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CATALYTIC ACTIVITY OF MANGANESE NODULE FOR OXIDATIVE DEHYDROGENATION OF ALCOHOLS AND HYDROCARBONS

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Various kinds of alcohols and hydrocarbons except chain hydrocarbon are oxidatively dehydrogenated on manganese nodule catalyst. The catalytic activity shows no decrease for long reaction time in the presense of oxygen in the reactant. The surface excess oxygen on manganese nodule is strongly concerned in these reactions as active spieces.

Manganese nodule which is present on the ocean floors in a great abundance has been noted as a new metal resource$^{1)}$. In addition, it can be expected to utilize the nodule as catalyst for chemical reactions, because it contains many kinds of transition metal oxides and its surface area is very large, that is, 100 to 300 $m^2/g^{2)3)}$. In this report, the catalytic activity of the nodule was investigated on dehydrogenation reactions of alcohols and hydrocarbons which were important in petrochemical industry. It was found that the nodule showed high catalytic activity for these reactions. The catalytic active sites on the nodule were also discussed.

Manganese nodule used in this work was collected from the sea-floor of the western Pacific Ocean(16°00.8'N, 153°50.5'E, 5590 m depth). The nodule, containing Mn(14.00 wt%), Fe(12.91 wt%), Co(0.42 wt%), Ni(0.21 wt%), Cu(0.16 wt), etc.$^{4)}$, was crushed to 24 to 42 mesh size after washing and then calcined in air for 4 h before use. The surface area of the nodule calcined at 400°C was 263 m^2/g. Hexane(NH), cyclohexane(CH), ethylbenzene(EB), isopropyl alcohol(IPA) and cyclohexanol(CHA) were employed for dehydrogenation reaction as representative reactants of chain hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, chain alcohols and alicyclic alcohols, respectively. All of them are commercial reagents of guaranteed grade and they were used after dehydrated by activated zeolite. The reaction was carried out in a flow reactor and a pulse microreactor. In the former, the feed gases were prepared by adding dried air to the reactant. The gases after the reaction were analysed by gas chromatography(column: PEG 1000 3 mm [i.d.] x 3 m, PEG 20M 3 mm [i.d.] x 2 m, and PORAPAK Q 3 mm [i.d.] x 1.5 m). In the latter, the reaction was carried out by use of helium as a carrier gas.

The amount of excess oxygen on the nodule surface was measured by the KI method at pH 7.5, 9.3 and 11.3[5].

Table 1 shows the conversions of alcohols and hydrocarbons and the selectivities for dehydrogenation reaction at various reaction temperatures. The conversions and selectivities were taken at the steady state in the flow reactor

Table 1 Conversion and Selectivity for Dehydrogenation of Hydrocarbon and Alcohol

Reactant and [Concentration]	Conversion(mol%) and [Selectivity(mol%)]					
	Reaction Temperature					
	200°C	250°C	300°C	350°C	400°C	500°C
IPA[a] [1.2 vol%]	23 [90]	72 [69]	84 [59]			
NH[a] [6.4 vol%]		0	0	0	10 [0]	
CH[a] [3.9 vol%]		0	12 [65]	42 [43]	72 [39]	
CHA[b] [1 μl]	9 [0]		35 [0]		85 [0]	89 [0]
EB[b] [1 μl]	6 [55]		16 [30]		64 [6]	68 [6]

a) Reaction in flow reactor, gas flow rate:60 ml/min, weight of catalyst: 200 mg, calcination temperature of catalyst:500°C.

b) Reaction in pulse reactor, gas flow rate:60 ml/min, weight of catalyst: 50 mg, calcination temperature of catalyst:500°C.

and at the first pulse in the pulse reactor. The dehydrogenation reaction of IPA, CH and NH were carried out in the flow reactor. The reaction products from IPA were acetone and water and those from CH were cyclohexene, benzene and water. In these reactions carbon dioxide was formed as the by-product, that is, deep oxidation also occurred. In the case of NH, any product except carbon dioxide and water was not detected. Dehydrogenation reactions of CHA and EB which have higher boiling points were carried out in a pulse microreactor. Although the desirable products of them are cyclohexanon and stylene respectively, deep oxidation of the reactants occurred at the initial pulse. The selectivity of the nodule for these dehydrogenation reactions increased with the pulse number; that is, the selectivity of CHA to cyclohexanon at the fifth pulse is 91% at 200°C and 68% at 300°C, though 0% at the first pulse at both temperatures. If these reactions are carried out in the flow system using air, the value of selectivities of CHA and EB in Table 1 are expected to become higher, since the selectivity of IPA in the first reaction for the deep oxidation was much higher than that of the flow reactor and after the tenth pulses the deep oxidation of IPA hardly occurred by addition of oxygen gas to the nodule catalyst, though the dehydrogenation occurred$^{3)}$.

The fact that the oxidative dehydrogenation occurs when oxygen is not present in a feed gas leads us to the conclusion that the oxygen used for the reaction is one on the surface of the nodule. In order to get information of the property of such oxygen, the amount of excess oxygen on the nodule surface was measured. The relation between the amount of surface excess oxygen and the catalytic activity was investigated and the results are shown in Fig.1. On the surface of the nodule calcined above 500°C, the oxygen having high oxidation power, which is measured in a solution buffered at pH 11.3, is hardly present. It is also clear from Fig.1 that the oxygen having higher oxidation power induces deep oxidation of reactants and that one having lower oxidation power does oxidative dehydrogenation, because the selectivity for dehydrogenation of IPA was higher on the catalyst calcined at higher temperature. The catalytic activity of the nodule for oxidative dehydrogenation of IPA was kept constant for more than 140 h. This indicates that the surface excess oxygen on the nodule is easily regenerated by oxygen in the feed gas.

The temperature at which reaction occurs elevated in the order of pKa value of the reactants, that is, the value of pKa is 18 for IPA, 45 for CH and >45 for NH. This may suggest that on the surface of the nodule the reactants were dissociated into H^+ and R^- or RO^-.

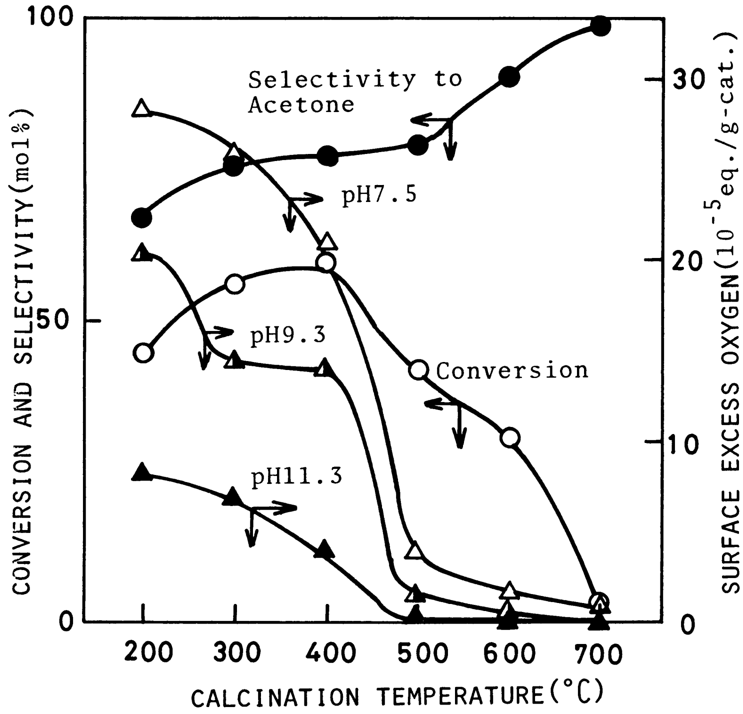

Fig.1 Change in Catalytic Activity$^{a)}$ for Dehydrogenation of Isopropyl Alcohol and Surface Excess Oxygen with Calcination Temperature

a) Reaction in pulse reactor at 200°C, helium flow rate:60 ml/min, weight of catalyst:20 mg, injected amount of one pulse:1 μl.

References and Notes

1) J. L. Mero, "The Mineral Resources of The Sea," Elsevier, New York, (1965).
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3) K. Matsuo, M. Nitta, K. Aomura, J. Japan Petrol. Inst., 19, 745(1976).
4) In general, manganese nodule contains more than thirty kinds of metals, but in this experiment only main metals were analysed.
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