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PROMOTING EFFECT OF SELENIUM ON THE CATALYSIS OF LIQUID TELLURIUM IN THE DEHYDROGENATION OF POLYNUCLEAR HYDROCARBONS

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An addition of small amount of selenium into the liquid tellurium has been found to bring about a pronounced elevation of the catalytic activity for the dehydrogenation of polynuclear hydrocarbons, i. e. tetralin, acenaphthene, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene.

With the purpose of finding a substance capable of promoting the activity of liquid tellurium catalyst for the dehydrogenation of polynuclear hydrocarbons, catalytic activities of various binary liquid alloys containing tellurium have been examined. The experimental result has shown that the promoting action of selenium is outstanding. The purpose of this letter is to provide the experimental data indicating the promoting action of selenium and to contribute to the advances in the chemistry of catalysis required to treat coal and coal extract[2-7].

Since the details of the experimental method had been reported on the preceding paper[1], only modified points will be described below.

1) Catalyst: The Te - Se catalyst was prepared in the following way. Namely, 70 g of granules of solid tellurium (1 - 2 mm size, 99.99 % purity) were taken in the reactor and a given amount of selenium (2 - 3 mm size, 99.999% purity) was added. Then purified helium was passed through the reactor (~ 20 ml/min) and the temperature was gradually raised to well above the melting point of the Te - Se alloy[8]. In order to ensure the complete mixing of tellurium and selenium, the streaming of helium in the reactor was continued for about 1 hr after the melting of the catalyst.

2) Protection from evolved hydrogen selenide: Since the formation of a poisonous compound containing selenium (e.g. H_2Se) was considered to be inevitable under the experimental condition, effluents from the reactor were forced to pass through a series of absorbers containing aqueous NaOH solution (1N). As illustrated in Fig. 1, condensable products (liquid products) were collected over the aqueous absorbent solution in the first absorber. Three absorbers were sufficient for the almost complete elimination of hydrogen selenide evolved during the activity test of ~20 hr.

The experimental results are summarized in Table 1. It is evident in this table that a pronounced elevation of the conversion for every reaction listed in the table has been brought about by adding selenium into the liquid tellurium catalyst. The high selectivities shown in the table have to be also pointed out.

An additional fact to be noted here is that, during the reaction, the color of the absorbent solution in the first absorber gradually turned to reddish brown. This indicates that the hydrogen selenide evolved in the reactor was oxidized to selenium in the absorbent solution. Thus there is no doubt that some reaction to form hydrogen selenide was taking place in the reactor and the concentration of selenium in the catalyst was gradually decreasing. Therefore, it is suspectable that a stoichiometric reaction between hydrocarbon and selenium (e.g. $Se + \underset{/}{C}H_2\text{-}\underset{\backslash}{C}H_2 \longrightarrow H_2Se + \underset{/}{C}H\text{=}\underset{\backslash}{C}H$) was causing the increase in the conversion.

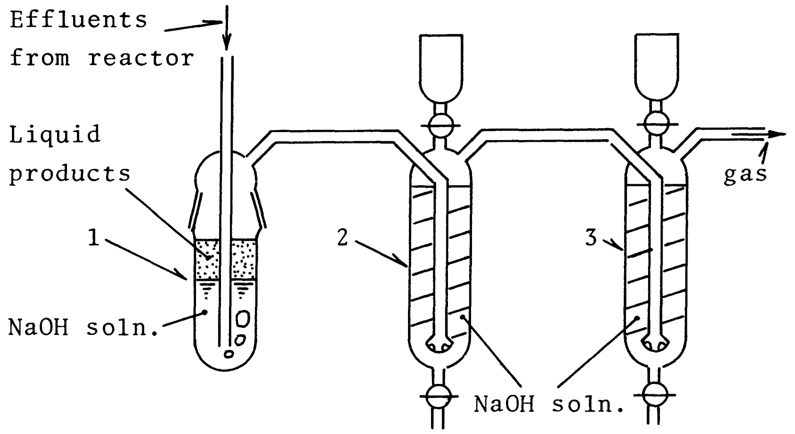


Fig. 1 Absorbers containing NaOH solution to remove H_2Se from the reaction product.

However, the suspicion disappears if we see the experimental result shown in Fig. 2. The experimental result shows that the elevation of the conversion due to the stoichiometric reaction of selenium with hydrocarbon was minor and insignificant. The high conversion was found to persist for a long time, and a little declining of the conversion was observed. Furthermore, the formation of the dehydrogenated product was found to amount well beyond the value predicted by assuming that the elevation of the conversion is due solely to the stoichiometric reaction as described above. If the observed elevation of the conversion is due to the stoichiometric hydrogen abstraction of selenium, the observed high conversion has to disappear at T_c indicated in the figure. Obviously, such is not the case with

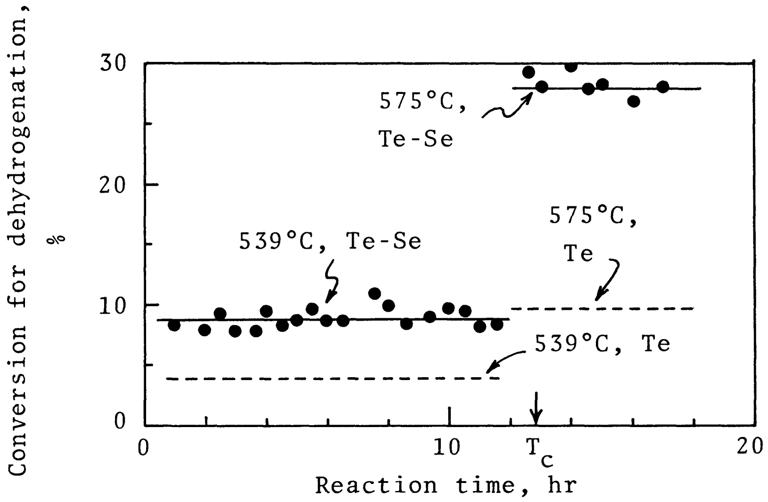
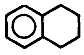
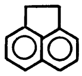
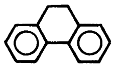
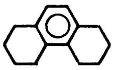
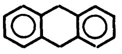
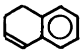


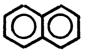
Fig. 2 The activity of the liquid Te - Se catalyst as a function of reaction time.

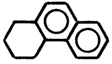
Table 1 Experimental Results Indicating the Catalytic Activity of the Liquid Te - Se Catalyst for the Dehydrogenation of Polynuclear Hydrocarbons

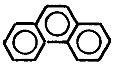
Catalyst (at% Se)	Reactant (mol/hr)	Solvent (mol/hr)	Temperature (°C)	Total conv. (%)	Selectivity (%)		
					to individual product		total
Te - Se (10)	 (0.059)		580	35.7 (10.6)[@]	11[*]	85[**]	96
			565	24.4 (8.0)	19	75	94
			550	12.6 (6.1)	34	58	92
			535	9.0 (4.5)	48	40	88
			515	5.9 (3.0)	54	26	80
Te - Se (10)	 (0.0033)	Benzene (0.06)	580	64.6 (6.0)			96
			568	50.1 (4.1)			96
			550	29.5 (1.6)			96
			535	19.2 (0.9)			97
			500	11.1 (0.5)			97
Te - Se (10)	 (0.0027)	Benzene (0.05)	580	96.7 (23.0)			99
			570	92.7 (19.8)			99
			555	81.8 (16.9)			99
			540	64.4 (14.2)			98
			520	41.4 (12.1)			95
			500	27.1 (11.3)			93
Te - Se (10)	 (0.0025)	Benzene (0.05)	580	92.4 (16.2)	22[#]	72[##]	94
			560	83.1 (10.1)	41	49	89
			545	66.3 (8.1)	49	29	88
			524	45.0 (7.2)	51	30	81
			505	34.0 (6.8)	40	26	66
Te - Se (10)	 (0.0031)	Benzene (0.06)	580	95.0 (19.0)			90
			560	92.3 (15.5)			93
			540	77.6 (12.8)			92
			520	60.9 (10.5)			95
			500	45.1 (8.2)			96

@ Conversion for the reaction over the liquid Te catalyst.

* Selectivity for 

** Selectivity for 

\# Selectivity for 

\## Selectivity for 

the present experimental result. Thus it can be said that the interference from the stoichiometric reaction was minor and the observed conversion was due mainly to the catalysis of the liquid Te - Se alloy.

References

1) K. Takahashi and Y. Ogino, Chem. Lett., 1978, 423.
2) R. F. Sullivan, C. J. Egan and G. E. Langlois, J. Catal., 3, 183 (1964).
3) C. W. Zielke, R. T. Struck, J. M. Evans, C. P. Costanza and E. Gorin, Ind. Eng. Chem., Process Des. and Develop., 5, 151 (1966).
4) W. H. Wiser, S. Singh, S. A. Qader, and G. R. Hill, Ind. Eng. Chem., Prod. Res. Develop., 9, 350 (1970).
5) S. Kikkawa, M. Nomura and K. Murase, Bull. Japan Petrol. Inst., 19, 863 (1976).
6) Y. Nakatsuji, S. Fujioka, M. Nomura and S. Kikkawa, Bull. Chem. Soc. Japan, 50, 3406 (1977).
7) Y. Nakatsuji, T. Kubo, M. Nomura and S. Kikkawa, Bull. Chem. Soc. Japan, 51, 618 (1978).
8) M. Hansen and K. Anderko, "Constitution of Binary Alloys", McGraw-Hill Book Company, New York, Toronto, London (1958), p.1188.

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