Oxidation of Carbon Monoxide over Transition Metal Ion-Zeolite Catalysts

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Adsorption of oxygen and oxidation of carbon monoxide was investigated on several X and Y type zeolites, their Na^+ being replaced by transition metal ions. Oxygen adsorption was observed on Cr(II), Cu(I), and Fe(II) ions whose oxidation potentials are high, giving an oxygen atom to metal ion ratio of 0.43—0.62 or nearly 0.5. A small amount of oxygen was adsorbed on Tl(I), Co(II), and Mn(II), as expected from their standard oxidation potentials. No oxygen was adsorbed on Cu(II) and Ni(II), their valences being difficult to increase. The activities of these transition metal ions for oxidation of carbon monoxide increased exponentially with the increase of their standard oxidation potential. Kinetic studies on CO oxidation over Fe(II)–X and –Y zeolites have been made, and a Rideal mechanism is suggested where CO molecules in the gas phase attack the oxygen atoms dissociatively adsorbed in the bridged form of Fe^{3+}–O^{2-}–Fe^{3+}. The difference in the activities of Fe(II)–X and –Y catalysts is discussed.

Since some transition metal ions are easily reduced by hydrogen and hydrocarbons and re-oxidized by oxygen, transition metal ion zeolites are inherently active for the oxidation of hydrocarbons. Some papers have recently been published on catalysis by the transition metal ions loaded on zeolites. They include studies by Van Sickle and Prest,[1] Mochida,[2] and others.[3–9]

Furthermore, fundamental studies of the transition metal ions on zeolite were published by Delgass *et al.*,[10] Garten and Boudart[11] and Ward.[12] Boudart has studied the reversible oxidation and reduction of iron supported on zeolite (Y-type faujasite and mordenite) by Mössbauer spectroscopy, demonstrating that Fe(II)–Y(or M) is converted into Fe(III) in oxygen at 400 °C and the Fe(III) is then reduced to Fe(II) by hydrogenation at 400 °C. In this case, the net oxygen adsorption due to the ion corresponded to an oxygen atom to iron ratio of 0.5.

From an interest in the catalysis of adsorbed oxygen on metal ions on zeolite, we prepared zeolite catalysts by replacing the original sodium ions with transition metal ions in their defined valence states, and used them to investigate the chemisorption of oxygen and activity for oxidation of carbon monoxide.

Experimental

Catalyst Preparation. The zeolites used in this study were 13X and 13Y type Linde Molecular Sieves. Catalysts were prepared by the exchange of sodium ions of the zeolite with transition metal ions, Cr(II), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(I), Cu(II), and Tl(I). The ion exchange with the transition metal ions in a higher valence state, namely Cu(II), Cr(III), and Ni(II), was carried out in atmosphere. On the other hand, the transition metal ions in a lower valence state, Co(II), Tl(I), Mn(II), and Fe(II), were incorporated into the zeolites by ion exchange in nitrogen stream following the procedure employed by Delgass *et al.* to prepare ferrous Y zeolite.[13]

Since chromous salts are unstable in oxidative atmosphere, Cr(II)-zeolites were prepared by ion exchange with the freshly prepared chromous chloride from chromic chloride[14] in nitrogen stream. Cu(I)-zeolites were prepared by ion exchange with cuprous iodide in liquefied ammonia according to the procedure by Reimlinger *et al.*[15]

After ion exchange, the transition metal ion zeolite were filtered and washed thoroughly with water. The zeolite was dried at 110 °C and compressed into a tablet under 300 kg/cm², and then crushed into 10—20 mesh. The cuprous zeolite was degassed at 400 °C for 3 hr under 10^{-3} mmHg to remove ammonia from the cuprous ammine complex ion before the catalytic activity test. The contents of the transition metal ion in the zeolites were determined, after ion exchange, by titration of the metal ion remaining in the filtrate with EDTA solution.

Oxygen Chemisorption. The oxygen chemisorption measurements were carried out on samples (2—3 g) of dehydrated zeolites using a conventional volumetric adsorption apparatus. The ion exchanged zeolite was admitted into the vessel and evacuated at 400 °C for 3 hr under 10^{-4} mmHg to remove the adsorbed water and gases. The zeolites prepared by ion exchange with transition metal ion in a lower valence state were further reduced in hydrogen at 400 °C and evacuated again at 400 °C for 3 hr under 10^{-4} mmHg.[13] After reduction, oxygen chemisorption on the transition metal ion in the zeolites was measured at 400 °C. The zeolites with the

1) D. E. Van Sickle and M. S. Prest, *J. Catal.*, **19**, 209 (1970).
2) I. Mochida, S. Hayata, A. Kato, and T. Seiyama, *ibid.*, **23**, 31 (1971).
3) T. Kubo, F. Kumada, H. Tominaga, and T. Kunugi, *Nippon Kagaku Kaishi*, **1972**, 1621.
4) J. Rouchand, P. Mulkey, and J. Fripiat, *Chem. Abstr.*, **70**, 77521y (1969).
5) J. Rouchand, L. Sondengam, and J. Fripiat, *Bull. Soc. Chim. Fr.*, **1968**, 4387.
6) D. G. Jones and N. J. Pennington, U. S., 3231134.
7) L. V. Skalkina, I. K. Kolchin, L. Ya. Ermolenko, S. A. Levina, and N. N. Mlashvich, *Kinet. Katal.* **12**, 242 (1971).
8) I. Mochida, T. Jitsumatsu, A. Kato, and T. Seiyama, This Bulletin, **44**, 2595 (1971).
9) T. Kubo, H. Tominaga, and T. Kunugi, *Nippon Kagaku Kaishi*, **1972**, 196.
10) W. N. Delgass, R. L. Garten, and M. Boudart, *J. Catal.* **18**, 90 (1970).
11) R. L. Garten and M. Boudart, *A. C. S. Preprints*, D7 (1972).
12) J. W. Ward, *J. Catal.*, **22**, 237 (1971).
13) W. N. Delgass, R. L. Garten, and M. Boudart, *J. Chem. Phys.*, **50**, 4603 (1969).
14) H. S. Booth, "Inorganic Synthesis," Vol. 1, p. 125 (1939).
15) H. K. Reimlinger, E. H. DeRuiter, and U. K. Kruerk, U.S. 3444253.

metal ions in the higher valence states were not pretreated by hydrogen to avoid proton formation.[16]

CO Oxidation. The activity test was carried out at catalyst temperatures 200—300 °C at atmospheric pressure by use of a flow reactor (17 mm in diameter) where 2 g of catalyst diluted with glass beads (2 mm in diameter) was placed. The gaseous reactants, carbon monoxide and oxygen, and the diluent nitrogen were supplied from the respective cylinders to the reactor. Carbon dioxide was analyzed at 80 °C by gas chromatography using a silica gel column, 2 m in length.

Results and Discussion

Oxygen Chemisorption. It was shown that Fe(II) ions on zeolite Y (or M) activated and adsorbed oxygen dissociatively, Fe(II) being oxidized to Fe(III) at 400 °C.[10,11] We have found that Fe(II) ions on zeolite seem to be more easily oxidized by molecular oxygen in the presence of water. This is suggested by the change in color of Fe(II) zeolite X (or Y) from pale green to brown when the ion exchanged zeolite was washed with water in the atmosphere at room temperature. The catalysis of the activated O^{2-} on this zeolite is of particular interest, since the electronic structure and hence the reactivity of these Fe(III) and O^{2-} might differ from those in the lattice of iron oxides.

The transition metal ions with high oxidation potential such as Cu(I), Cr(II), Tl(I), Co(II), are supposed to exhibit a similar catalytic behavior to that of Fe(II) ions. Cu(I) and Cr(II) ion on zeolites were presumed to be oxidized in the atmosphere from the change of color in filtrating and washing procedures after ion exchange. However, no color change was observed in the zeolites incorporated with Tl(I) and Co(II).

The oxygen chemisorption data are shown in Tables 1 and 2. No oxygen was chemisorbed on either X or Y type Na^+. Accordingly, any oxygen chemisorption on the zeolites loaded with transition metal ions was attributed to the presence of metal ions. The amount of oxygen chemisorption on Co(II), Mn(II), or Tl(I) of both types was less than the other zeolite loaded with Fe(II), Cu(I), or Cr(II). All the latter transition metal ions are in their lower valence state in the ion exchange. The results are in line with the relative ease of oxidation predicted from the levels of oxidation potentials of the metal ions. On Fe(II), Cu(I), or Cr(II) zeolites of both X and Y type, oxygen chemisorption due to the metal ions gave an oxygen atom to metal ion ratio 0.430—0.618, which is not far from 0.5 observed for Fe(II)–Y(or M).[10,11] This may permit the supposition that the oxygen chemisorption in a bridged form like M^{n+1}–O^{2}–M^{n+1} applies for Cu(I) and Cr(II) as for Fe(II).

As shown in Table 2, the oxygen chemisorption on Fe(II) is affected by the degree of ion exchanged for the original sodium ion with Fe(II), namely the ratio of oxygen atom to Fe(II) approaches 0.5 with a rise in the ion exchange degree. An exceedingly high dispersion of Fe(II) in low concentration on zeolite might not be favorable for the formation of the bridged oxygen atom such as Fe(III)–O^{2-}–Fe(III) due to more frequent occurrences of an unduly long distance from neighbouring Fe(II) ions in zeolite.

Table 1. Oxygen chemisorption on the transition metal ion in the Y type zeolite at 400 °C and at 100 mmHg

Zeolite	Na(I) exchanged (%)	Oxygen chemisorbed, 10^{-4} mol/g-cat.	Oxygen atom to metal ion ratio
Na(I)	0	0.00	0.000
Co(II)[a]	48	0.53	0.106
Tl(I)[a]	54	0.07	0.006
Fe(II)[a]	36	1.89	0.500
Cu(I)[a]	34	3.12	0.436
Cr(II)[a]	34	1.52	0.430
Cu(II)	54	0.00	0.000
Cr(III)	38	3.54	0.795
Mn(II)[a]	40	0.70	0.100
Ni(II)	39	0.00	0.000

a) Employed for its catalytic activity for oxidation of carbon monoxide.

Table 2. Oxygen chemisorption on the transition metal ion in the X type zeolite at 400 °C and at 100 mmHg

Zeolite	Na(I) exchanged (%)	Oxygen chemisorbed, 10^{-4} mol/g-cat	Oxygen atom to metal ion ratio
Na(I)	0	0.00	0.000
Co(II)[a]	41	0.07	0.013
Tl(I)[a]	26	0.00	0.000
Fe(II)	12	0.76	0.360
Fe(II)	35	3.00	0.488
Fe(II)[a]	42	3.62	0.490
Cu(I)[a]	18	3.86	0.618
Cr(II)[a]	28	2.33	0.474

a) Employed for its catalytic activity for oxidation of carbon monoxide.

Among the Y zeolites prepared by ion exchange with the transition metal ions in higher valence states (Table 1), oxygen chemisorptions were negligibly small for Cu(II) and Ni(II) whose valences are energetically difficult to enlarge. However, for Mn(II) whose valence can step up to a higher state, a slight oxygen chemisorption was observed.

CO Oxidation. The activities of catalysts for CO oxidation, tested under given conditions for 4 hr, were confirmed to be fairly constant for the duration of the experiment except for Fe(II)–Y catalyst which showed a slight decrease in its initial activity within the first 40 min.

Figure 1 shows the relative activity of transition metal ions, expressed by conversion of CO per metal ion, compared to that of Fe(II)–Y for oxidation of carbon monoxide. The standard oxidation potentials of the transition metal ions are chosen as the abscissa. The catalytic activities of the metal ions are closely related with their oxidation potentials. A very small amount of oxygen was adsorbed on Co(II), Mn(II), and Tl(I) standard oxidation potentials of which are −1.82, −1.51, and −1.25, respectively. The catalytic

16) L. Riekert, *Ber. Bunsenges. Phys. Chem.*, **73**, 331 (1969).

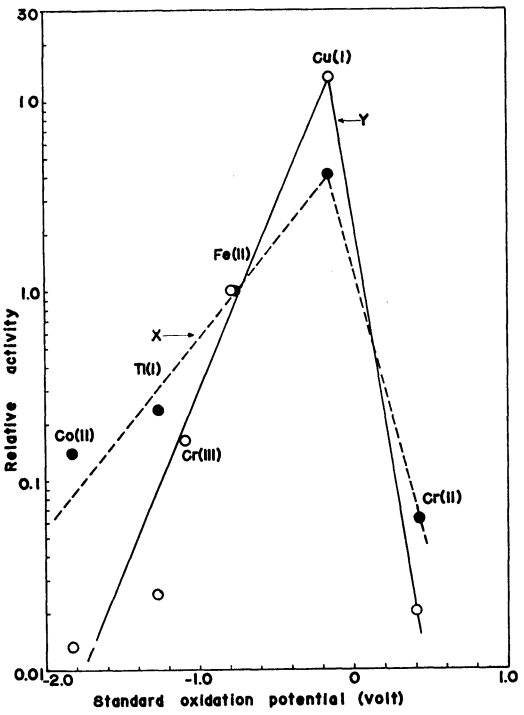


Fig. 1. Dependence of the relative activity on standard oxidation potenital.
●: X type, ○: Y type.
Conditions: P_{CO} 0.099 atm, P_{O_2} 0.179 atm, W/F 7.4 g-cat. hr/mol.
Temperature 280 °C, except for the comparison between Cu(I) and Fe(II) carried out at 200 °C.

activities of these metal ion zeolites were also lower than those of Cu(I) and Fe(II) as expected from oxygen chemisorption data.

The activities of the transition metal ions increased exponentially with the increase in their standard oxidation potential. But the X and Y zeolite ions replaced by Cr(II) showed extremely low activities for CO oxidation. Reduction of bulk α-Cr_2O_3 and chromia on silica or alumina to CrO by hydrogen or carbon monoxide is known to be difficult below 500 °C.[17] Similarly, the oxidized chromic ion Cr(III)–O^{2-}–Cr(III) on zeolite does not seem to be reduced by carbon monoxide below 300 °C.

The marked difference in catalytic activities expressed in the term (produced CO_2 mol/Fe(II)·hr) of Fe(II) on X and Y type is described in the following section. The difference was also confirmed with other transition metal ions when they were on either X or Y zeolite. The key factor which controls the catalytic activity of a given transition metal ion should be ascribed to the structure of zeolite as ligand. Because of limited data obtained on only two types of zeolite, X and Y type, the correlation between catalytic activity and the structure has not been fully established yet.

The catalytic activities of some zeolite catalysts which were exchanged with transition metal ions in a higher valence state, Cu(II), Cr(III), Ni(II), were also examined (Table 3). The oxidation activity of Cu(II)

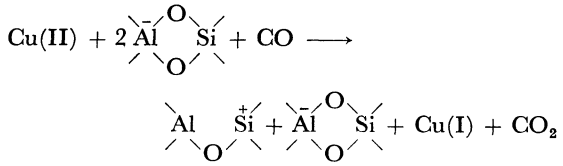
17) R. L. Burwell, Jr., G. L. Haller, K. C. Taylor, and J. F. Read, *Advan. Catal.*, **20**, 12 (1969).

Table 3. Catalytic activities of some zeolite Y catalysts for oxidation of carbon monoxide
Conditions: CO partial pressure 0.099 atm, O_2 partial pressure 0.179 atm
W/F 7.4 g-cat·hr/mol

Catalyst	Na(I) exchanged (%)	Reaction temperature (°C)	Conversion (%)
Fe(II)	36	280	17.2
Cu(I)	34	200	38.7
Cu(II)	54	200	0.8
Cr(III)	38	280	5.4
Ni(II)	39	300	0.93

and Ni(II) was much lower than that of Fe(II) and Cu(I). This is in line with the fact that oxygen is not adsorbed on Cu(II) and Ni(II) whose valences are difficult to enlarge.

A small amount of carbon monoxide was converted into carbon dioxide over Cu(II) zeolite Y, but the carbon monoxide does not seem to have reacted with oxygen activated by Cu(II) since no chemisorption of oxygen is observed (Table 1). Naccache and Taarit[18] showed that Cu(II) Y reduced by carbon monoxide gave no ESR signal of Cu(II) and that Cu(I) were detected by chemical analysis. They proposed a scheme for the reduction of Cu(II) Y by carbon monoxide as follows:



We have confirmed carbon dioxide formation when carbon monoxide was passed over the Cu(II) Y zeolite at 340 °C in the absence of oxygen. The amount of carbon dioxide produced was gradually reduced and the color of the Cu(II) Y catalyst turned from green to white. When the catalyst was allowed to stand in contact with air at room temperature its greenish color slowly reappeared.

It is not strange that Cr(III) showed a fairly good activity, because there is the possibility that heating of Cr(III) in the presence of oxygen can convert all or a part of it into Cr(VI).

Kinetics of CO Oxidation over Fe(II) Zeolite Catalysts. Some kinetic experiments have been made on the oxidation of carbon monoxide over Fe(II)–X and Fe(II)–Y catalysts, their degrees of sodium ion exchange being 42 and 36%, respectively. Experiments were carried out to study the difference in their activities quantitatively as a function of temperatu re (Fig.2). Dependence of the rate on carbon monoxide pressure was found to be nearly unity for both catalysts, while that on oxygen pressure was fractional, approximately 0.1 and 0.4 for Fe(II)–X and Fe(II)–Y, respectively (Fig. 3). These observations, together with the fact that no CO chemisorption was found on the catalysts, lead to a hypothesis that the reaction proceeds *via* the

18) C. M. Naccache and Y. B. Taarit, *J. Catal.*, **22**, 171 (1971).

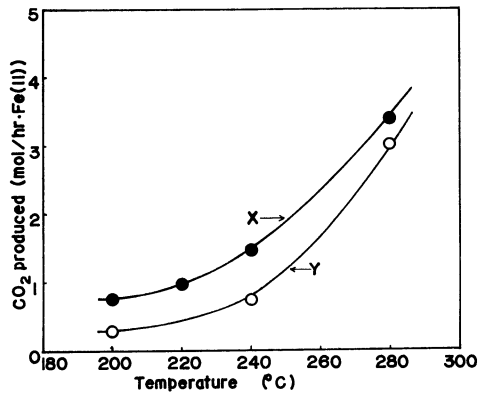


Fig. 2. Change of CO conversion against reaction temperature.
●: Fe(II)X, ○: Fe(II)Y
Conditions: P_{CO} 0.099 atm, P_{O_2} 0.179 atm
W/F 7.4 g-cat. hr/mol.

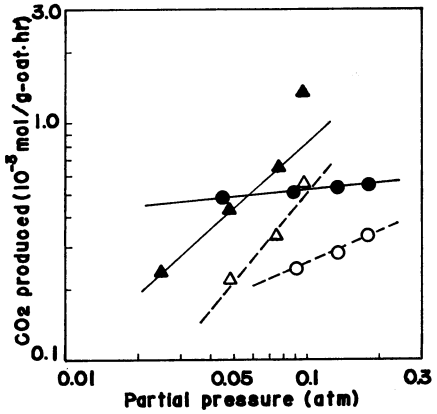


Fig. 3. Dependence of the rate on carbon monoxide and oxygen partial pressure.
Dependence on P_{CO}: ▲: Fe(II)X (220 °C), △: Fe(II)Y (240 °C) P_{O_2} 0.179 atm, W/F 7.4 g-cat. hr/mol
Dependence on P_{O_2} ●: Fe(II)X (220 °C), ○: Fe(II)Y (240 °C) P_{CO} 0.074 atm, W/F 7.4 g-cat. hr/mol

Rideal mecahnism, where carbon monoxide in the gas phase attacks oxygen which is adsorbed dissociatively on the catalysts. This is supported by the fact (Fig. 4) that the plot of reciprocal of the rate *vs.* reciprocal of the root of the oxygen partial pressure gives a straight line. Thus the following rate law holds.

$$r_{CO_2} = \frac{k\sqrt{K \cdot P_{O_2}}}{1+\sqrt{K \cdot P_{O_2}}} \cdot P_{CO}$$

By rearrangement we get

$$\frac{1}{r_{CO_2}} = \frac{1}{k\sqrt{K} \cdot P_{CO}} \cdot \frac{1}{\sqrt{P_{O_2}}} + \frac{1}{k \cdot P_{CO}}$$

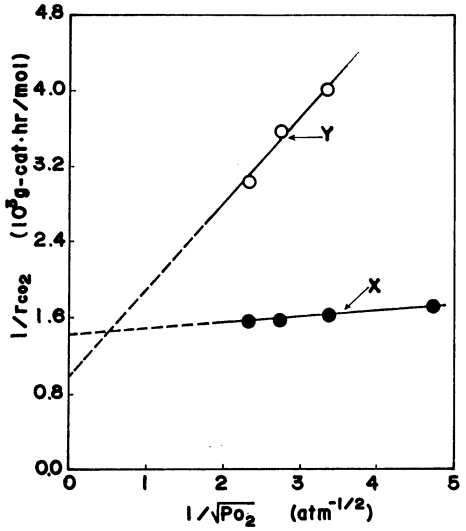


Fig. 4. Dependence of the rate on oxygen partial pressure.
●: Fe(II)X, (220 °C) ○: Fe(II)Y (240 °C)
Conditions: P_{CO} 0.074 atm, W/F 7.4 g-cat. hr/mol

The kinetic parameters obtained by a numerical analyis of the data are:

	Fe(II)X (220°C)	Fe(II)Y (240°C)
k(mol/g-cat.·hr·atm^{-1})	1.95×10^{-2}	2.73×10^{-2}
K(atm^{-1})	365	1.16

Because of the difference in reaction temperatures of the experiments for Fe(II)–X and Fe(II)–Y, comparison and interpretation of these kinetic parameters for carbon monoxide oxidation over the two catalysts would leave some ambiguities.

It might be tentatively concluded that Fe(II)–X catalyst adsorbs a larger amount of oxygen than Fe(II)–Y in their working states at temperatures 200—300 °C. This is supported by further findings on oxygen adsorption.

Skalkina *et al.*[7] reported that catalytic activity of X type zeolite incorporated with Fe(III) was higher than that of Y type for ammoxidation of propylene. Some reports suggested the difference to lie in the strength of electrostatic field near the metal ion for the corresponding X and Y types.[19,20] For carbon monoxide oxidation, the strength of electrostatic field may affect the catalytic activity.

19) P. E. Pickert, J. A. Rabo, E. Dempsey, and V. Schomaker, *Actes Congr. Intern. Catalyse.* 3, *Amsterdam*, **1964**, 714 (1965).
20) C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, **70**, 1413 (1966).