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Catalytic Oxidation over Molecular Sieves Ion Exchanged with Transition Metal Ions

III. Catalytic Activities of Molecular Sieves Ion Exchanged with Transition Metal Ions in the Oxidation of Propylene and Ethylene

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Oxidation activities of molecular sieves ion exchanged with 12 kinds of transition metal ions for propylene and ethylene were observed by an ordinary flow reactor in order to explore the role of the metal ion in the oxidation of olefins. The order of catalytic activity of the metal ions was $Pd \simeq Pt > Cu > Tl > Ag > Mn > Ni > Co > Zn > V > Cr > Na$. The reaction orders in oxygen over these catalysts were all around 0.5, but those in propylene varied considerably. The adsorption of olefin accordingly seemed more important in this oxidation, so the activity sequence was correlated with the Y parameter proposed by Misono *et al.* to express the tendency of the metal ion to form a dative π-bond. With this parameter, reasonable linear relationships were obtained with both the activity and the reaction order. The differences between the ion-exchanged molecular sieve catalysts and conventional oxide catalysts are discussed.

INTRODUCTION

In a previous paper (*1*), molecular sieve Y ion exchanged with cupric ion (Cu(II)-Y) was found to be a very active catalyst for propylene oxidation. It would be interesting to know how active molecular sieves ion exchanged with other transition metal ions are and to discover whether there are more active catalysts than Cu(II)-Y, whose activity was 10 times higher than that of the ordinary cupric oxide catalyst. It may also be of value to study why Cu(II)-Y has a high catalytic activity and how the metal ion exists in the molecular sieve.

The catalytic activities of metal oxide catalysts have been examined for various oxidation reactions. Activity data were tested for correlations with the so-called table properties of the catalysts in the oxidation reactions of propylene (*2*), ethylene (*3*), and hydrogen (*4*). Boreskov has reviewed these subjects (*5*). These trials may be useful not only for the estimation of the catalytic activity, but also to give some information leading to an understanding of the reaction mechanism. This approach should be valuable to adapt to the oxidation over ion-exchanged molecular sieve catalysts.

In the present work, the catalytic activities of the molecular sieves ion exchanged with transition metal ions other than cupric ion, viz., Ag, Pt, Pd, Co, Ni, Tl, Mn, V, Zn, and Cr, have been observed in the oxidation of propylene and ethylene. The catalytic activities have been correlated with properties of the metal ions using a linear free-energy relationship (LFER) approach

(*6*). Together with kinetic studies, this approach may solve the high activity of the ion-exchanged molecular sieve catalyst.

EXPERIMENTAL

Catalysts

The ion-exchanged molecular sieves examined are listed in Table 1 together with some of their properties. They were prepared by the ion exchange of the Y molecular sieve (Linde), Na-Y, with aqueous solutions of metal sulfates or nitrates except for cupric, palladium, and platinum ions, for which ammine complexes were used. A sufficient amount of metal ion was passed through the cylindrically shaped Na-Y in a column. The ion-exchanged sieves were then washed thoroughly with decationized water and dried at 100°C, followed by calcination at 400°C for 7 hr in the air. The amount of metal ion exchanged into the molecular sieve was determined by extraction of the metal ion with hot nitric acid and titration of this solution. Approximately 80–90% of the sodium ions were exchanged, except for Tl, where only 10.9% of the sodium ions were exchanged.

The silica-supported palladium catalyst (Pd(II)-S) was prepared by impregnation of silica gel (Wako Co.) with ammonical palladium chloride solution, and then calcination at 400°C for 7 hr in the air. Cu(II)-S was described in a previous paper (*1*).

Apparatus and Procedure

Catalytic activities were determined by a conventional flow method, with the fixed catalyst bed diluted by carborundum (Nakarai Co.). The thermowell was located in the middle of the catalyst bed packed in a glass tube of 25 mm diameter. For the investigation of the catalytic activities, the reactant gas consisted of 2% propylene, 50% oxygen, and 48% nitrogen, while in the case of kinetic studies, two series of experiments characterized by different propylene concentrations in the reactant gas were undertaken. In one series, the concentration was below the explosive range, whereas in the other it was above this range. These two series were designated L and H series, according to Moro-oka and Ozaki (*2*). The reactant gas compositions for both series were normally as follows:

Series	Propylene (%)	Oxygen (%)	Nitrogen	Constant to be determined
L	2	20–70	Balance	*m*
	0.2–3.5	50	Balance	*n*
H	20	10–25	Balance	*m*
	15–30	15	Balance	*n*

TABLE 1

THE CATALYSTS AND THEIR ACTIVITIES FOR PROPYLENE OXIDATION

Catalyst	Color	Rate at 350°C[a] (ml/g · min)	m^b	n^b	$-\Delta H_f$ (kcal/O g-atom)	Y
Ag(I)-Y	White	6.80×10^2	0.52	−0.1	7.31	3.99
Pt(II)-Y	Black	6.80×10^4			18.0	4.82
Pd(II)-Y	Black	9.69×10^4	0.6	−0.8	20.4	4.27
Cu(II)-Y	Light blue	1.37×10^3	0.6	0.2	37.1	2.89
Tl(II)-Y	White	1.70×10^3			41.9	3.78
Co(II)-Y	Pink	2.13×10^2			57.2	2.96
Ni(II)-Y	Green	2.60×10^2	0.57	0.60	58.4	2.82
Mn(II)-Y	Light pink	3.0×10^2			62.2	3.03
V(IV)-Y	White	1.2×10^2			74.7	2.18
Zn(II)-Y	White	1.41×10^2			83.2	2.34
Cr(III)-Y	Green	2.10×10^2			90.0	2.70
Cu(II)-S		1.28×10^2	0.50	0.50		
Pd(II)-S		6.58×10^2	0.4	1.1		

[a] Reactant gas composition; 2% propylene, 50% oxygen, and 48% nitrogen.

[b] $V = kP_{O_2}^{m}P_{C_3H_6}^{n}$; observed for the low propylene concentration.

The catalytic activity for ethylene oxidation was observed with the gas composition of 2% ethylene, 50% oxygen, and 48% nitrogen.

Reactant and product gases were analyzed by means of gas chromatography, using a Porapak Q column (Water Associates) for carbon dioxide and olefins, and a PEG column (Japan Chromato Co.) for acetaldehyde. Details were described in a previous paper (*1*).

Results

Products

Carbon dioxide and water were the main products in both series for both olefins with all the catalysts. In the case of Cu(II)-Y, formaldehyde was formed besides carbon dioxide to the extent of 10% of the oxidized propylene, as described in a previous paper (*1*). On catalysts other than Cu(II)-Y, a slight odor of aldehyde was noticed in the effluent gas from the reactor in some cases. Even in such cases, however, none of the oxygenated olefin products was detected on the gas chromatogram. Material balance in carbon was satisfactory as described in a previous paper (*1*).

Determination of Catalytic Activities

In order to compare the catalytic activities of the molecular sieves ion exchanged with different transition metal ions, the reaction rate at a common temperature, 350°C, was observed, since the measurements of the oxidation rate of propylene were practicable around this particular temperature for every catalyst tested here.

The dependency of the conversion of propylene on the contact time is shown in Fig. 1, where Cu(II)-Y and Cu(II)-S were used as catalysts. The conversion increased linearly with the contact time below 15% conversion, so that the principle of the differential reactor could be applied. Thus the reaction rate V was obtainable from the straight line at low conversion,

$$V = [F/(1 + r)We]x,$$

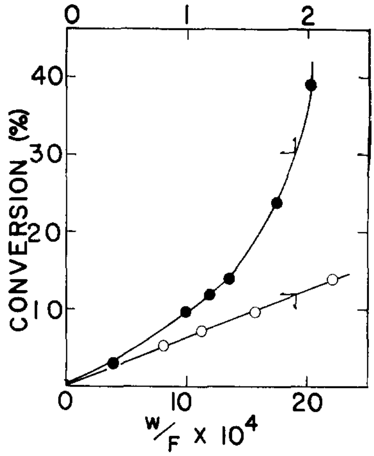

FIG. 1. Oxidation of propylene over Cu(II)-Y and Cu(II)-S at 350°C. Reactant gas composition; 2% propylene, 50% oxygen, and 48% nitrogen. ●, Cu(II)-Y; ○, Cu(II)-S.

where x is the conversion of propylene, F is total flow rate, W is the weight of molecular sieve, r is the ratio of oxygen plus nitrogen to propylene, and e is the degree of ion exchange. The surface area will be equal in all catalysts since the exchange of cations in the molecular sieve causes no change in the base structure.

The activities of ion-exchanged molecular sieves for the ethylene oxidation were obtained by the same procedure as described above. The results are shown in Table 2.

Kinetic expression

The rate equation was studied for Ag(I)-Y, Pd(II)-Y, Cu(II)-Y, Ni(II)-Y, Pd(II)-S, and Cu(II)-S. They were the representatives of the catalyst groups described in the latter part of this work.

The reaction rate of the differential re-

TABLE 2
ACTIVITIES FOR ETHYLENE OXIDATION

Catalyst	Rate at 350°C[a] (ml/g · min)	$-\Delta H_f$ (kcal/O g-atom)
Ag(I)-Y	2.65×10	7.31
Pd(II)-Y	1.93×10^3	20.4
Cu(II)-Y	1.39×10^2	37.1
Ni(II)-Y	6.77	57.2
Cu(II)-S	1.45×10^2	
Pd(II)-S	7.26×10^3	

[a] Reactant gas composition; 2% ethylene, 50% oxygen, and 48% nitrogen.

actor may be generally expressed by the following equation

$$V = kP_{O_2}{}^{m}P_{C_3H_6}{}^{n},$$

where k is the rate constant, P_{O_2} and $P_{C_3H_6}$ are the partial pressures of oxygen and propylene, respectively. The reaction orders m and n were determined under such concentration ranges as shown above by varying one of P_{O_2} or $P_{C_3H_6}$ and keeping the other constant.

$$\log V = \log k + m \log P_{O_2} + n \log P_{C_3H_6}.$$

An example of log V — log P plots is shown in Fig. 2. The values of m and n for the L series are shown in Table 1, and for the H series in Table 3. The catalysts suffered no change in their color after the reaction.

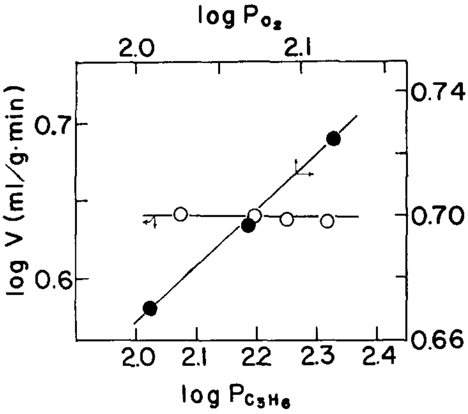

FIG. 2. Log-log plot of the reaction rate against the partial pressure of the reactant gases on CU(II)-Y. (H series). ●, plots as for oxygen; ○, plots as for propylene.

TABLE 3
REACTION ORDERS OF PROPYLENE OXIDATION FOR THE H SERIES GAS COMPOSITION

	m^a	n^a
Pd(II)-Y	0.44	0.0
Cu(II)-Y	0.50	0.0
Cu(II)-S	0.50	0.0

[a] $V = kP_{O_2}{}^{m}P_{C_3H_6}{}^{n}$.

Propylene Oxidation under a Very High Propylene Concentration

The oxidation at a very high propylene concentration of 70% was studied on Cu(II)-Y and Cu(II)-S at 350°C. On both catalysts, the activities were small in comparison with those for the low propylene concentration, and the main product turned out to be acrolein rather than carbon dioxide, as shown in Table 4. In marked contrast to the case of the low propylene concentration, where a distinct difference between these catalysts was observed, they behaved similarly and were dark brown after the reaction under this high propylene concentration.

DISCUSSION

Catalytic Activity Order of Molecular Sieves Ion Exchanged with Transition Metal Ions

The volcano-shaped relationships between the catalytic activities for the oxidations of olefins and the heats of formation of the corresponding metal oxides per oxygen atom were observed in the same manner as found in their oxidations on oxide catalysts (*2*, *3*), where Pd and Pt

TABLE 4
OXIDATION OF PROPYLENE AT HIGH-PROPYLENE CONCENTRATION[a]

	$W/F \times 10^4$ (g · min/ml)	Conversion (%)	$V_1{}^b$ (ml/g · min)	$V_2{}^c$ (ml/g · min)	Ratio[d]
Cu(II)-Y	5.68	4.50	3.92×10	8.00×10	2.05
Cu(II)-S	12.5	5.78	1.37×10	5.24×10	3.80

[a] Reactant gas composition: 70% propylene, 10% oxygen, and 20% nitrogen.
[b] Rate of carbon dioxide formation at 350° (on a propylene basis).
[c] Rate of acrolein formation at 350°.
[d] Acrolein/carbon dioxide.

were most active. However, there was no dependence of the reaction orders in oxygen on the metal ion, indicating that such correlations were only apparent in the present cases. In contrast, the reaction orders in propylene varied very much from one catalyst to another, as shown in Table 1. This fact is taken to mean that the adsorption of propylene is an important process in its oxidation on the ion-exchanged molecular sieves. So a better parameter should be explored for a description of the activity of such a catalyst.

In order to reveal the nature of the metal ion, the parameter, Y, has been proposed (7). The value of this parameter is calculated by the following equation

$$Y = 10(I_n/I_{n+1})(r/n^{1/2}),$$

where I_n is the n-th ionization potential, r is the ionic radius of the metal ion, and n is its formal charge. Y can be considered to express the tendency of the metal ion to form a dative π-bond, and to correspond consequently to its "softness." Misono *et al.* correlated this parameter with the shift of the ir absorption of ethylene by the adsorption on the metal ion (7). The adsorption of the olefin on the metal ion was considered to depend on its softness as revealed in organometallic or coordination chemistry (8) so that the plot of log V_{350} against Y may be of value. There was a good linear correlation between them as shown in Fig. 3, where the catalytic activity of ion-exchanged molecular sieve increased with Y.

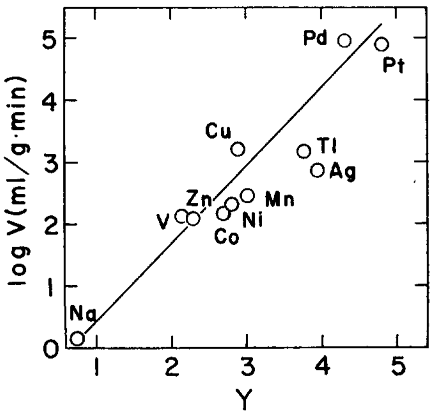

FIG. 3. Correlation between the catalytic activity and the parameter Y in propylene oxidation. The catalytic activity was the reaction rate shown in Table 1. The values of Y were taken from Ref. (7).

As a relation exists between the catalytic activity and n, the reaction order for propylene, there must be a linear correlation between n and Y as shown in Fig. 4, but m, the reaction order for oxygen, is invariable with Y, as expected. The decrease of n accompanying the increase of Y may mean that the adsorption of propylene onto the metal ion is strengthened by increasing Y, and that the catalytic activity of ion-exchanged molecular sieves mainly depends on the ease of the formation of the dative π-bond with propylene. Carter *et al.* (9) reported a strong adsorption of ethylene on Ag-Y using ir. This observation supports the above interpretation.

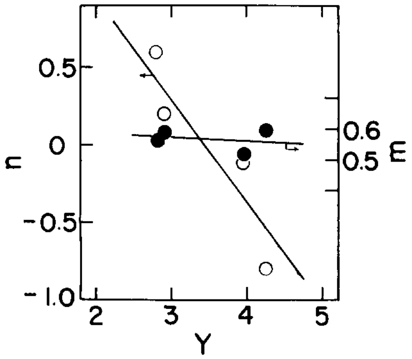

FIG. 4. Correlation between the reaction orders and the parameter Y in propylene oxidation. The values of Y were taken from Ref. (7). ●, plots as for oxygen; ○, plots for propylene.

Characterization of the Ion-Exchanged Molecular Sieve Catalysts

Though the catalytic activity of the ion-exchanged molecular sieves for olefin oxidation showed similar trends to that of oxide catalysts, there were distinct differences between these catalyst groups. The ion-exchanged molecular sieve had the color of the hydrated or the anhydrous metal ion, which was clearly different from that of the corresponding metal oxide. To make clear the state of the metal ions in the molecular sieve, some complementary studies were carried out. Cupric ion in the molecular sieve was coordinated by ethylenediamine, and a dark blue complex which had an ir absorption band at 1048 cm^{-1} was obtained (*10*). This band has been identified as the deformation of the chelate ring (*11*). In the cases of palladium and platinum, the color was similar to that of the respective silica-supported catalyst; however the metal ion had the ability to form a coordination bond with ethylenediamine as did Cu(II)-Y (*10*). Thus, the metal ion on the molecular sieve kept its isolated ionic state. The oxidation activities for propylene and ethylene of Pd(II)-Y and Pd(II)-S are compared in Tables 1 and 2. Ethylene was more reactive than propylene on Pd(II)-S, as reported for the olefin oxidation on an evaporated Pd film (*12*). In marked contrast, propylene is 50-times as reactive as ethylene on Pd(II)-Y. A similar role of the molecular sieve was observed for cupric ion, as described in a previous paper (*1*). Such a δ_R LFER approach (*6*) for the olefin reactivity may elucidate the adsorbed intermediate of olefin on the metal ion of the molecular sieve (*12*).

The following differences were also found in the reaction orders between the molecular sieve and the oxide catalysts. The first is the constancy of the reaction order for oxygen on the ion-exchanged molecular sieves, in contrast to the considerable variation observed on the oxide catalysts (*2*, *3*). The second is the notable smallness of the values of the reaction order for propylene on the ion-exchanged molecular sieves. This fact implies a strong adsorption of propylene and may be compatible with the results using ir spectroscopy of ethylene adsorbed on Ag(I)-Y (*11*).

The above differences may mean that the state of the metal ion on the molecular sieve differs significantly from that of the oxide on the metal, and seems to suggest new applications for the catalyst such as reported in a previous paper (*1*b).

At the very high propylene concentration, the difference between the molecular sieve and the oxide catalyst of copper disappeared, as shown in Table 4. This is because the cupric ion was reduced to the metal on both catalysts.

The Kinetic Equation

The oxygen may adsorb on the ion-exchanged molecular sieve in a dissociated form because its reaction orders were around 0.5 on every sieve. In the L series, the values of n varied from 0.6 on Ni(II)-Y, the largest, to -0.8 for Pd(II)-Y, the smallest. These reaction orders are interpreted by the Langmuir-Hinshelwood equation (Eq. 1) where the dissociated oxygen and propylene adsorb on the same active site. The latter species may adsorb so tightly that the second term can be neglected in comparison with the third in the denominator.

$$V = k\frac{P_{O_2}{}^{1/2}P_{C_3H_6}}{(1 + K_1P_{O_2}{}^{1/2} + K_2P_{C_3H_6})^2} \qquad (1)$$

For the H series, the reaction orders of n were zero, whereas the values of m were also around 0.5 as shown in Table 3. The following equation may be applied. This equation would imply a Rideal mechanism with the rate-controlling step a collision of propylene onto the dissociated oxygen, where the former adsorption is strong and the latter one is weak (*13*).

$$V = kP_{O_2}{}^{1/2}\frac{P_{C_3H_6}}{1 + K_2P_{C_3H_6}} \qquad (2)$$

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