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The Activities of Manganese Nodules and Manganese–Iron Mixed Oxide for Decomposition of Isopropyl Alcohol

The vast deposits of manganese modules (Mn-nod) found on ocean floor have been noted as a valuable mineral resource of the future. Many investigations have been made on the mining and extraction of valuable metals and their genesis (*1*, *2*). Recently, several studies on the catalytic activity of Mn-nod have been also made based on the fact that Mn-nod possesses a porous structure and consists of a variety of transition metal oxides (*3–5*). However, the nature of active sites of Mn-nod is not at all clear, perhaps due to the complexity of the structure arising from the presence of many metals. Mn-nod generally contains 30 kinds of metals or more, in the form of oxides or hydroxides, although the main components are manganese and iron. If we wish to obtain some information on the nature of active sites of Mn-nod, the catalytic properties of the main components should be investigated first and then the role of minor components in them.

TABLE 1

Metal Content of Manganese Nodules

Acid-soluble part (wt%)		Acid-insoluble part (wt%)
Mn	14.00	
Fe	12.91	
Co	0.42	
Ni	0.21	18.57
Cu	0.16	
Oxygen, water and other metals	53.73	
Total	81.43	18.57

EXPERIMENTAL

The Mn-nod used was collected from the seafloor of the western Pacific Ocean (16°00.8′N, 153°50.5′E, 5590-m depth). The results of analysis of the main metal contents are shown in Table 1. Most of the acid-insoluble components are silica and alumino-silicate. Mn-nod was dried at 110°C for 10 hr after washing, crushed to 24 to 42-mesh size, and then calcined at 200 to 600°C for 4 hr in air before use.

The hydroxide and oxide of manganese and iron were prepared by precipitation from the solutions of metal chlorides and sodium hydroxide under conditions as similar as possible to sea water. The precipitates were washed and dried at 110°C for 10 hr. The prepared powdered sample was pressed, crushed to 24 to 42-mesh size, and treated in the same manner as Mn-nod. The specific surface area of the catalyst was measured by adsorption of nitrogen at liquid nitrogen temperature.

The decomposition reaction of isopropyl alcohol, which was dehydrated by molecular sieves, was chosen to test the catalytic property of the samples. The apparatus used was a conventional pulse microreactor connected to a gas chromatograph (column: PEG 1000, 3 mm [i.d.] × 4 m, and Porapak Q, 3 mm [i.d.] × 1.5 m). Dehydrated and deoxygenated helium was

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used as a carrier gas. The conversion of isopropyl alcohol at the first pulse was taken as the activity of catalyst, because the conversion decreased gradually with pulse number.

RESULTS AND DISCUSSION

The results of decomposition of isopropyl alcohol over Mn-nod calcined at 200 to 600°C are shown in Fig. 1. The reaction products were acetone, carbon dioxide, and water, but propylene was not detected. When the calcination temperature exceeds 400°C, the activity decreased though the selectivity to acetone formation increased. It is clear from this result that Mn-nod possesses the active sites on which isopropyl alcohol is dehydrogenated and oxidized. The surface area of Mn-nod was considerably large, 300 m^2/g, when calcined at 200 to 300°C, and it is comparable to a commercial alumina or silica–alumina.

The results of the catalytic properties of manganese and iron oxides prepared are shown in Fig. 2. In the case of manganese oxide, the reaction products were the same as for Mn-nod. On the other hand, in the case of iron oxide the products included propylene instead of carbon dioxide. This suggests that manganese plays a more important role than iron in the catalytic action of Mn-nod. These single metal oxides have a surface area much smaller than that of Mn-nod: That is, the largest values for manganese oxide and iron oxide were about one-eighth and one-fifth of that for Mn-nod, respectively. However, the difference in surface area may not explain the difference in their activities.

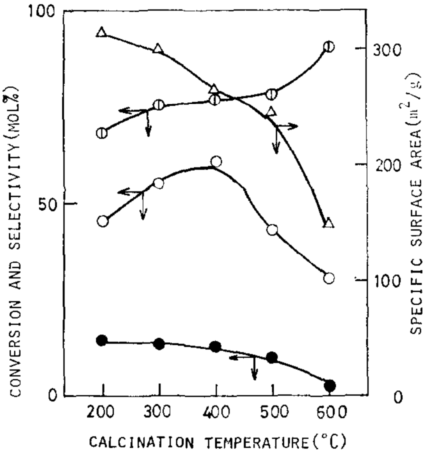

FIG. 1. Catalytic activity and surface area of Mn-nod. ○, conversion of isopropyl alcohol; ●, conversion of IPA to carbon dioxide; ⦶, selectivity to acetone; Δ, surface area. Catalyst weight 20 mg; He flow rate, 60 ml/min.

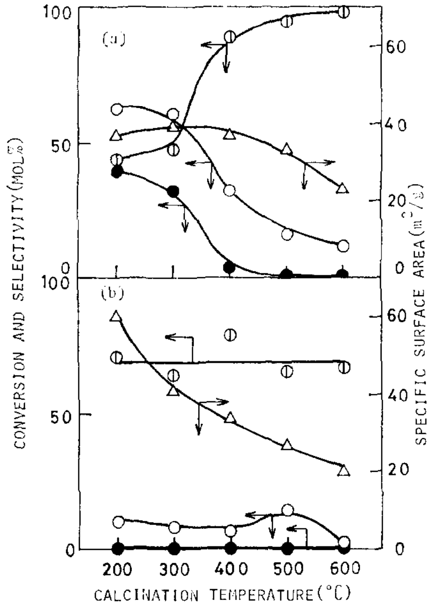

FIG. 2. Catalytic activity and surface area of manganese and iron oxides: (a) manganese oxide; (b) iron oxide. Symbols are the same as in Fig. 1.

When manganese and iron were coprecipitated as mixed oxides with the same atomic ratio (Fe/[Mn + Fe] = 0.5) as that of Mn-nod, the mixed oxides showed a larger activity and surface area than each single metal oxide (Table 2). The reaction products for the mixed oxide catalyst showed the same distribution pattern as Mn-nod and manganese oxide, not iron oxide. The high activity of the mixed oxide is closer to that of Mn-nod. The increase in surface area of the mixed oxide, compared to single metal oxide, is based on an interaction between manganese oxide and iron oxide. In order to confirm this estimation, X-ray powder diffraction patterns of the oxides were determined. The mixed oxide was amorphous, even when calcined at 400°C, while the patterns of manganese oxide and iron oxide showed the presence of γ-Mn_2O_3 and/or Mn_3O_4 and α-Fe_2O_3, respectively. This indicates that the mixed oxide is prevented from crystallization by alternate bonding between manganese and iron oxide particles during the formation of precipitate. Also Mn-nod may be such a precipitate because of its amorphous structure.

It is also important to know the role of minor metal components, contained perhaps as oxides, in the catalytic properties of Mn-nod. The effects of addition of small amounts of cobalt, copper, and nickel oxides to manganese and iron oxides on their catalytic activities and surface areas were investigated. The results are shown in Table 2. The addition of minor metals to iron oxide had a considerable influence on both the surface area and activity per weight, although their addition, except for Ni, to manganese oxide resulted in hardly any change. In all cases of iron–minor metal mixed oxides, the catalytic products were very different from those of Mn-nod and manganese oxide, as has been expected.

Of all the prepared catalysts, the mixed oxide containing most of the major metals (Mn, Fe, Co, Ni, Cu, Si, and Al) had an activity most like that of Mn-nod, a larger surface area, and the same distribution pattern of products as Mn-nod. Figure 3 shows change in surface area and catalytic activity of the mixed oxide with calcination temperatures. The curves are almost the same as those of Mn-nod in Fig. 1. From the results in Fig. 3 and Table 2, it can be said that the mixed oxide prepared by coprecipitation of manganese, iron, and

TABLE 2

Effect of Adding Transition Metals to Manganese and Iron Oxide on Activity and Surface Area

Catalyst[a]	Specific surface area (m^2/g)	Conversion of IPA			
		Total		To carbon dioxide	
		(mol%)	(mol%/m^2)	(mol%)	(mol%/m^2)
Mn	31	32.1	52	3.5	5.6
Mn–Co	25	29.3	59	3.1	6.2
Mn–Ni	63	46.6	37	8.7	6.9
Mn–Cu	35	33.0	47	4.3	6.1
Fe	34	6.1	9.0	1.0[b]	1.5[b]
Fe–Co	204	29.2	7.2	6.6[b]	1.6[b]
Fe–Ni	174	39.6	11	3.3[b]	0.95[b]
Fe–Cu	180	44.5	12	2.4[b]	0.67[b]
Mn–Fe[c]	134	59.8	22	11.9	4.4
Mn–Fe–Co–Ni–Cu[d]	259	85.6	17	31.3	6.0
Mn–Fe–Co–Ni–Cu–Si–Al[e]	280	41.0	7.0	5.7	1.0
Mn–nod	263	61.0	12	13.1	2.5

[a] Calcined at 400°C for 4 hr. Mn(or Fe):M = 1:0.1

[b] This value is for conversion not to carbon dioxide but to propylene.

[c] Mn:Fe = 1:1.

[d] Mn:Fe:Co:Ni:Cu = 1:1:0.1:0.1:0.1.

[e] Mn:Fe:Co:Ni:Cu:Si:Al = 1:1:0.02:0.02:0.02:0.1:0.1.

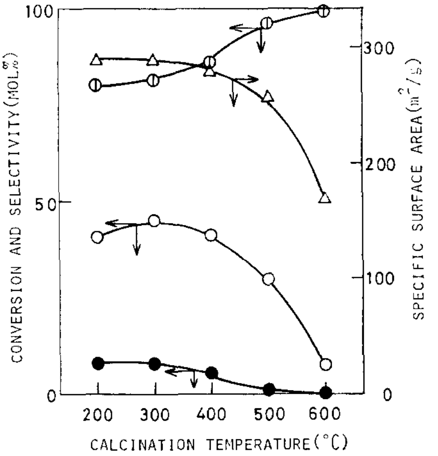

FIG. 3. Catalytic acitivity and surface area of mixed oxide of Mn:Fe:Co:Cu:Ni:Si:Al = 1:1:0.02:0.02:0.02:0.1:0.1. Symbols are the same as in Fig. 1. Catalyst weight, 20 mg; He flow rate, 60 ml/min.

other component metals represents well the characteristics of the active centers of Mn-nod. In other words, this catalyst may be called "synthetic Mn-nod."

Isopopyl alcohol is converted to carbon dioxide and water by oxidation on the catalysts containing manganese. There is, however, no oxygen in the reactant and carrier gas. The reactive oxygen on the catalyst surface must be used in the oxidation of the reactant. Such an oxygen is usually called surface excess oxygen on the catalyst. In fact, it is known that manganese oxide has large amount of surface excess oxygen (*6*). A measurement of surface excess oxygen of the mixed oxide catalysts and Mn-nod may reveal the nature of the active sites on Mn-nod. This is under investigation and will be reported a later date.

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