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CATALYTIC ACTIVITY OF THE LIQUID Na-Pb ALLOY SYSTEM

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The liquid Na-Pb alloy system has been found to catalyze the dehydrogenation of several alkylbenzenes, i.e. ethylbenzene, cumene, and p-cymene. It has also been found that the alloy catalyzes the dehydrogenation of tetralin. In every reactions, the selectivity has been found to be satisfactorily high.

The use of liquid sodium as a catalyst seems to be interesting, but the strong reactivity of this metal hinders the experimental work especially at high temperature where the metal is in a liquid state. In this connection it seems promising to use any stable alloy containing sodium as a component. According to literature[1-6] a commercial Na-Pb (1 : 1) alloy which is called " Drynap " has frequently been used as a mild reducing agent in place of sodium for a reduction of organic substances. Thus the present authors have attempted to test the catalytic activity of the liquid Na-Pb alloy system.

Since the experimental method is essentially the same as that reported in the previous papers[7,8], only important points are described below.

1) Catalyst; The Na-Pb (1 : 1) alloy was obtained commercially (Wako Pure Chemical Industries, Ltd.). Alloys of lower sodium contents were made by mixing the 1 : 1 alloy with lead (99.99 %) in the reactor (Pyrex glass; bubbling type[8,9]).

2) Reactants; Ethylbenzene, cumene and p-cymene each was purified by a vacuum distillation prior to the activity measurement.

3) Pretreatment of catalyst; Under a streaming of purified helium through the reactor, the temperature was gradually raised to melt the catalyst alloy. In order to remove oily contaminants contained in the commercial Na-Pb alloy, the streaming of helium was continued for about 1 hr after the melting of the alloy.

Experimental results are shown in Figs. 1 - 4. It can be seen in Fig. 1 that ethylbenzene was effectively dehydrogenated to styren with sufficiently high selectivity[*1]. Pure lead was almost inactive and the catalytic activity was found to depend on the sodium content in the liquid alloy. Both the dehydrogenation of cumene[*2] and the dehydrogenation of p-cymene[*3] were also catalyzed by the liquid alloy (Fig. 2). The conversions and the selectivities for these reactions were satisfactorily high. Moreover, as can be seen in Fig. 3, the activity of the liquid Na-Pb alloy was stable[*4]. It appears worth reporting that the liquid Na-Pb alloy catalyzed the dehydrogenation of tetralin[*5](Fig. 4).

It must be noted here that the catalytic activity found in the present work,

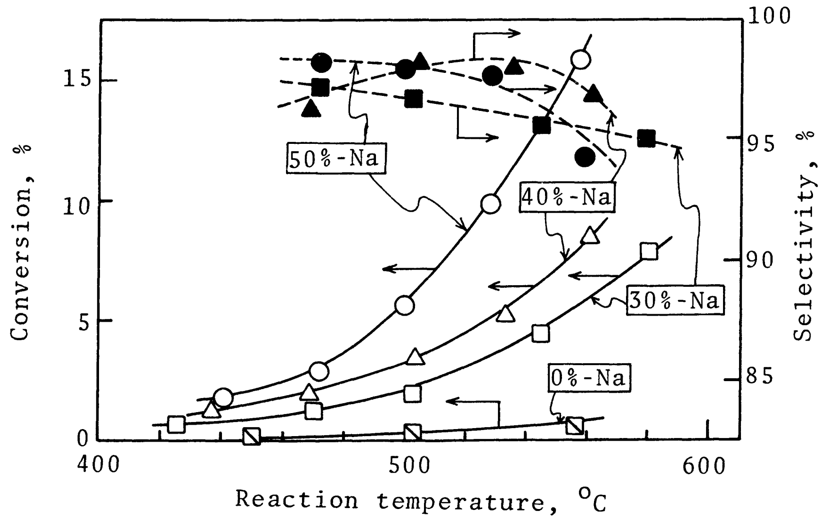

Fig. 1
Catalytic activity of liquid Na-Pb alloy for the dehydrogenation of ethylbenzene; feed rate = 0.044 mol/hr, carrier gas = He 0.054 mol/hr, catalyst wt. = 70g.

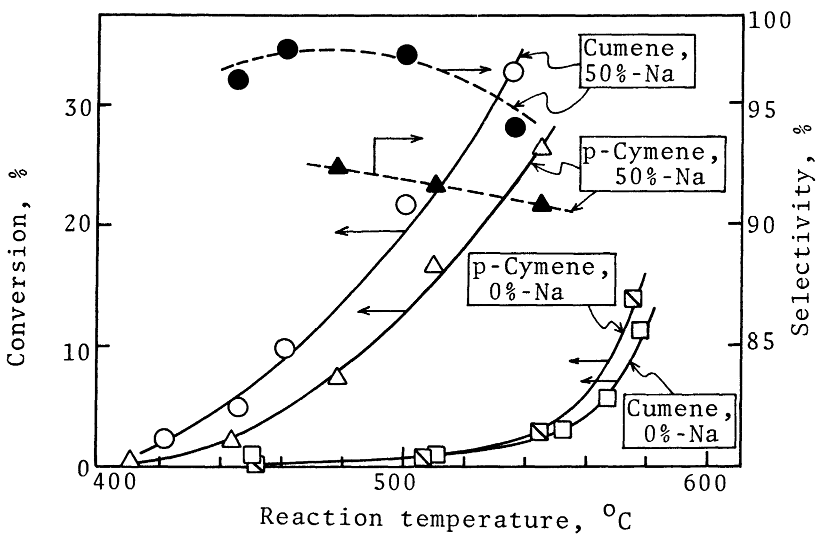

Fig. 2
Catalytic activities of liquid Na-Pb alloy for the dehydrogenation of cumene and of p-cymene; feed rate of cumene = 0.038 mol/hr, feed rate of p-cymene = 0.034 mol/hr, carrier gas = He 0.054 mol/hr, catalyst wt. = 70g.

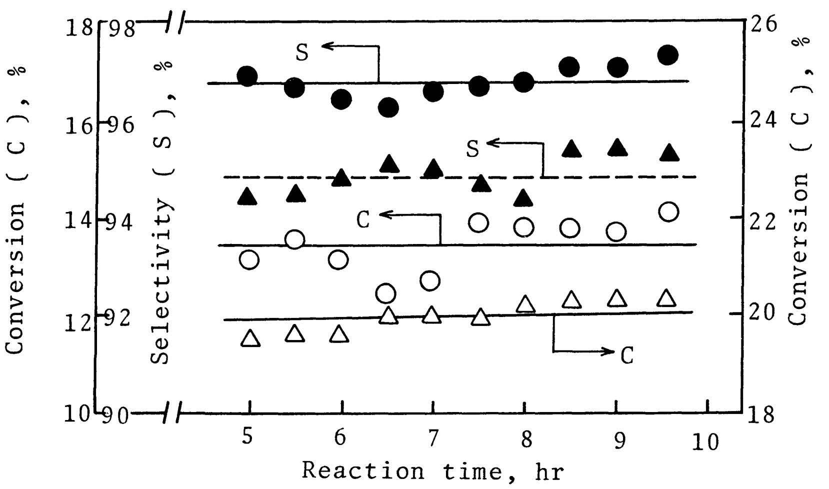

Fig. 3
Catalytic activities of liquid Na-Pb (50%-Na) alloy as a function of reaction time (○, ● ~ ethylbenzene, feed rate = 0.031 mol/hr, temperature = 523 °C; △, ▲ ~ cumene, feed rate = 0.038 mol/hr, temperature = 516 °C), catalyst wt. = 70g.

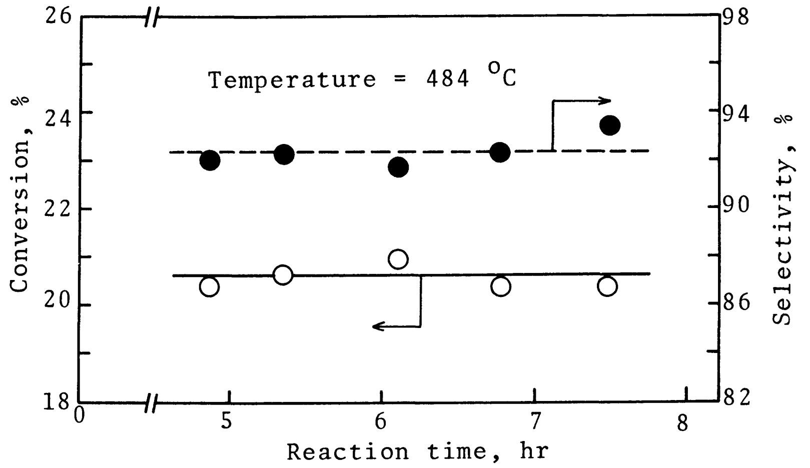

Fig. 4
Catalytic activity of liquid Na-Pb (50%-Na) alloy for the dehydrogenation of tetralin;
feed rate = 0.059 mol/hr, carrier gas = He 0.054 mol/hr, catalyst wt. = 70g.

i.e. the activity of the " liquid Na-Pb alloy ", is an overall activity which presumably includes the activity of the sodium vapor. In order to estimate the activity of the sodium vapor and to determine the extent of the contribution from the surface catalysis, further works are necessary. Nevertheless the characteristic activity of the Na-Pb alloy liquid seems to be worth reporting. The most unique point in the catalysis of the liquid Na-Pb alloy system is its special ability to dehydrogenate selectively the side chain in the alkylbenzene molecule. Liquid tellurium had been found[9] to catalyze the dehydrogenation of certain polynuclear hydrocarbons, but its activity to dehydrogenate alkylbenzenes had been poor. Other liquid metals such as In, Tl, Ga, Al and Zn had been reported to be active only for the dehydrogenation of alcohols or of amines[7,8,10] and not active for the reaction of hydrocarbons. Thus it can be said that the finding of the catalytic activity of the liquid Na-Pb alloy system may open a new field of the catalysis of the liquid metal or of the liquid alloy.

References and Notes

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*1 The selectivity was defined as follows:
Selectivity = C_{st} /(C_{st} + C_{bp}), where C_{st} is the concentration of styrene in the

products and C_{bp} is the total concentration of byproducts in the products. According to the gaschromatographic analysis, the byproducts were mainly benzene and toluene.

*2 The byproducts were benzene, toluene, ethylbenzene and styrene.

*3 The byproducts were benzene, toluene, p-xylene, cumene, p-ethyltoluene and p-methyltoluene.

*4 Although data for p-cymene were not given in Fig. 3, the activity for this reaction was found to be stable at least for 7 hr.

*5 Similar to the results for the liquid Te catalyst and for the liquid Te-Se catalyst, naphthalene and 1,2-dihydronaphthalene were formed. However, the formation of 1,2-dihydronaphthalene over the Na-Pb catalyst was very small even at a temperature where the formation of this compound over the Te (or Te-Se) catalyst was significant.

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