JOURNAL OF CATALYSIS **36**, 361–370 (1975)

Catalytic Oxidation over Molecular Sieves Ion-Exchanged with Transition Metal Ions

VI. A Kinetic Study of the Oxidative Dehydrogenation of Cyclohexane over Y Sieve Ion-Exchanged with Cupric Ion

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Received September 5, 1973; revised September 9, 1974

Kinetics and adsorption in the oxidative dehydrogenation of cyclohexane over Cu(II)-Y were studied to elucidate the reaction mechanism and the key to the high selectivity of Cu(II)-Y catalyst among the molecular sieves ion-exchanged with transition metal ions. Rate equations for benzene and carbon dioxide formation were $V(\text{benzene}) = k_1p_2$, and $V(CO_2) = k_2p_2^{1/2}$ (p_2, partial pressure of oxygen) under partial pressures of 0.05 to 0.95 (oxygen) and 0.01 to 0.18 atm (cyclohexane) at 320°C.

Adsorption of reactants measured by means of the pulse gas chromatographic technique revealed the following results: (a) an oxygen pulse converted preadsorbed cyclohexane exclusively into carbon dioxide, but a cyclohexane pulse was converted by preadsorbed oxygen into benzene; (b) adsorption of oxygen was saturated, whereas that of cyclohexane increased with partial pressure in the same pressure range as used in the kinetic measurements; (c) reactivity of adsorbed oxygen was much higher than that of adsorbed cyclohexane; (d) no adsorbed oxygen was observed during the oxidation reaction in spite of (b) above.

The results indicate that adsorption of oxygen is rate determining in the oxidative dehydrogenation for benzene formation. The high benzene yield of Cu(II)-Y is assumed due to its high adsorption ability for oxygen. Catalytic activities of the Y sieves ion-exchanged with cupric ion at several levels were also studied to discuss the location of the active site for this oxidation.

INTRODUCTION

Interesting catalytic activities of molecular sieves have recently been reported for oxidation reactions (*1*). We have described (*2,3*) high catalytic activities of molecular sieve Y ion-exchanged with transition metal ions (abbreviated as metal ion-Y) for the oxidation of olefins and oxidative dehydrogenation of cyclohexane. In the oxidative dehydrogenation of cyclohexane, Cu(II)-Y was found to be the best selective catalyst for benzene formation among Pd(II), Ag(I), Ni(II), Zn(II), and Cr(III)-Y, although Pd(II)-Y had the largest activity for carbon dioxide formation. Kubo, Tominaga and Kunugi (*4*) found recently that the metal ions of lower valence, such as ferrous ion, held on the molecular sieve catalyzed cyclohexene formation from cyclohexane through oxidative dehydrogenation under low oxygen pressure and pointed out the catalytic role of the dissociatively adsorbed oxygen, which was detected on Fe(II)-Y by means of Mössbauer spectroscopy (*5*).

In the present work, the kinetics of this oxidative dehydrogenation reaction and

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the quantities of adsorbed cyclohexane and oxygen on Cu(II)-Y under the reaction conditions were studied, using both flow and pulse reactors, respectively, in order to clarify the role of cupric ion in this selective oxidation and to elucidate the mechanism. Catalytic activities of the Y sieves with different copper content were also studied to discuss the location of the active sites.

EXPERIMENTAL METHODS

Materials

The ion-exchanged molecular sieve catalysts were prepared by ion-exchange of Y-molecular sieve (Linde, SK-40), Na(I)-Y, with an aqueous solution of metal ion in a suitable form not too acidic nor too basic. The exchange levels were, 1, 10, 30, 60, and 100%. This treatment was followed by a thorough washing with deionized water, drying at 100°C and calcination at 400°C for 7 hr in the atmosphere. Details were described in previous papers (*2,3,6*).

Cyclohexane (G. R. grade) was obtained from Wako Junyaku Co.; neither benzene nor cyclohexene was detectable in it by gas chromatography.

Apparatus and Procedure

The catalytic activity and kinetics were observed by an ordinary flow reactor with a fixed catalyst bed diluted with carborundum (Nakarai Co.) to enlarge the heat capacity of the catalyst bed. The exchange level of the catalyst used for the kinetic measurements was 100%. The total flow rate was 100 ml/min and the weight of catalyst was around 30 mg. The thermowell was located in the middle of catalyst bed packed in a glass tube of 25 mm diameter.

Two series of experiments were undertaken for the kinetic study to obtain the reaction orders in cyclohexane and oxygen, respectively. In one series, the partial pressure of cyclohexane was changed in the range between 0.01 and 0.18 atm under the fixed oxygen pressure of 0.30 atm. Cyclohexane was fed by means of a nitrogen flow passed through a cyclohexane saturator. Desired partial pressures were obtained by changing the temperature of the saturator. In another series, the partial pressure of oxygen was changed from 0.05 to 0.95 atm under the fixed cyclohexane pressure of 0.05 atm. In both series, the reactant gas was balanced to 1 atm by nitrogen.

Cyclohexane, cyclohexene, benzene, and carbon dioxide were analyzed by means of gas chromatography. A column of 4 m TCP (Japan Gaschro Co.) – 1 m PEG-1000 (Japan Gaschro Co.) was used at 80°C for the first three and a Porapak Q (Waters Associates Inc.) column of 2 m was used at room temperature for CO_2. The conversion of cyclohexane to benzene and carbon dioxide increased linearly with the contact time below 10% conversion, so that the principle of the differential reactor could be applied. Thus, the reaction rate V(ml/g min) was obtainable from the straight line at low conversions,

$$V = [F/(1 + r)W]\ X,$$

where X is the conversion of cyclohexane into benzene or carbon dioxide, F is the total flow rate, W is the weight of catalyst, and r is the ratio of oxygen plus nitrogen to cyclohexane. Catalytic activities of Cu(II)-Y of different exchange levels were compared at 320°C, using a reactant gas mixture of 3.7% cyclohexane, 50% oxygen and 46.3% nitrogen.

The amounts of adsorbed cyclohexane and oxygen and their reactivities on Cu(II)-Y were studied by the pulse gas chromatographic technique (*7*). One of the reactant gases was passed onto the catalyst in the glass tube reactor at 320°C for 1 hr together with nitrogen gas as a carrier. Afterwards, helium gas was passed in order to elute out the unadsorbed reactant for 25 min, and then the other reactant was pulsed into the helium carrier (60 ml/min) in order to have the adsorbed species react with it; the reaction products, benzene and carbon dioxide, were analyzed by a gas chromatograph directly attached to the reactor. The consecutive pulses were injected until no product was detected. Another analytical method in which all products were condensed by a liquid nitrogen trap attached to the reactor and then were evaporated to a gas chromatograph, gave the same results. This coincidence implies that the slow desorption of the products in this reaction was not important.

RESULTS

Kinetic Expression

The reaction rate of the differential reactor for benzene and carbon dioxide formation may be generally expressed by Eq. (1),

$$V = k\, p_2{}^m p_1{}^n, \qquad (1)$$

where k, p_1, and p_2 are the rate constant and partial pressures of cyclohexane and oxygen, respectively.

$$\log V = \log k + m \log p_2 + n \log p_1. \qquad (2)$$

Relations between log V and log p are shown in Fig. 1 and Table 1. The values of m and n (the reaction orders in oxygen and cyclohexane, respectively) are calculated for benzene and carbon dioxide formation from Fig. 1 and Table 1, respectively. The rate equations thus obtained are described by Eqs. (3) and (4) for benzene and carbon dioxide formation, respectively.

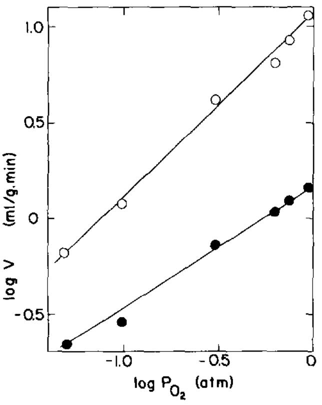

FIG. 1. Log–log plot of reaction rates against partial pressures of oxygen on Cu(II)-Y at 320°C. The partial pressure of cyclohexane was kept at 0.05 atm. (○) plots as for benzene formation; (●) plots as for carbon dioxide formation.

TABLE 1

DEPENDENCE OF BENZENE AND CARBON DIOXIDE FORMATION RATES ON THE PARTIAL PRESSURE OF CYCLOHEXANE[a]

Partial pressure of cyclohexane (atm)	Reaction rate (ml/g min)	
	$V(C_6H_6)$	$V(CO_2)$
0.01	3.73	0.77
0.03	3.75	0.83
0.05	4.10	0.72
0.10	4.40	1.18
0.14	4.70	1.00
0.18	3.77	0.88

[a] Catalyst, Cu(II)-Y; partial pressure of oxygen: 0.30 atm; reaction temp, 320°C.

$$V(\text{benzene}) = k p_2 p_1{}^0, \qquad (3)$$

$$V(CO_2) = k'\, p_2{}^{1/2}\, p_1{}^0. \qquad (4)$$

Adsorption of Cyclohexane and Oxygen on Cu(II)-Y

a. Oxygen adsorption. The reactivities of adsorbed oxygen with cyclohexane pulsed are shown in Fig. 2, where the reaction rate is shown by the conversion of cyclohexane into benzene and carbon dioxide. Seven pulses of 2 μl cyclohexane were necessary to consume all adsorbed oxygen on Cu(II)-Y of 100 mg as shown in Fig. 2. The total amounts of benzene and carbon dioxide produced gave the amount of adsorbed oxygen based on Eqs. (5) and (6):

$$O_2 + 2/3C_6H_{12} = 2/3C_6H_6 + 2H_2O, \qquad (5)$$

$$O_2 + 1/9C_6H_{12} = 2/3CO_2 + 2/3H_2O. \qquad (6)$$

It is very interesting that the reaction of adsorbed oxygen with pulsed cyclohexane

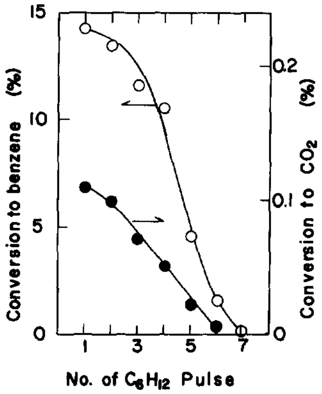

FIG. 2. Reactivity of adsorbed oxygen on Cu(II)-Y with cyclohexane at 320°C. Partial pressure of oxygen of the adsorbate gas, 1 atm; pulse size of cyclohexane, 2 μl; used catalyst: Cu(II)-Y, 100 mg. (○) benzene formation; (●) carbon dioxide formation. Conversion in the ordinate: produced benzene/pulsed cyclohexane (2 μl).

produced benzene almost exclusively; its selectivity reached 99% as shown in Fig. 2.

The thermal desorption of adsorbed oxygen on Cu(II)-Y during the helium elution is shown in Fig. 3, where the amount of oxygen adsorbed was determined at each elution time from the quantity of benzene produced by sufficient cyclohexane pulses (in this case, three pulses of 2 μl cyclohexane) to consume all adsorbed oxygen. The adsorption levels of oxygen expressed by the conversion of pulsed cyclohexane in Fig. 3 were essentially constant during the first 30 min, so that the thermal desorption can be neglected if the reaction of adsorbed oxygen with pulsed cyclohexane was finished within this period. The adsorption of oxygen was found to be almost saturated above 0.12 atm oxygen partial pressure, as shown in Fig. 4. The amount of saturated adsorption was 1.7×10^{-7} mole/mg catalyst, which corresponds to 8% of total cupric ion on the molecular sieve if one assumes the oxygen molecule to be associatively adsorbed on the metal ion.

b. Cyclohexane adsorption. The reactivity of adsorbed cyclohexane with pulsed oxygen is shown in Fig. 5. In marked contrast to the reaction of adsorbed oxygen, carbon dioxide was the only product. The total amount of adsorbed cyclohexane under 0.03 atm cyclohexane was 0.9×10^{-7} mole/mg catalyst or 1 cyclohexane molecule/25 cupric ions.

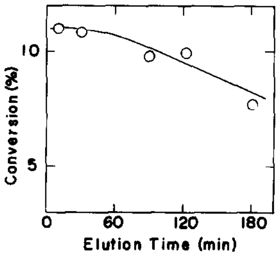

FIG. 3. Desorption of adsorbed oxygen on Cu(II)-Y by the elution of helium gas at 320°C. Used catalyst: Cu(II)-Y, 24.5 mg; temperature of adsorption, 320°C. Conversion in the ordinate: produced benzene/pulsed cyclohexane (6 μl).

The dependence of cyclohexane adsorption on partial pressure was observed in the same way as described above for oxygen. The amount of adsorption increased linearly with the partial pressure, as shown in Fig. 4, showing that the adsorption was not saturated on Cu(II)-Y at partial pressures of 0.03–0.12 atm, a range which includes the partial pressure employed in the kinetic measurement of the oxidative dehydrogenation.

The reactivities of the two adsorbed species can be compared by the amounts of the counter reactant necessary to consume all adsorbed species when the same

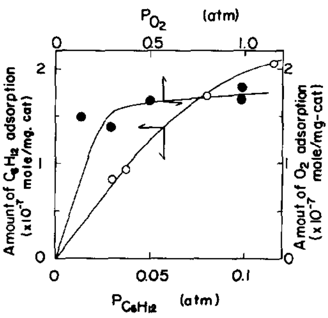

FIG. 4. Adsorption isotherm of oxygen and cyclohexane on Cu(II)-Y at 320°C. (●) oxygen, (○) cyclohexane.

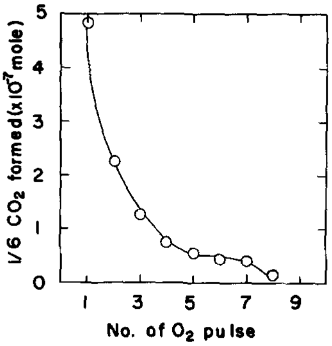

FIG. 5. Reactivity of adsorbed cyclohexane on Cu(II)-Y at 320°C. Adsorbate gas, 3% cyclohexane in helium; pulse size of oxygen, 5 ml; used Cu(II)-Y, 11.1 mg.

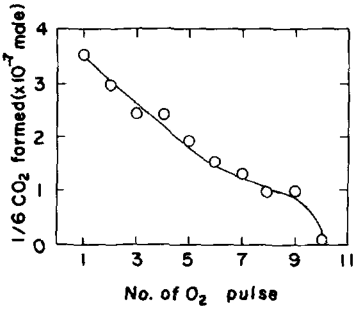

FIG. 6. Adsorption of cyclohexane during oxidation reaction at 320°C. Reaction gas; 13% cyclohexane, 50% oxygen, 37% helium. Pulse size of oxygen, 5 ml; used Cu(II)-Y, 11.8 mg. No product was observed by cyclohexane pulses.

amount of the sieve was used. Seven pulses of 5 ml oxygen (1.4×10^{-3} mole) were necessary for the oxidation of cyclohexane adsorbed on 11.1 mg Cu(II)-Y (1.0×10^{-6} mole of adsorbed cyclohexane), whereas only three pulses of 2 μl cyclohexane (7.2×10^{-5} mole) were needed for adsorbed oxygen (1.9×10^{-6} mole). These values indicate a higher reactivity of adsorbed oxygen compared with adsorbed cyclohexane.

c. Adsorption of cyclohexene on Cu(II)-Y. The adsorption and reactivity of cyclohexene, one of the possible intermediates (*8*) in this oxidative dehydrogenation, were investigated at 200°C because the decomposition reactions mainly took place at 320°C. After five pulses of cyclohexene (10 μl) were injected to the catalyst, oxygen pulses were introduced to the system. Adsorbed cyclohexene was oxidized exclusively into carbon dioxide by oxygen, as with cyclohexane. On the other hand, the reaction of oxygen adsorbed under 1 atm with pulsed cyclohexene produced a minor amount of benzene in addition to decomposed products, and the selectivity for benzene increased with decreasing reaction temperature, or the repeat of cyclohexene pulses.

d. Adsorption under the flow of the reaction gas mixture. In order to measure the adsorption during the reaction, the catalyst (11.8 mg) was treated by a reactant gas mixture composed of 13% cyclohexane, 50% oxygen, and 37% nitrogen at 320°C and then a cyclohexane or oxygen pulse was injected at the same temperature. Although no reaction was observed from the cyclohexane pulse, carbon dioxide was formed from the oxygen pulse, the reactivity of which is shown in Fig. 6. This feature is consistent with a persistent adsorption of cyclohexane (in view of the fact that the adsorbed cyclohexane was converted exclusively to carbon dioxide) and indicates that adsorbed oxygen does not persist on Cu(II)-Y catalyst during the oxidative dehydrogenation reaction. The amount of adsorbed cyclohexane under the reaction mixture was 1.5×10^{-7} mole/mg cat, which is a little below the value (2.1×10^{-7} mole/mg cat as shown in Fig. 4) of the adsorption without oxygen under the same cyclohexane concentration. The lower partial pressure of cyclohexane over the catalyst than that at the reactor inlet due to the steady consumption by the reaction may explain a small decrease of adsorption amount.

Adsorption of Cyclohexane and Oxygen on the Y Sieves Ion-Exchanged with Other Metal Ions than Copper

Catalytic (at 290°C) (*3*) and adsorption (at 320°C) activities of molecular sieves

TABLE 2
CATALYTIC AND ADSORPTION ACTIVITIES OF MOLECULAR SIEVES ION-EXCHANGE WITH TRANSITION METAL IONS

Catalyst	Catalytic activity[a] (ml/g min) × 10^2		Adsorption activity[b]	
	$V(C_6H_6)$	$V(CO_2)$	C_6H_{12}	O_2
Cu(II)-Y	52.0	22	100	100
Pd(II)-Y	4.4	7250	>200	<1[c]
Cr(III)-Y	2.3	9.6	<1	<1
Zn(II)-Y	0.4	3.2	<1	<1
Ni(II)-Y	1.4	7.3	<1	<1
Ag(I)-Y	0.2	2.5	<1	<1

[a] Reaction rate at 290°C; reaction gas: 1% cyclohexane, 50% oxygen, 49% nitrogen. Details refer to Ref. (3).

[b] Relative value of adsorbed amount at 320°C [Cu(II)-Y = 100]. Adsorbate gases are composed of 3.7% cyclohexane in nitrogen for cyclohexane adsorption and 100% O_2 for O_2 adsorption, respectively.

[c] Benzene was formed by simple dehydrogenation, not by oxidative dehydrogenation.

ion-exchanged with transition metal ions (Me-Y) are summarized in Table 2. Adsorption activities were observed by the same method as described above. Except for Pd(II)-Y and Cu(II)-Y, the Me-Y catalysts showed only small adsorption activities for both reactants and also small catalytic activities. Among the Me-Y catalysts examined, Pd(II)-Y showed the highest activity for benzene formation by cyclohexane pulses after adsorption treatment of oxygen. However, the absence of water in the products and the absence of a decrease in catalytic activity (provided the interval between pulses is sufficiently long) indicates the occurrence of the simple dehydrogenation, and also indicates that oxygen adsorption is small. The catalytic activity of Pd(II)-Y for the dehydrogenation was, however, very small by the flow reactor in accordance with the marked decrease of activity by the successive pulses at short pulse intervals.

The adsorption of cyclohexane on Pd(II)-Y was much larger than that on Cu(II)-Y, but adsorbed cyclohexane was oxidized exclusively to carbon dioxide on Pd(II)-Y as well as on Cu(II)-Y. The maximum catalytic activity for carbon dioxide formation shown by Pd(II)-Y (Table 2) may be connected with its maximum activity for cyclohexane adsorption.

Catalytic Activity of Cu(II)-Y at Various Ion-Exchange Levels

Catalytic activity for the oxidative dehydrogenation of cyclohexane was measured over Na(I)-Y and five samples of Cu(II)-Y in which sodium ions were exchanged with cupric ions at the five different levels of 1, 10, 30, 60, and 100%. The characteristic features of the catalytic activities of the sieves ion-exchanged at low and high levels are shown in Fig. 7a and b. The formation of cyclohexene was observed with a considerable selectivity over the sieves of low cupric ion concentration, as shown

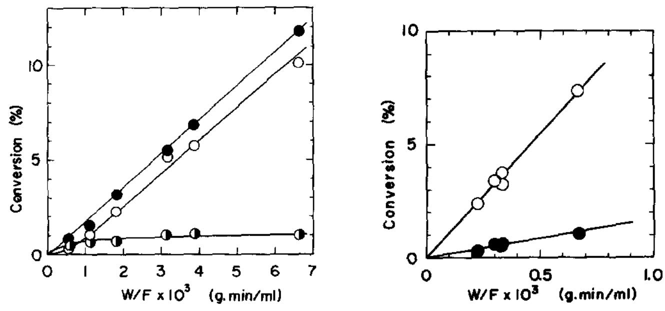

FIG. 7. Oxidation of cyclohexane over Cu(II)-Na(I)-Y catalyst at 320°C. (a) Cupric ion exchange 10%; (b) Cupric ion exchange, 60%. (○) benzene formation; (●) carbon dioxide formation; (◑) cyclohexene formation.

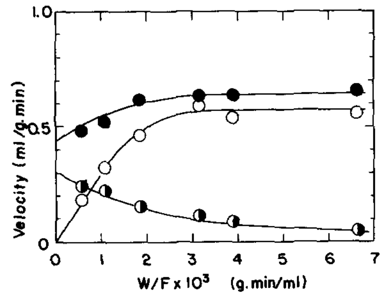

FIG. 8. Formation rates of products in the oxidation of cyclohexane over Cu(II)-Na(I)-Y catalyst at 320°C. Cupric ion exchange, 10%; (○) benzene; (●) carbon dioxide; (◑) cyclohexene.

in Fig. 7a. The figure indicates a consecutive reaction in which cyclohexene is converted into benzene. The consecutive reaction is clearly shown by Fig. 8, where the formation rates of each product are plotted against the contact time. The formation rate of cyclohexene is extrapolated to a definite value, whereas that of benzene is zero at the zero contact time.

Over the sieve of a high exchange level, no cyclohexene was detected in the products by gas chromatography and yields of benzene and carbon dioxide increased linearly with the contact time below 15% conversion, as shown in Fig. 7b, denying consecutive formation of benzene from cyclohexene.

The formation rates of each product are shown as a function of percentages of the ion-exchange in Fig. 9, where the rates were calculated at 10% conversion of cyclohexane. The rate of benzene formation increased rather abruptly beyond 30% cupric ion-exchange, whereas only a small variation is observed in that of carbon dioxide formation, and the formation rate of cyclohexene decreased gradually to zero as the percentage of exchanged cupric ion increased.

Neither silica–alumina, alumina nor NaOH–silica gel[2] showed any catalytic activity of oxidation of cyclohexane at a contact time of 5×10^{-3} g min/ml, but Na(I)-Y showed a 16% conversion of cyclohexane to carbon dioxide under the same conditions. These facts imply that the oxidation activity of Na(I)-Y cannot be connected simply to its acid–base character.

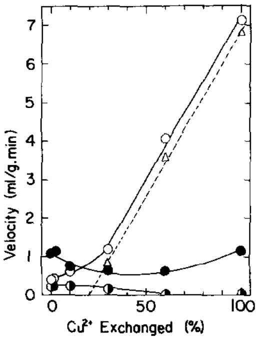

FIG. 9. Rates of oxidation over Cu(II)-Na(I)-Y catalysts at 320°C vs catalyst compositions of copper. (○) benzene; (●) carbon dioxide; (◑) cyclohexene; (△) benzene formation rate due to cupric ions on the molecular sieve (see text).

DISCUSSION

Reaction Mechanism of Benzene Formation on Cu(II)-Y

Five reaction mechanisms (*10*) which are distinguished by the rate-determining step may possibly explain the rate equation shown by Eq. (3). Mechanism 1: Oxygen adsorption step is rate-determining. Mechanism 2 (Langmuir-Hinshelwood mechanism I): The rate-determining step is the surface reaction of two adsorbed species on the separate active sites of the catalyst. Mechanism 3 (Langmuir-Hinshelwood mechanism II): The surface reaction of two adsorbed species on the same active site is rate determining. Mechanism 4 (Rideal mechanism I): The reaction of adsorbed cyclohexane with oxygen in the vapor phase is rate determining. Mechanism 5 (Rideal mechanism II): The reaction of adsorbed oxygen with cyclohexane in the vapor phase is rate determining, but adsorption of cyclohexane is

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[2] For a description of these catalysts, see Mochida *et al.* (*9*).

fairly strong and inhibits oxygen adsorption.

To satisfy the observed rate Eq. (3), strong adsorption of cyclohexane and molecular adsorption of oxygen on the active sites of the catalyst should be assumed under the reaction conditions for mechanisms 2–5. However, the results revealed the following facts: (a) the adsorbed cyclohexane which was held on the catalyst strongly enough not to be eluted by the helium carrier gas was converted exclusively into carbon dioxide; (b) saturated adsorption of cyclohexane cannot be assumed under the reaction conditions (Fig. 4), but saturated adsorption of oxygen can be assumed. These results indicate the small contribution of strongly adsorbed cyclohexane to benzene formation, and imply that mechanisms 2–5 should be abandoned. On the other hand, the following observations support mechanism 1 in which the adsorption step of oxygen is rate determining:

a. adsorbed oxygen produced benzene by cyclohexane pulses;

b. Cu(II)-Y, the best selective catalyst for benzene formation, showed the highest adsorption ability for oxygen;

c. the adsorbed oxygen was much more reactive than adsorbed cyclohexane;

d. no adsorption of oxygen was observed during the reaction although saturated adsorption occurred under the same partial pressure in the absence of cyclohexane.

The facts (c) and (d) may be consistently explained by the assumed mechanism, where the surface reaction following the rate-determining step consumed immediately all adsorbed oxygen during the reaction.

Dissociative as well as associative oxygen on the catalyst is possible for the adsorbed species in mechanism 1. Wang and Lunsford (*11*) found O_2^- species on molecular sieves by ESR. Kubo, Tominaga and Kunugi (*4*) connected fair selectivities for the cyclohexene formation of metal ions of lower valence on the molecular sieve with dissociative oxygen species; whereas metal ions of higher valence produced no cyclohexene at all (*3,4*), except for the sieve of very low ion-exchange levels. Associative as well as dissociative oxygen may be present on Cu(II)-Y; however, it is plausible to assume associative oxygen as the reactive species for benzene formation in this oxidative dehydrogenation.

On the other hand, cyclohexene is unlikely to be an intermediate for benzene formation because it gave mainly decomposed products in its reaction with adsorbed oxygen at 320°C.

Thus, one of the possible reaction series for benzene formation is the following:

$$O_2 + \text{catalyst} \longrightarrow O_2\text{–catalyst}, \tag{7}$$

$$C_6H_{12} + O_2\text{–catalyst} \longrightarrow C_6H_8 + 2H_2O + \text{catalyst}, \tag{8}$$

$$C_6H_8 \xrightarrow{\text{rapid}} C_6H_6 + H_2, \tag{9}$$

$$2H_2 + O_2\text{–catalyst} \xrightarrow{\text{rapid}} 2H_2O + \text{catalyst}, \tag{10}$$

where the rate-determining step is Eq. (7). This conclusion may be checked by measuring the adsorption rate of oxygen and comparing it with the reaction rate.

Active Sites for Oxidative Dehydrogenation of Cyclohexane into Benzene

The results revealed in the previous (*3*) and present studies lead us to conclude that the active sites of Cu(II)-Y for the oxidative dehydrogenation of cyclohexane into benzene are closely associated with cupric ions in the sieves, similarly to the oxidation of olefins (*2,12*) and carbon monoxide (*12*). The X-ray diffraction studies suggest that charge-balancing cations may be found in seven different regions of space within the structure of faujasite (*13*). The problem as to which sites are catalytically active has been studied by many researchers. Some effects of ion-exchange levels of cations on catalytic and adsorption activities have been explained by a strong preference of alkaline earth (calcium) ions for catalytically inactive Site I such that a large fraction of Site I positions is filled first before sodium ions at the potentially catalytic active sites (Sites II and III) can be replaced (*14*).

However, the situation seems somewhat different in the case of transition metal cations, which have no overwhelming preference for Site I (*15*). Thus, some cupric ions may be distributed outside the hexagonal prism even at the low exchange level before all Site I are exchanged, and they may be involved in the catalytic reactions. Such a deduction is consistent with the present result of rather high activity of 60% exchanged Cu(II)-Y, because it should have little activity if the preference of Site I is as overwhelming for cupric ion as for calcium cations.

Catalytic activities due to cupric ions were calculated by subtracting the activity of Na(I)-Y from those of Cu(II)-Y and the results are plotted in Fig. 9. The activity due to cupric ion appeared essentially beyond 30% ion-exchange, and increased linearly with increasing extent of ion-exchange. The straight line intersects with the abscissa at 20% ion-exchange. This linear relation may be explained in terms that the catalytically active sites on the sieve were ion-exchanged by cupric ion in a constant ratio to the exchangeable sites beyond 20% preferential exchange of Site I, consistent with the fact that only 8% of total cupric ions on the sieve adsorbed oxygen.

The linear relation in Fig. 9 rejects the sextet reaction scheme (*16*) for benzene formation on Cu(II)-Y.

Some General Remarks on Oxidation Over Molecular Sieve

The rate equation for carbon dioxide formation [Eq. (4)] and the reactivity of adsorbed cyclohexane by the oxygen pulse into carbon dioxide indicates that the rate-determining step of the complete oxidation of cyclohexane is the surface reaction of dissociative oxygen and strongly adsorbed cyclohexane. However, a quite high oxidation activity of nontransition metal ions for paraffins (*17*) into carbon dioxide has been reported. Miale and Weisz (*18*) found highly selective dehydrocyclization activity of Na(I)-X for *n*-hexane at elevated temperatures, whereas silica–alumina, alumina or H-X showed only negligible activity (*19*). Complete oxidation in the present study seemed to occur rather independently of the level of cation exchange as shown in Fig. 9. Such facts indicate that the nontransition metal cation of the sieve regardless of its kind has an oxidation activity of hydrocarbons to some extent, and that cations may begin the oxidation reaction by the abstraction of hydrogen, which leads to cyclohexene and benzene with a certain selectivity in the case of cyclohexane oxidation. Thus, a total reaction profile of the oxidative dehydrogenation of cyclohexane over the sieve may be summarized as follows:

$$\begin{tikzcd}
\text{cyclohexane} \arrow[r, "V_1"'] \arrow[rr, bend left, "V_4"] \arrow[dr, "V_3"'] & \text{cyclohexene} \arrow[r, "V_2"'] \arrow[d, "V_5"] & \text{benzene.} \arrow[dl, "V_6"] \\
 & \text{carbon dioxide} &
\end{tikzcd} \tag{11}$$

On a sieve of low cupric ion exchange, V_1 catalyzed by sodium ions is larger than V_4 catalyzed by copper ions, so that benzene formation occurs via a consecutive reaction. With increasing amounts of cupric ion at sites outside the hexagonal prisms, however, V_1 decreases and V_4 increases. In contrast, V_3 is constant regardless of the ion-exchange level.

The molecular oxygen assumed as an active species on the Cu(II)-Y catalyst is consistent with the reaction profile proposed here because cyclohexene does not seem to be an intermediate for a principal benzene formation on cupric ion in the present study. Cyclohexadiene possibly formed by the reaction of cyclohexane with molecular oxygen may be an intermediate, as shown in the reaction schemes [Eqs. (8) and (9)].

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