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Catalytic Oxidation over Molecular Sieves Ion-exchanged with Transition Metal Ions. IV. The Oxidative Dehydrogenation of Cyclohexane

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The oxidative dehydrogenation of cyclohexane over molecular sieves ion-exchanged with cupric ion (Cu(II)-Y) was investigated by means of an ordinary flow reactor with a reactant gas composed of 1.0% cyclohexane, 50% oxygen, and 49% nitrogen. The reaction was studied at temperatures between 210—350°C; here, carbon dioxide and benzene were the main products. The Cu(II)-Y was found to be a very active catalyst for the oxidation of cyclohexane as well as for that of olefins, in comparison with an ordinary cupric oxide catalyst supported on silica gel; the selectivity for benzene formation was as high as 80% below 10% conversion. Both products were found to be formed in competitive reactions. The catalytic activities were also studied on molecular sieves ion-exchanged with other transition metal ions, such as palladium (II), silver (I), and zinc (II). The relations between the catalytic activities and the heats of formation of the corresponding metal oxides per g-atom oxygen were examined; volcano-shaped correlations were observed for both benzene and carbon-dioxide formations for these catalysts. The most active catalyst was Cu(II)-Y for benzene formation, whereas it was Pd (II)-Y for the carbon dioxide formation. The meaning of the correlations was discussed according to Balandin's explanation, based on thermochemistry, although no satisfying explanation was found. The compensation effects were observed between the activation energies and the frequency factors in these oxidations.

In previous papers, it was reported that the molecular sieves ion-exchanged with transition metal ions have very high catalytic activities for the oxidation of olefins.[1-3] It may be interesting to investigate the catalytic activities of these catalysts for the saturated hydrocarbons. Agudo *et al.*[4] reported the oxidations of heptanes on Na-X, Ca-X, and Mn-X, but homogeneous processes were predominant, so the character of the transition metal on the molecular sieve appeared only obscurely.

In the present work, the oxidative dehydrogenation of cyclohexane was studied over molecular sieves ion-exchanged with several transition-metal ions. Although the dehydroisomerization (reforming, in other words) of saturated hydrocarbons by Pd- or Pt-molecular sieves has been reported and applied in industrial processes,[5] regarding oxidative dehydrogenation only a few works have been reported, those using alcohols and alkylbenzenes as the reactants.[6,7]

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[1] I. Mochida, S. Hayata, A. Kato, and T. Seiyama, *J. Catalysis*, **15**, 314 (1969).

[2] I. Mochida, S. Hayata, A. Kato, and T. Seiyama, *ibid.*, **19**, 405 (1970).

[3] I. Mochida, S. Hayata, A. Kato, and T. Seiyama, *ibid.*, in press.

[4] A. L. Agudo, F. R. Badcock, and F. S. Stone, *Proc. Inter. Congr. Catalysis, 4th Moscow*, No. 59 (1968).

[5] J. A. Rado, P. E. Pickert, D. Stmir, and J. E. Bogles, *Actes Congr. Intern. Catalyses, 2e, Paris*, 1960, 2055 (1961); Mays, R. C., *Ind. Eng. Chem.* **53**, 733 (1967).

[6] P. N. Galich, A. A. Gutyrya, V. S. Gutyrya, and I. E. Neimark, *Dokl. Akad. Nauk SSSR* **144**, 147 (1962); P. N. Galich, V. S. Gutyrya, O. P. Egorov, I. E. Neimark, Il'in. Golobchenko, and V. S. Frolova, *Neftkhimiya Akad. Nauk, Soedin.* (Ukr. SSR Inst. Khim. Vysckomolekul.), **1964**, 13.

[7] J. Turkevich, *Catalysis Rev.* **1**, 1 (1968); P. B. Venuto and P. S. Landnis, *Advan. Catalysis*, **18**, 259 (1968).

Cyclohexane can be thought to be transformed easily into benzene, and the benzene thus produced is relatively stable against further oxidations, so the oxidative dehydrogenation of cyclohexane can be expected to occur with a high activity and selectivity over molecular sieves ion-exchanged with transition-metal ions, since high activities of these catalysts were found with regard to the oxidation of olefinic hydrocarbons.[1,3)]

Experimental

Catalyst. The ion-exchanged molecular-sieve catalysts were prepared by the ion-exchange of the Y-molecular sieve (Linde), Na–Y, with an aqueous solution of metal sulfates or nitrate except for the cases of cupric and palladium ions, for which amine complexes were used. A sufficient amount of the metal ion was passed through a cylindrically-shaped column of Na–Y. The ion-exchanged sieves were then washed thoroughly with decationized water, dried at 100°C, and calcined at 400°C for 7 hr in the air. The amount of metal ion-exchanged onto the sieve was determined by extraction with nitric acid and by the titration of the solution. 80—90% of the sodium ions were exchanged. The cupric oxide catalyst supported by silica gel was described in a previous paper.[1)]

Reagent. The cyclohexane used was of a G. R. grade and was obtained from the Wako Junyaku Co. It was used without further purification. No benzene or cyclohexene was detected by the gas chromatography.

Apparatus and Procedure The oxidative dehydrogenation was studied by the ordinary flow method, with a fixed catalyst bed diluted with 1% cyclohexane, 50% oxygen, and 49% nitrogen. Cyclohexane was fed by means of a nitrogen flow passed through an alumina bed impregnated with a sufficient amount of cyclohexane kept at 0°C. The cyclohexane, cyclohexene, benzene, and carbon dioxide were analyzed by means of chromatography. For the first three, 2 m TCP (Japan Gaschro Co.) and 1 m PEG (Japan Gaschro Co.) columns were used at 80°C, and for the last, a Porapak Q (Waters Associates, Inc.) column of 2 m was used at room temperature. The conversions and the selectivity were calculated in the following ways:

$$\text{Conversion for carbon dioxide} = \frac{(1/6)\ \text{carbon dioxide}}{\text{cyclohexane fed}}$$

$$\text{Conversion for benzene} = \frac{\text{benzene}}{\text{cyclohexane fed}}$$

$$\text{Selectivity for benzene} = \frac{\text{benzene}}{\text{benzene} + (1/6)\ \text{carbon dioxide}}$$

The activity of the catalyst was corrected to that on a fixed amount of the metal ion.

Results

Oxidation of Cyclohexane on a Y Molecular Sieve Ion-exchanged with Cupric Ions (Cu(II)-Y). The oxidation of cyclohexane over Cu(II)–Y of 300 mg began to occur at 210°C under a flow rate of 50 m*l*/min. Up to 350°C, benzene and carbon dioxide were the main products, plus a small amount of cyclohexene. The carbon balance was better than 95% (on an inlet cyclohexane basis) after 2 hours' reaction, although a carbon deposit was observed on the catalyst. The catalyst recovered its original color of light blue when the carbon deposited on the catalyst was burned in the air. This means that the cupric ions maintain the ionic state on the molecular sieve during the oxidation reaction, as was previously observed in the oxidation of propylene.[1,2)]

Above 350°C, products other than carbon dioxide and benzene were observed. Acetic acid and propionic acid were detected in the products. However, a detailed analysis was not made.

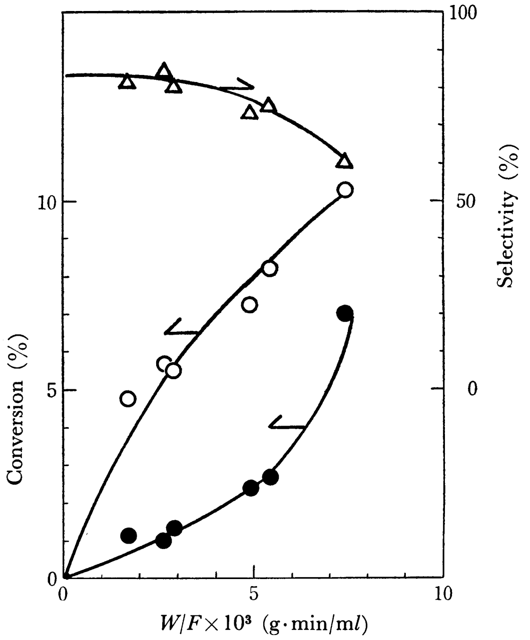

Fig. 1. The oxidation of cyclohexane over Cu(II)-Y at 260°C.
The reactant gas composition; 1% cyclohexane, 50% oxygen, 49% nitrogen.
○: benzene formation, ●: carbon dioxide formation, △: selectivity of benzene formation.

The oxidation at 260°C is shown in Fig. 1 as a function of the contact time. Benzene and carbon dioxide were formed in linear relations with the contact time below a 10% conversion. Above this conversion, however, the carbon dioxide formation increased rapidly and the benzene formation was surpressed. The former fact may suggest the competitive formations of these products below a 10% conversion, while the latter may do the successive oxidation of benzene into carbon dioxide above a 10% conversion. The selectivity of the benzene formation was as high as 80% in the competitive region. The selectivity in the region of the competitive reactions varied little with the reaction temperature between 210 and 350°C, although the rates increased considerably.

A Comparison of Cu(II)-Y with Cupric Oxide Supported on Silica Gel in the Oxidative Dehydrogenation of Cyclohexane. The catalytic activity of Cu(II)–Y was compared with that of the ordinary cupric oxide mounted on silica gel (Cu(II)–S). The two catalysts had nearly equal surface areas.[1)] The reactions on these catalysts in the competitive region at 310°C are shown in Fig. 2 as a function of the contact time. The catalytic

Table 1. INITIAL RATES, ACTIVATION ENERGIES, AND FREQUENCY FACTORS OF MOLECULAR SIEVES ION-EXCHANGED WITH TRANSITION METAL IONS FOR THE OXIDATION OF CYCLOHEXANE

Catalyst	Rate at 290° [a)] (m*l*/g·min)		Activation energy (kcal/mol)		Frequency factor (m*l*/g·min at $T=\infty$)	
	C_6H_6	CO_2	C_6H_6	CO_2	C_6H_6	CO_2
Ag(I)-Y	0.2	2.5	9.6	12.4	3.3	5.2
Pd(II)-Y	4.4[b)]	7250[b)]	15.6	35.6	6.6	16.9
Cu(II)-Y	59.0	22	26.9	29·1	12.3	12.5
Ni(II)-Y	1.4	7.3	—	—	—	—
Zn(II)-Y	0.4	3.2	—	—	—	—
Cr(III)-Y	2.3	9.0	14.3	19.5	6.0	8.5
Cu(II)-S	7.4	6.4	20.6	14.5	9.2	6.3

a) (Conversion observed below 10% conversion)/contact time.
b) Estimated from the Arrhenius plots between 200 and 260°C.

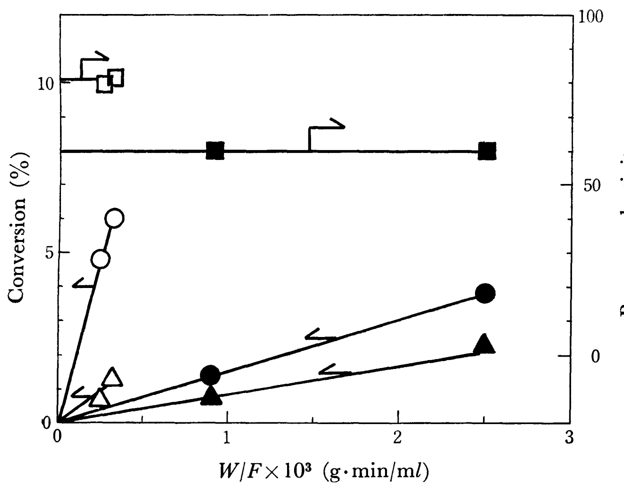

Fig. 2. Comparison between Cu(II)-Y and Cu(II)-S in the oxidation of cyclohexane at 310°C.
○: benzene formation, △: carbon dioxide formation, □: selectivity of benzene formation.
Open plots are for Cu(II)-Y and closed ones are for Cu(II)-S.

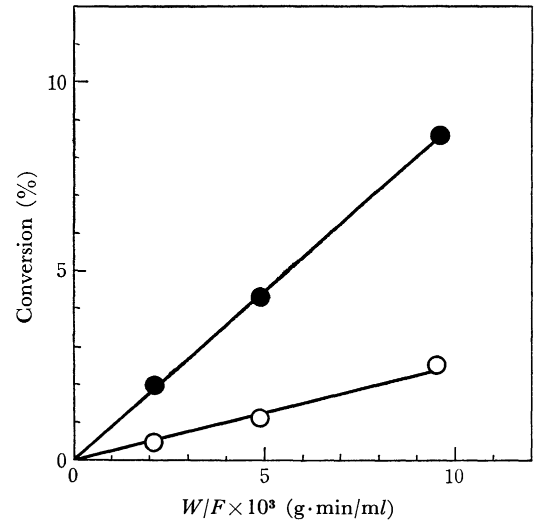

Fig. 3. The oxidation of cyclohexane on Cr(III)-Y at 290°C.
○: benzene formation, ●: carbon dioxide formation.

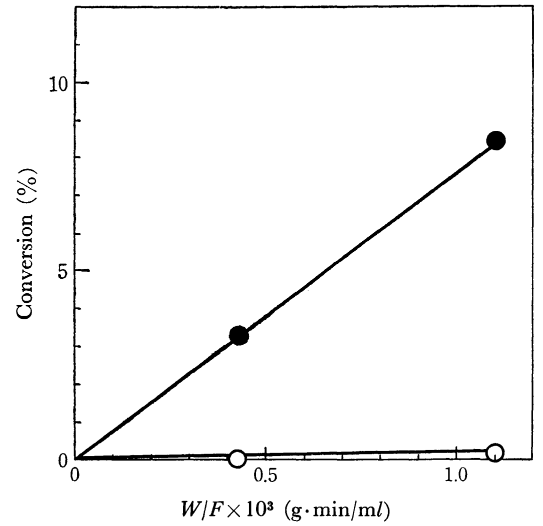

Fig. 4. The oxidation of cyclohexane on Pd(II)-Y at 230°C.
○: benzene formation, ●: carbon dioxide formation.

activity of Cu(II)-Y was much larger than that of Cu(II)-S, being fifteen times as much for the benzene formation and four times as much for the carbon-dioxide formation. The selectivity for the benzene formation in the competitive reactions was also better (80% for Cu(II)-Y, but 60% for Cu(II)-S). The activation energies and frequency factors of these two catalysts are shown in Table 1. It is interesting that Cu(II)-Y had a very high catalytic activity for the oxidations of saturated hydrocarbon as well as of olefinic hydrocarbons at such temperatures.[1-3)]

The Oxidations of Cyclohexane over Molecular Sieves Ion-exchanged with Other Transition-metal Ions. The catalytic activities of molecular sieves ion-exchanged with five kinds of transition-metal ions other than the cupric ion were also studied in order to investigate the roles of metal ions in the oxidative dehydrogenation based on the δ_C LFER approach.[8)] The reactions over Cr(III)-Y at 290°C and over Pd(II)-Y at 230°C are shown in Figs. 3 and 4 respectively as examples. It should be mentioned that the selectivities for the benzene formation of such sieves were much smaller than that of Cu(II)-Y, although the reactions also seemed competitive on these catalysts below a 10% conversion, as was shown by the linearity of the con-

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[8)] I. Mochida and Y. Yoneda, *J. Catalysis*, **7**, 386 393, **8**, 223 (1967).

version plotted against the contact time. On Pd(II)-Y, the benzene formation was too small to be detected at low conversions, as is shown in Fig. 4, but it became measurable beyond a 10% conversion. This mean that the small value of the selectivity cannot be ascribed to the occurrence of the successive reaction at these conversion levels because of the high activity of this catalyst, and that the formations of benzene and carbon dioxide also take place competitively on Pd(II)-Y.

In Table 1, the rate data of the catalysts used are summarized; the activation energies and frequency factors here were calculated from the rates at reaction temperatures between 230 and 350°C, except for the case of Pd(II)-Y, which was too active for the oxidation rates to be observed in this temperature range, so the observation was made between 200 and 260°C. The catalytic activities of these catalysts at 290°C were in the following orders: Pd>Cu>Cr>Ni>Zn>Ag for the carbon dioxide formation, and Cu>Pd>Cr>Ni>Zn>Ag for the benzene formation (the activity of Pd(II)-Y at this temperature was extrapolated in the Arrhenius plots). The former activity order was analogous to that observed in the deep oxidations of olefins except for the small activity of Ag(I)-Y.[3)]

Discussion

The Correlation of the Catalytic Activities with the Heats of Formation of the Corresponding Metal Oxides. The correlation of the catalytic activities for the oxidation of the metal oxides with their heats of formation per oxygen atom was reported on by Moro-oka and Ozaki, Seiyama *et al.*, Komuro *et al.*, and Boreskov and Balandin.[9)] Recently, Aonuma and Nakada discussed such a correlation in the oxidative dehydrogenation of cyclohexene on the oxide catalyst.[10)] A similar examination of the activities of molecular-sieve catalysts may be of value. In a previous paper,[3)] volcano-shaped correlations were found in the oxidations of propylene and ethylene on the molecular-sieve catalysts. Such plots are made for the carbon dioxide and benzene formations in Fig.5, where volcano-shaped correlations were observed for both formations, showing the maximum activity at the palladium ion for carbon dioxide and at the cupric ion for benzene. It is interesting that the heat of the formation of the metal oxide could also be a parameter describing the catalytic activity in the present oxidation.

According to Balandin's explanation of such relations, the most active catalyst can be predicted on the basis of the thermochemical data on the reaction.[11)] If the oxidation reaction of cyclohexane can be assumed to proceed through the following two steps, which consist of the dissociative adsorption of oxygen on the metal ion and the successive oxidation of cyclohexane by this adsorbed oxygen, the formation rate of carbon dioxide or benzene is at a maximum when ΔH_1 is equal to ΔH_2 or to ΔH_3 respectively:

$$\text{Me} + 1/2\,\text{O}_2 = \text{Me-O},\ \Delta H_1 \tag{1}$$

$$\text{Me-O} + 1/24\,\text{C}_6\text{H}_{12} = \text{Me} + 1/4\,\text{CO}_2 + 1/2\,\text{H}_2\text{O},\ \Delta H_2 \tag{2}$$

$$\text{Me-O} + 1/2\,\text{C}_6\text{H}_{12} = \text{Me} + 1/3\,\text{C}_6\text{H}_6 + \text{H}_2\text{O},\ \Delta H_3 \tag{3}$$

(ΔH_1, ΔH_2, and ΔH_3 are the heats of Reactions (1), (2), and (3) respectively.)

Since the sum of ΔH_1 and ΔH_2 or of ΔH_1 and ΔH_3 is equal to the heat of carbon-dioxide formation per g-atom oxygen (ΔH_{CO_2}) or that of benzene formation ($\Delta H_{\text{C}_6\text{H}_6}$) respectively, the above rule means that the formation rate is at a maximum at $\Delta H_1 = 1/2\,\Delta H_{\text{CO}_2}$ for carbon dioxide or at $\Delta H_1 = 1/2\,\Delta H_{\text{C}_6\text{H}_6}$ for benzene. The values of the heats of oxidation per g-atom oxygen are -42 kcal/mol for the benzene formation and -49 kcal/mol for the carbon-dioxide formation respectively. If the heat of adsorption of oxygen on the metal ion of the molecular sieve, ΔH_1, can be assumed to be equal to that of the formation of the metal oxide, ΔH_f°, the most active catalyst is the one whose ΔH_f° is -21 kcal/mol for the benzene formation and -24.5 kcal/mol for the carbon-dioxide formation respectively. Thus, if the assumptions are appropriate, Pd(II)-Y should be the most active for both formations among the catalysts examined here. The results for the carbon—dioxide formation support the above discussion. However, the cupric ion, not the palladium ion, was most active for the benzene formation. Even if the cyclohexyl radical rather than benzene is considered to be the intermediate product in Eq. (3), the situation is not improved. Other reaction schemes such as dehydrogenation in the first step, followed by the oxidation of the hydrogen with oxygen, may also be considered. However, sufficient thermodynamic data are lacking for further discussion.

Correlation as for Activation energies and Frequency Factors. The reaction rate should be connected with the thermochemical data of the reaction through its activation energy, according to Balandin's explanation.[11)] The relations of the activation energies to the parameters used above are shown in Fig. 6 for both formations in order to make possible a discussion of the relations shown in Fig. 5 from another point of view. Similar volcano-shaped correlations were observed for the reaction rates in both formations. Such correlations for activation energies, however, were contradictory to those observed in the usual cases, where the most active catalyst has the smallest value of activation energy.[8,12)] The frequency factors are often constant when a linear relation holds between the reaction rate and the thermochemical data.[8)] The values of the present case, however, varied considerably from one to another. They were also correlated with the present parameter, as is shown in Fig. 7 for both for-

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[9)] I. Komuro, H. Yamamoto, and T. Kwan, This Bulletin, **36**, 1532 (1963); Y. Moro-oka, and A. Ozaki, *J. Catalysis*, **5**, 116 (1966); T. Seiyama, S. Kagawa and H. Tokunaga, *Shokubai (Catalyst)*, **8**, 306 (1966); G. K. Boreskov, *Advan. Catalysis*, **15**, 285 (1965); A. A. Balandin, *ibid.*, **19**, 1 (1969).

[10)] T. Aonuma and Y. Nakada, *Shokubai (Catalysts)*, **12**, 20 (1970).

[11)] A. A. Balandin, *Advan. Catalysis*, **10**, 120 (1957).

[12)] a) J. E. Leffler, and E. Grunwald, "Rates and Equilibria of Organic Reactions" Wiley, New York (1963), p. 315. b) E. Cramer, *Advan. Catalysis*, **7**, 75 (1955).

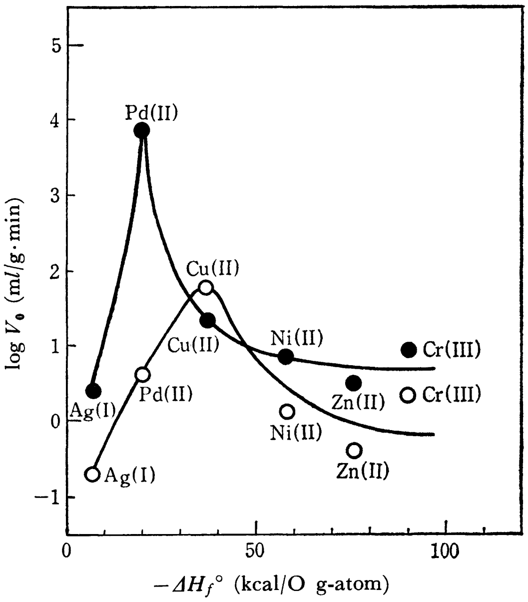

Fig. 5. Correlations of the initial rates of the carbon dioxide and benzene formations with the heats of formation of metal oxides per g-atom oxygen. The reaction temperature was 290°C.
○: benzene, ●: carbon dioxide.

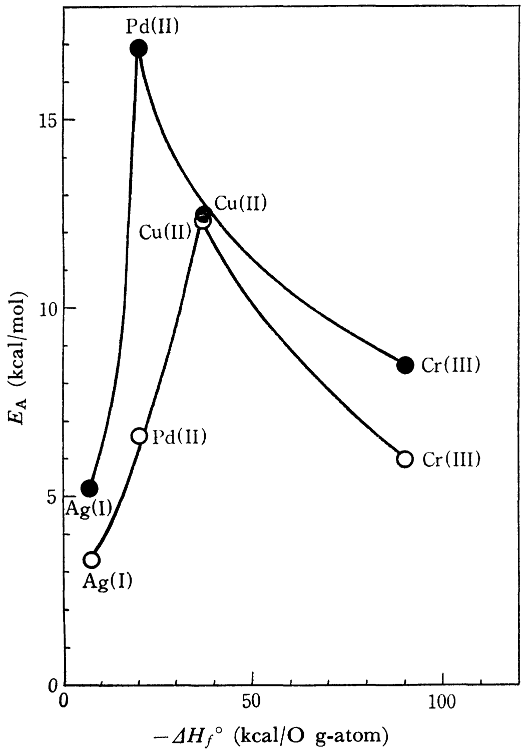

Fig. 6. Correlations of activation energy of the carbon dioxide and benzene formations with the heats of formation of metal oxides per g-atom oxygen.
○: benzene, ●: carbon dioxide.

mations. The relations were in volcano shapes similar to those observed in the activation energies, so that the most active catalyst had the largest frequency factor. This situation was defined as frequency-factor-controlling.12)

The analogous relations of the activation energy and the frequency factor with the same heat of formation suggest the existence of compensation effects in this oxidation. In fact, the compensation effects in the formations of both carbon dioxide and benzene are shown in Fig. 8. Thus, the frequency-factor-controlling mentioned above implies that the oxidation reaction was observed above the isokinetic temperature.12)

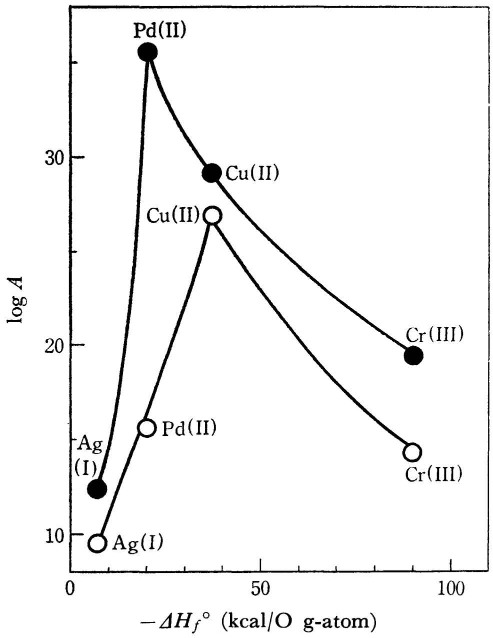

Fig. 7. Correlations of frequency factors of the carbon dioxide and benzene formations with the heats of formation of metal oxides per g-atom oxygen.
○: benzene, ●: carbon dioxide.

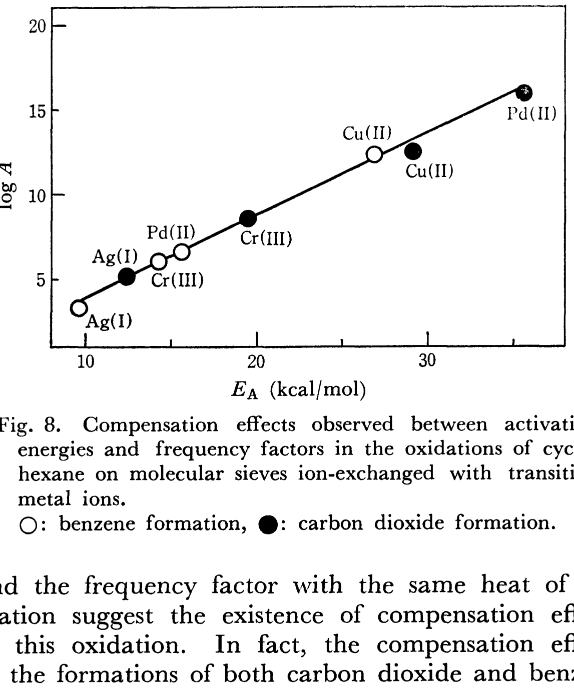

Fig. 8. Compensation effects observed between activation energies and frequency factors in the oxidations of cyclohexane on molecular sieves ion-exchanged with transition metal ions.
○: benzene formation, ●: carbon dioxide formation.

In a previous paper,3) the reaction orders as well as the catalytic activity of the ion-exchanged molecular-sieve catalysts for olefin oxidations were reasonably correlated with the parameter of Y,13) which is thought to represent the softness of the metal ion, but no reasonable relation was found in the present oxidation of

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13) M. Misono, E. Ochiai, and Y. Yoneda, *J. Inorg. Nucl. Chem.* **29**, 2685 (1967).

cyclohexane by the use of such a parameter.

In conclusion, the catalytic activities of ion-exchanged molecular-sieve catalysts for the oxidation of cyclohexane into benzene and carbon dioxide can be correlated with the heats of the formation of the corresponding metal oxides per g-atom oxygen at any of the reaction temperatures examined in the present study, because the compensation effects were present. Therefore, the activity of the ion-exchanged molecular sieve can be well estimated from the table values of the metal oxides, although the meaning of such a correlation is yet in question with regard to the reaction mechanism.

We should also mention the possibility of improving the selectivity for the benzene formation, even at the high conversion level, by adopting a better gas-composition of the reactant.

Our thanks are due to Mr. Shinji Hayata for his experimental assistance.