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ISOMERIZATION AND DEHYDROGENATION OF CYCLOHEXENE OVER TaS_2 AND TRANSITION METAL INTERCALATED TaS_2

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Over TaS_2 and $M_{1/3}TaS_2$ (M = Ni, Fe, and Co), cyclohexene undergoes dehydrogenation to benzene and isomerization to 1-methylcyclopentene selectively in nitrogen and hydrogen atmosphere, respectively. Considerable promoting effects on catalytic activity are exerted by the intercalation of Ni and Fe. Moreover, metal intercalation has an effect to prolong a catalyst life.

It is known that many transition metal dichalcogenides with layer structure produce so called intercalation compounds by containing bases, Lewis bases and metal atoms between layers.[1] The physical properties of these compounds have been studied extensively,[2] but little is known about their catalytic properties. In this paper, we examined the catalytic isomerization and dehydrogenation of cyclohexene over TaS_2 and its intercalation compounds $M_{1/3}TaS_2$ (M = Fe, Co, or Ni).

TaS_2 (α-Type) was synthesized by heating tantalum powder in sulfur vapor (ca. 1 atm) at 900°C in a sealed quartz tube.[3] Three intercalation compounds, $M_{1/3}TaS_2$ with M=Fe, Co, and Ni, were prepared in a similar way starting from the stoichiometric compositions of metal powder mixtures. The catalytic reaction was carried out in a pulse reactor with a fixed catalyst bed in either a hydrogen or a nitrogen flow (30 cm^3/min). Cyclohexene (2×10^{-3} cm^3) was injected as a pulse into the reactor. The products were analyzed by gas chromatography with a column of TCP (tricresyl phosphate) supported on uniport-B.

Over any catalysts examined, catalytic reaction of cyclohexene was significant at temperatures above 100°C, as illustrated in Fig. 1. Reaction products were benzene, 1-methylcyclopentene (1-MCP') and methylcyclopentane

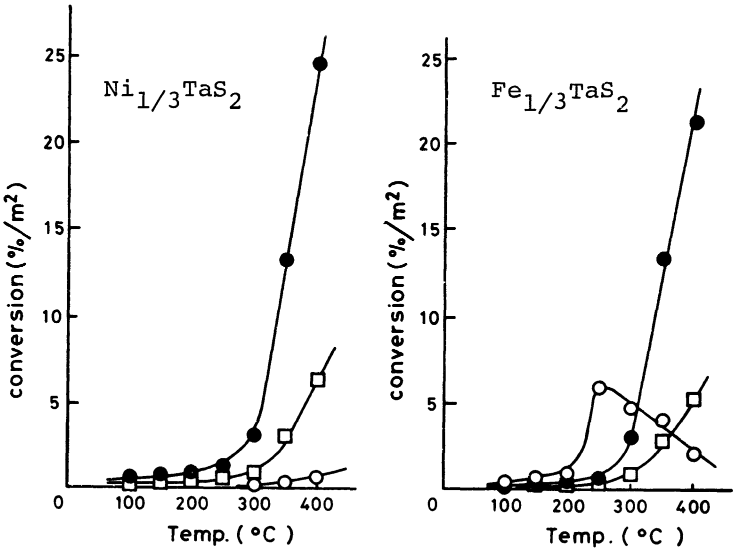

Fig. 1 Dehydrogenation and isomerization of cyclohexene in H_2 flow.
●; 1-MCP', □; MCP, ○; Benzene

(MCP). Table 1 summarizes the results over the four catalysts. In the nitrogen flow, dehydrogenation to benzene far exceeded isomerization to 1-MCP' or further hydrogenation to MCP. In the case of hydrogen carrier, the main products were 1-methylcyclopentene and methylcyclopentane at all temperatures examined except for the case of $Fe_{1/3}TaS_2$, in which the dehydrogenation of cyclohexene proceeded below ca.300°C in preference to isomerization. There were no significant differences in selectivity among the catalysts. In the catalytic activity, however, a sequence $Ni_{1/3}TaS_2 \simeq Fe_{1/3}TaS_2 > \alpha\text{-}TaS_2 > Co_{1/3}TaS_2$ was obtained in both flow at 400°C, indicating promoting effects of Ni and Fe.

Table 1. Catalytic isomerization and dehydrogenation of cyclohexene.

	Catalyst	temp(°C)	conv.(%/m^2)	selectivity*		
				MCP	1-MCP'	Benzene
N_2 flow	$Fe_{1/3}TaS_2$	400	14	2	5	93
	$Co_{1/3}TaS_2$	400	7.2	5	13	82
	$Ni_{1/3}TaS_2$	400	15	7	15	78
	$\alpha\text{-}TaS_2$	400	9.1	7	10	83
H_2 flow	$Fe_{1/3}TaS_2$	400	24.8	18	75	7
		250	5.7	6	6	91
	$Co_{1/3}TaS_2$	400	11.7	16	83	1
	$Ni_{1/3}TaS_2$	400	26.2	19	80	1
	$\alpha\text{-}TaS_2$	400	14.5	22	77	1

* MCP = methylcyclopentane, 1-MCP' = 1-methylcyclopentene

As mentioned above, cyclohexene undergoes dehydrogenation and isomerization reactions selectively in the nitrogen and hydrogen atmosphere, respectively. It is noted that cyclohexane was not detected even in the hydrogen flow. These facts show that the presence of hydrogen promotes the isomerization while suppressing the dehydrogenation. The isomerization of cyclohexene to 1-MCP' is a reaction which is believed to proceed via carbonium ion intermediates.4) In the present case, hydrogen adsorption on sulfide catalysts probably facilitates the formation of the carbonium intermediates. As for the effects of metal intercalation, Ni and Fe promotes catalytic activity while Co acts oppositely. In addition, metal intercalation had an effect to prolong the catalyst life; while the catalytic conversion over TaS_2 gradually declined to almost half an initial level in 2 hr at 400°C, such a decline was scarecely observed over the intercalation compounds. In the crystal structure of intercalation compounds, the intercalated metal atoms are located in the layer spacings of TaS_2. The latter effect suggests that the structure is stabilized by metal intercalation. The intercalated metal atoms may be exposed to surface at the edge of layers. However, it is unlikely that the promoting effect of intercalated Ni or Fe is associated with catalysis by such exposed metals, since there were no significant changes in selectivity. Probably intercalated metals modify the catalytic properties of TaS_2 electronically or structurally.

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