

LIQUID TELLURIUM AS A CATALYST FOR THE DEHYDROGENATION OF  
SEVERAL POLYNUCLEAR HYDROCARBONS

Katsumi TAKAHASHI and Yoshisada OGINO

Department of Chemical Engineering, Faculty of Engineering,  
Tohoku University, Aramaki Aoba, Sendai 980

Liquid tellurium has been found to catalyze selectively the dehydrogenation of certain polynuclear hydrocarbons, i.e. tetralin, indane, acenaphthene, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene.

Although much information about the dehydrogenation of alcohols over the liquid metal catalysts has been accumulated by the present authors and their co-workers<sup>1)</sup>, little information about the catalyses of liquid metals or semimetals for the reactions of hydrocarbons has been accumulated. The majority of those liquid metals which catalyze the dehydrogenation of alcohols had been found to be inactive for the reactions of hydrocarbons. However, the research has entered into a new-stage at the present work in which liquid tellurium (a liquid semimetal) has been found to catalyze the dehydrogenation of several polynuclear hydrocarbons. The purpose of this letter is to describe the experimental results.

The activity measurements were carried out in a flow apparatus equipped with a bubbling type reactor<sup>2)</sup>. The reactant was supplied from a microfeeder into the reaction system and was mixed with helium streaming in the reaction system at a rate of 0.057 mol/hr. Then the mixture of helium and the reactant vapor was forced to bubble into the catalyst liquid maintained at a reaction temperature. The effluent from the reactor was cooled and the liquid products were separated from gaseous products. The products were analyzed by gaschromatography (for liquids: HITACHI-163, column = PEG20M-2m, temperature = 180 - 220 °C, carrier = He-30 ml/min, detector = FID; for gases: YANACO-G-800, column = activated carbon-2m, temperature = 100 °C, carrier = He-20 ml/min, detector = TCD). When the reactant and/or product were in solid states at room temperature, they were dissolved in benzene before the reaction and/or analysis. Materials (catalysts and reagents) of the highest quality were used in this work. They were obtained commercially.

The experimental results for the tetralin dehydrogenation are shown in Fig. 1, where the total conversion of tetralin to 1,2-dihydronaphthalene and naphthalene is shown as a function of the reaction temperature. A superior catalytic activity of liquid tellurium is evident in this figure. Although liquid zinc showed activity comparable to that of liquid tellurium at high temperatures, its activities at low temperatures were poor. Liquid lead and liquid cadmium were only slightly active at high temperatures. Liquid bismuth, liquid indium and liquid tin

were inactive, i.e. these liquid metals gave approximately the same conversions as those obtained in the thermal decomposition.

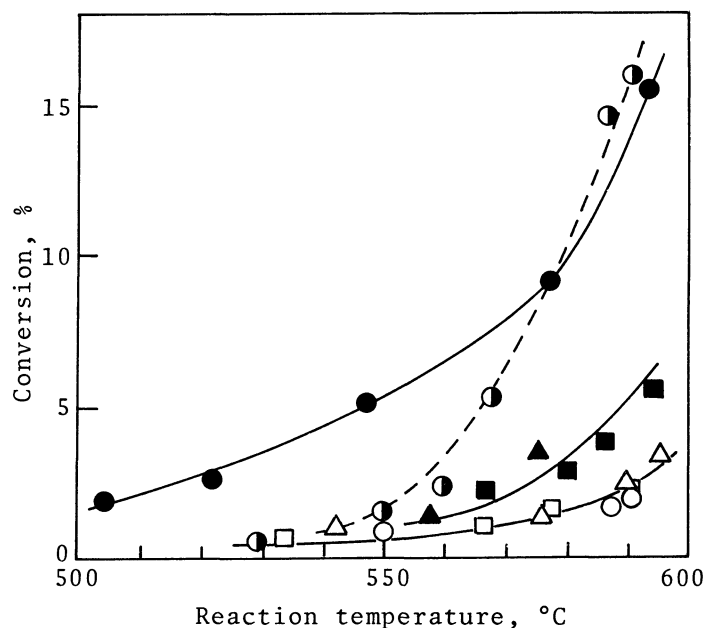









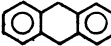
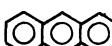
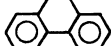
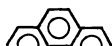

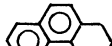
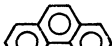
Fig. 1 Results of dehydrogenation reaction over several liquid state catalysts (● Te, ◐ Zn, ▲ Pb, ■ Cd, △ Bi, □ In, ○ Sn).

The dehydrogenation of tetralin is considered to be a consecutive reaction in which 1,2-dihydronaphthalene is a primary product and naphthalene is a secondary product. In the reaction over the liquid tellurium catalyst (over the liquid zinc as well), the formation of 1,2-dihydronaphthalene was predominant at low temperatures while the formation of naphthalene was predominant at high temperatures. Both of these compounds can be considered to be the dehydrogenation products, and hence the total conversion to these compounds was taken as the basis to evaluate the selectivity. In the reaction over the liquid tellurium catalyst, the selectivity was found to be satisfactory at high temperature where the conversion was considerable, i.e. 96 % (593 °C, 15.4 % conversion). Additional information about the catalytic activity of liquid tellurium is given under the other items in Table 1.

The experimental data which demonstrate the catalytic activity of liquid tellurium for the reaction of hydrocarbons other than tetralin are also given in Table 1. It is obvious from these data that liquid tellurium is active at least for the dehydrogenation of polynuclear hydrocarbons listed in the table. It must be noted that the selectivities were fairly good at high temperatures where the conversions were considerable.

In connection with the utilization of coal and coal extract, reactions of polynuclear hydrocarbons, especially hydrocracking, have been the objects of intensive studies. Certain molten salts have been reported<sup>3,4)</sup> to be effective for the hydrocracking. However, no successful use of the molten metal catalyst (or the molten semimetal catalyst) has been reported. Thus the present finding is valuable and probably contribute to the advances in the chemistry of catalysis required to treat the raw materials containing a wide variety of polynuclear hydrocarbons.

Table 1. Results of Reaction of Polynuclear Hydrocarbons on Liquid State Catalysts

Catalyst	Reactant (mol/hr)	Solvent (mol/hr)	Reaction temperature ( °C )	Total conversion ( % )	Selectivity ( % ) to individual product			total
Te, 70g			593	15.4	24	72	96	
			578	9.0	36	39	75	
Zn, 70g			590	17.1	36	45	81	
			568	5.3	44	20	64	
Cd, 70g	 (0.039)	—	594	5.4	 55	 18	73	
Pb, 70g			576	3.4	49	21	70	
Bi, 70g			596	3.3	38	34	72	
In, 70g			591	2.4	51	18	69	
Sn, 70g			591	1.9	44	21	65	
	 (0.041)	—	574	9.4	 90		90	
	 (0.0033)	Benzene (0.06)	571	3.9	 88		88	
	 (0.0031)	"	586	20.4	 ~99		~99	
	 (0.0027)	Benzene (0.05)	581	17.8	 79		79	
Te, 70g	 (0.0025)	Benzene (0.05)	588	18.2	 70	 13	83	

## References and Notes

- 1) Eleven papers on this article have been published, the last one of them is A. Miyamoto and Y. Ogino, J. Catal., 43, 143 (1976).
- 2) K. Kashiwadata, Y. Saito, A. Miyamoto and Y. Ogino, Bull. Chem. Soc. Japan, 44, 3004 (1971).
- 3) N. Choudhary and D. N. Saraf, Ind. Eng. Chem., Prod. Res. Dev., 14, 74 (1975).
- 4) Y. Nakatsuji, S. Fujioka, M. Nomura, and S. Kikkawa, Bull. Chem. Soc. Japan, 50, 3406 (1977).

(Received February 20, 1978)