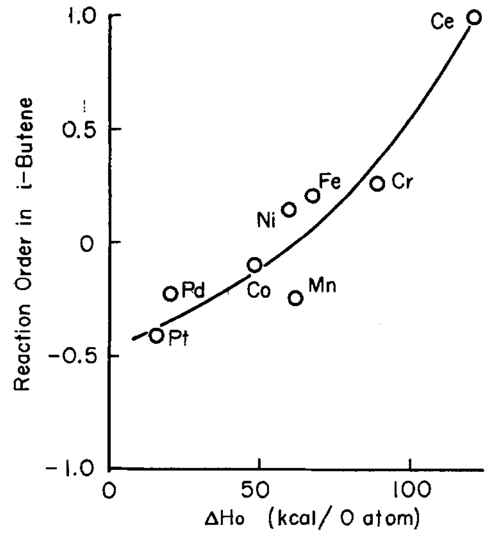


FIG. 6. Correlation of the reaction order in isobutene with ΔH_O.

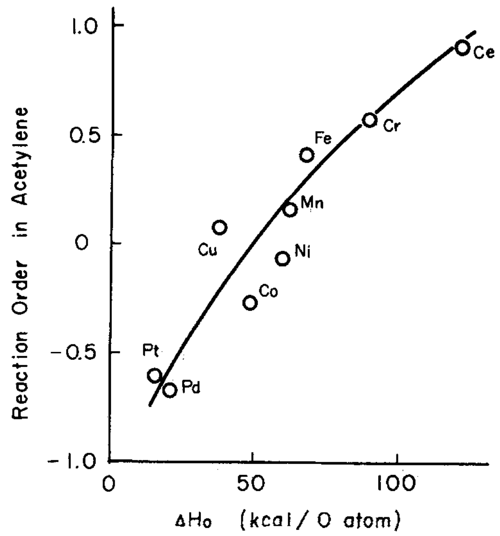


FIG. 8. Correlation of the reaction order in acetylene with ΔH_O.

Co_3O_4, NiO, and MnO_2 of lower ΔH_O value was virtually independent of acetylene pressure and half-order in oxygen. The increase in ΔH_O from CuO, etc., to Fe_2O_3 and Cr_2O_3 is accompanied by an increase in the acetylene order and decrease in the oxygen order. Over CeO_2, which has the highest value of ΔH_O, the kinetics were first order in acetylene and independent of oxygen. This dependency of the reaction orders on ΔH_O and the compensation between two kinds of orders, i.e., in hydrocarbon and in oxygen, are identical with the results previously reported in the oxidation of propylene.

Such variation in reaction order from one catalyst to another catalyst may be explained on the basis of adsorption strength. The results obtained in the competitive oxidation of hydrocarbons strongly support this

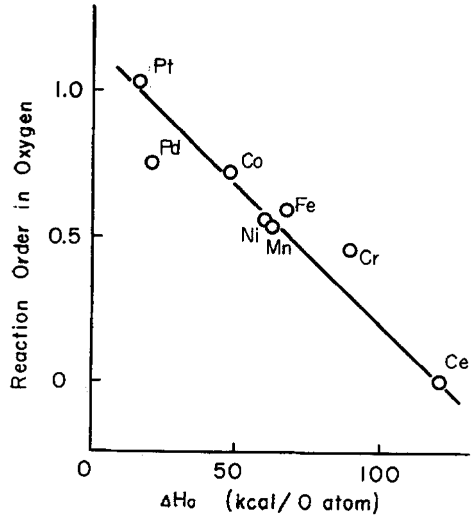


FIG. 7. Correlation of the reaction order in oxygen with ΔH_O in the oxidation of isobutene.

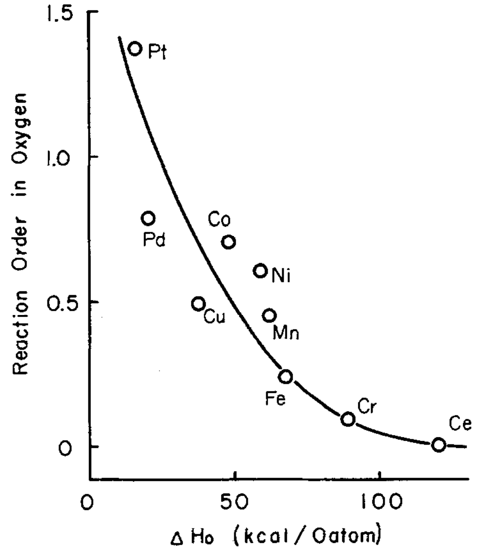


FIG. 9. Correlation of the reaction order in oxygen with ΔH_O in the oxidation of acetylene.

view, according to which the surface state of the catalyst is discussed as follows:

(1) A group of catalysts of low ΔH_O value, such as Pt and Pd, is characterized by negative order in hydrocarbon and nearly first order in oxygen. This suggests that the surface is fully covered by hydrocarbon and the slow step of the oxidation is the chemisorption of oxygen on the surface covered by hydrocarbon.

(2) Another group of catalysts of medium ΔH_O value, such as Co_3O_4 and Fe_2O_3, is characterized by a nearly zero or positive low order in hydrocarbon and a nearly half-order in oxygen. This suggests that hydrocarbon and oxygen occupy the surface and the slow step is the surface reaction between adsorbed species. On the basis of reaction order change, it seems that the surface coverage of hydrocarbon decreases and that of oxygen increases with increase in ΔH_O.

(3) The third group of catalysts of higher ΔH_O value is characterized by first order in hydrocarbon and zero order in oxygen. This suggests the surface of catalyst is fully covered by oxygen. The slow step of the oxidation over this type of catalyst would be either the chemisorption or the reaction of hydrocarbon on the oxygen-covered surface. The absence of interaction between hydrocarbons in the competitive oxidation is consistent with this view.

Summarizing, the catalyst surface is increasingly covered by oxygen and decreasingly by hydrocarbon as the ΔH_O value increases. The slow step of the oxidation correspondingly shifts from the step of oxygen chemisorption to the surface reaction. Since ΔH_O can be taken to signify the bond strength between metal and oxygen, as discussed in the preceding paper, this change of the surface state of working catalyst and of the slow step of oxidation with ΔH_O seems to be reasonable. When the metal-to-oxygen bond is weak, the adsorbed oxygen would readily react on the attack of hydrocarbon, while the catalyst may be unfavorable for chemisorption of oxygen. Such a catalyst is likely to be reduced, forming a surface deficient in oxygen. This situation will be reversed as ΔH_O increases.

The trend in the variation of reaction order with ΔH_O of the catalyst discussed above is less significant in the oxidation of ethylene and propane, as shown in Figs. 10 to 13. Particularly in the case of propane, the reaction kinetics are virtually first order in hydrocarbon and independent of oxygen irrespective of catalyst. This insensitiveness of the reaction order to the variation of ΔH_O is probably due to the weakness of the adsorption of propane and ethylene, which is evidenced in the competitive oxidation. The weakness of hydrocarbon adsorption seems to favor an oxygen-covered surface.

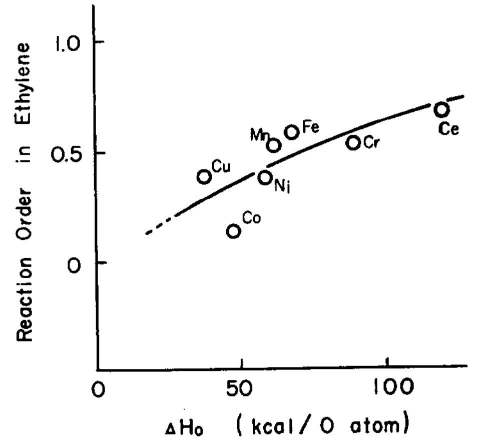


FIG. 10. Correlation of the reaction order in ethylene with ΔH_O.

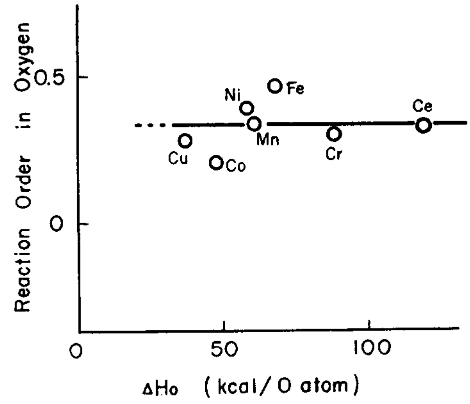


FIG. 11. Correlation of the reaction order in oxygen with ΔH_O in the oxidation of ethylene.

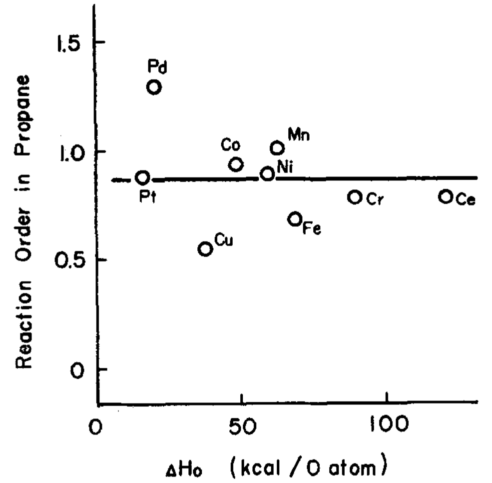


Fig. 12. Correlation of the reaction order in propane with ΔH_O.

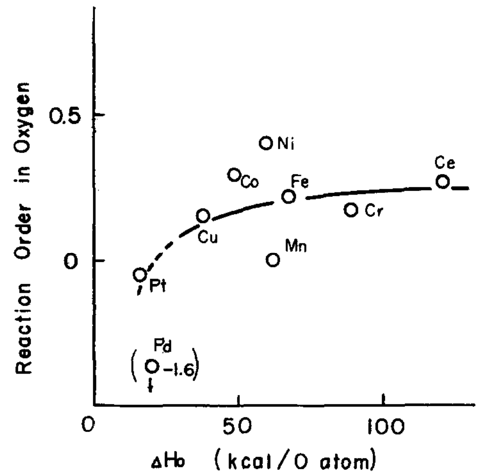


Fig. 13. Correlation of the reaction order in oxygen with ΔH_O in the oxidation of propane.

3. Activity of Catalysts

The reaction rates, V_{300}, for isobutene, ethylene, and propane, and V_{220} for acetylene against ΔH_O are plotted in Figs. 14–17. As can be seen in those figures, the higher the ΔH_O, the less active the catalyst. This variation in activity with ΔH_O is essentially identical with those found by Sachtler *et al.* (*5*) and by the authors (*6*) in propylene oxidation, and by Komuro *et al.* (*4*) in a rearrangement of the data of Popovskii and Boreskov (*17*) on hydrogen oxidation.

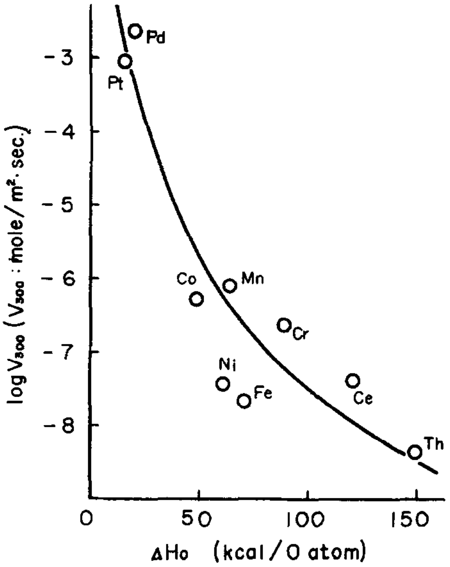


Fig. 14. Correlation of the catalytic activity V_{300} with ΔH_O in the oxidation of isobutene.

This consistent variation of catalytic activity with ΔH_O should refer to the reaction mechanism, particularly to the type of rate-determining step. As discussed in the preceding paragraph, the probable slow step of this reaction seems to depend upon the ΔH_O of the catalyst. However, over most catalysts the slow step seems to be the surface reaction between adsorbed oxygen and adsorbed hydrocarbon whereas, in the case of acetylene and isobutene over Pt and Pd, it seems to be the step of oxygen adsorption. The

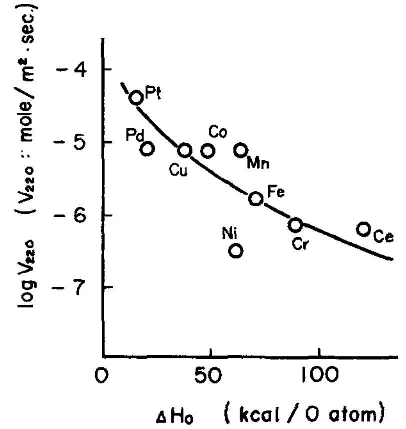


Fig. 15. Correlation of the catalytic activity V_{220} with ΔH_O in the oxidation of acetylene.

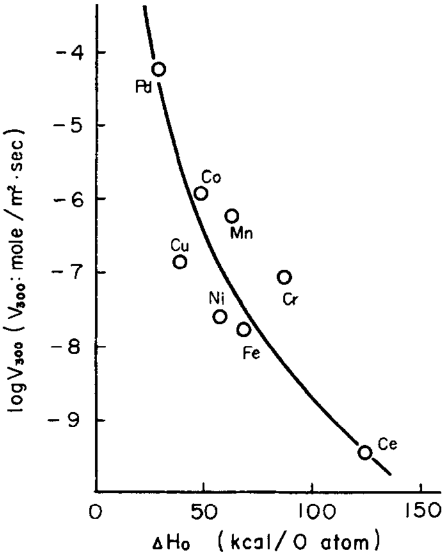


FIG. 16. Correlation of the catalytic activity V_{300} with ΔH_O in the oxidation of ethylene.

surface reaction involves the breaking or loosening of a metal–oxygen bond, whereas the oxygen adsorption is just the formation of this bond. Since ΔH_O signifies the strength of the metal–oxygen bond, the surface reaction would be slower, whereas the oxygen adsorption would be faster, as ΔH_O is increased. On the basis of the above considerations, it was concluded that the expected trend in the variation of catalytic activity with ΔH_O is the so-called volcano-shaped variation, with the slow step being different on both sides of the maximum, while the maximum position probably depends on the nature of reactant. As shown in Figs. 14 to 17, the left side of the maximum seems to be missing. The slow step over the most active catalysts, Pt or Pd, is the oxygen adsorption as suggested by the observed kinetic feature. This is in agreement with the above prediction.

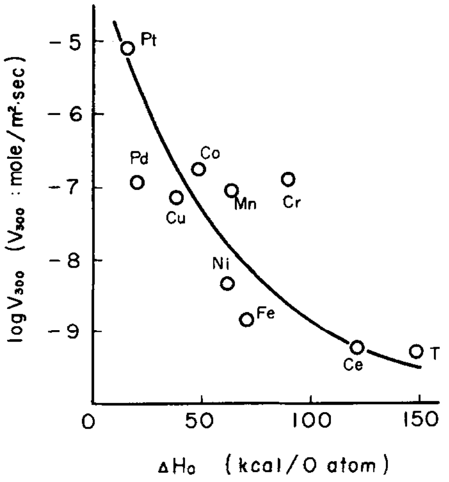


FIG. 17. Correlation of the catalytic activity V_{300} with ΔH_O in the oxidation of propane.

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