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DEHYDROCYCLIZATION OF HEXANE TO BENZENE CATALYZED BY REDUCED ZIRCONIUM OXIDE TREATED WITH SULFATE, SELENATE,AND TELLURATE IONS[1)]

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Dehydrocyclization catalysts for paraffinic hydrocarbons were obtained by exposing $Zr(OH)_4$ to 0.5 M H_2SO_4, 0.05 M H_2SeO_4,or 0.05 M H_2TeO_4 followed by calcination in air at 600-700 °C and reduction at 500-550 °C. The catalytic properties were highly dependent on metal oxides used as supports; ZrO_2 was most effective. The catalyst converted hexane into benzene with selectivity up to 84%.

We have previously reported that solid superacid catalysts were obtained by exposing hydroxides or oxides of Fe, Ti, Zr, and Hf, prior to the crystallization, to sulfate ion followed by calcination in air over 500 °C.2,3) This preparation method of catalyst was applied to selenate and tellurate ions; the ZrO_2 catalyst thus prepared showed the selective dehydrogenation activity for alcohols without any acidic action.4) In continuation of our interest in the catalytic ability of these sulfate-, selenate- and tellurate-treated materials, the catalysts were found to be quite effective for dehydrogenation of hydrocarbons when they were reduced. In the present work, we studied the catalytic action for dehydrocyclization of paraffinic hydrocarbons which are catalyzed by Cr_2O_3, MoO_3, or Pt, Pd, and Rh supported on alumina,5) and found that the ZrO_2 catalysts treated with sulfate, selenate, and tellurate ions followed by reduction are active for the dehydrocyclization of hexane to benzene.

Zirconium hydroxide was obtained by hydrolyzing $ZrOCl_2 \cdot 8H_2O$ with aqueous ammonia, washing, drying at 100 °C, and powdering the precipitate (32-60 mesh). The hydroxide (2 g) was exposed to a 0.05 M aqueous solution (30 ml) of selenic acid (H_2SeO_4) or telluric acid (H_6TeO_6) for 30 min followed by filtering, drying, and calcining the solid in air for 3 h; 0.5 M H_2SO_4 was poured into $Zr(OH)_4$ on a filter paper followed by the same procedures. Reactions were carried out in a microcatalytic pulse reactor with a fixed-bed catalyst (flow rate of He carrier gas 10 ml/min; pulse size 0.4 μl; catalyst 0.2 g). The reduction of catalyst was performed by injection of H_2 (2 cm^3) ten times at 500-550 °C before reaction. Effluent products were directly introduced into a gas chromatographic column for analysis (Bentone 34+DIDP, 2 m, 70 °C).

The ZrO_2 catalyst which was obtained by treating $Zr(OH)_4$ with selenic or telluric acid followed by calcination caused the oxidative dehydrogenation to convert propan-2-ol into acetone selectively.4) Reactions with hydrocarbons over the catalyst formed large quantities of carbon oxides in the beginning, but the

Table 1. Reaction of hexane at 550 °C

Catalyst	Calcination temp /°C	Products /%[a)]	
		Benzene	By-products[b)]
ZrO_2[c)]	650	1.6	1.5
Se/ZrO_2	600	27.3	8.7
	650	37.6	11.9
	700	34.4	9.0
	750	16.1	6.6
Te/ZrO_2	600	30.0	6.1
	650	30.3	6.1
	700	29.0	5.3
	750	20.1	5.6
	800	9.4	3.3
S/ZrO_2	600	21.0	2.5
	650	43.0	12.4
	700	37.8	11.3
	750	27.5	9.9
Pt/Al_2O_3[d)]	700	2.9	35.4
Pd/Al_2O_3[e)]	700	12.2	44.9
Rh/Al_2O_3[f)]	700	35.9	46.4
$Pt\text{-}Re/Al_2O_3$[g)]	700	9.1	25.2

a) Conversions were taken as the average of the eleventh to the fifteenth pulse value. b) Mainly cracked C_1 and C_2 compounds. c) Support only. d,e,f) Reference catalysts supplied from Catalysis Society of Japan: d) JRC-A4-0.5Pt, e) JRC-A4-0.5Pd, f) JRC-A4-0.5Rh. g) A commercial reforming catalyst, $0.27\%Pt\text{-}0.27\%Re/Al_2O_3$, supplied from Nippon Mining Co., Ltd.

catalyst was effective for dehydrogenation of hydrocarbons afterward. Thus, the ZrO_2 catalysts treated with selenic or telluric acid and calcined at 500-800 °C were reduced with injection of H_2 (2 cm^3) ten times at 550 °C and then used for the reaction of hexane. As shown in Table 1 the catalysts were quite effective for the dehydrocyclization of hexane to benzene. High activities were observed on calcination at 600-700 °C following treatment with selenic or telluric acid, the selectivity being up to 84%. The superacid, which was obtained by treating $Zr(OH)_4$ with 0.5 M H_2SO_4 followed by calcination at 600-750 °C, was also reduced in the same manner as the above; the catalyst showed high activity and selectivity for the formation of benzene from hexane. By-products were mainly cracked materials, C_1 and C_2, the isomerized products, isohexanes, being negligible. It seems likely that isohexanes formed were cracked under the condition without hydrogen. Reforming catalysts, Pt/Al_2O_3, Pd/Al_2O_3, Rh/Al_2O_3, and $Pt\text{-}Re/Al_2O_3$, were much lower in selectivity under the present conditions; the different results from the reported ones[6)] were probably caused by the reduction at the high temperature,

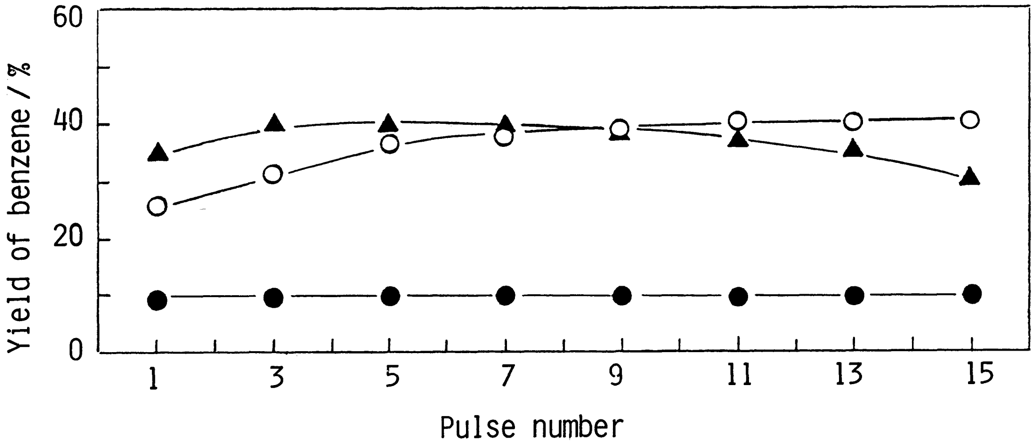


Fig. 1. Reaction of hexane at 550 °C.
(○) Se/ZrO_2 calcined at 650 °C, (▲) Rh/Al_2O_3,
(●) Pt-Re/Al_2O_3

550 °C, and by the condition without hydrogen.

The yields of benzene over several catalysts are shown as a function of pulse number in Fig. 1. It is seen that the Se/ZrO_2 catalyst kept its activity almost constant during reaction. The commercial Pt-Re/Al_2O_3 catalyst was also constant in activity, but the selectivity for benzene was quite low in comparison with those of the present catalysts.

The present catalyst also converted heptane into toluene together with small amount of benzene under the same conditions. Namely, the catalysts prepared by treatment with selenic or telluric acid followed by calcination at 650 °C led to 14.8 and 11.8% conversions for the formation of toluene at 500 °C in company with 0.6 and 0.5% benzene, respectively, the selectivity for the dehydrocyclization being 62 and 75%. Octane was converted into 5.0% benzene, 4.4% toluene, 4.1% ethylbenzene, and 9.8% xylenes (o- : m- : p- = 84 : 9 : 7) by the former catalyst, the selectivity for the cyclization being 56%; those by the latter were 4.4, 3.6, 3.7, and 8.1% (o- : m- : p- = 92 : 6 : 2), respectively, the selectivity being 63%.

Other metal oxides were also examined; the catalytic action was found to be highly dependent on metal oxides used as supports. Table 2 shows the activities of catalysts prepared from several oxides for the reaction of hexane to benzene at 550 °C. The catalysts were prepared from $TiCl_4$, $HfCl_4$, $Al(NO_3)_3$, $SnCl_4$, and $Bi(NO_3)_3$ as starting materials in the same manner as the ZrO_2 catalyst; commercial SiO_2-Al_2O_3 (Shokubai Kasei Co.) was also used. All the materials were calcined at 650 °C. It is seen from Table 2 that ZrO_2 is most effective.

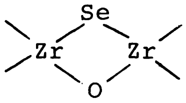
The ZrO_2 catalysts treated with selenic acid and calcined at 500, 650, and 800 °C were shown to contain 3.1, 1.7, and 0.4 wt% in the quantity of Se, that of Te of the ZrO_2 catalysts treated with telluric acid being 4.0 and 3.8 wt% after calcination at 500 and 800 °C, respectively. In the case of the sulfate-treated ZrO_2, the quantity of S was estimated to be 2.8, 2.2, and 0.2 wt% with calcination at 500, 650, and 800 °C, respectively.[7)] The surface properties of the Fe_2O_3 catalyst prepared by the addition of sulfate ion and of the subsequently reduced

Table 2. Catalytic effect of metal oxides for the reaction of hexane to benzene at 550 °C

Metal oxide	Conversion to benzene /%[a)]		
	Treatment		
	H_2SO_4[b)]	H_2SeO_4[c)]	H_2TeO_4[c)]
TiO_2	7.2	7.2	10.5
HfO_2	20.4[d)]	18.8[e)]	7.9
Al_2O_3	1.6	1.3	1.7
SnO_2	0.1	0.1	0.1
Bi_2O_3		0.1	0.1
SiO_2-Al_2O_3		0.5	0.6
ZrO_2	28.2[f)]	36.7[g)]	29.0[h)]

a) The tenth pulse values. b,c) Reduction temperature: b) 550 °C, c) 500 °C. Selectivity for benzene: d) 65%, e) 81%, f) 72%, g) 81%, h) 82%.

material were recently studied in detail using XPS and IR by Tanabe et al.[8)] Our XPS experiment of Se/ZrO_2 calcined at 650 °C showed to be 54.8 eV for the binding energy of Se 3d, which was closer to 55.9 eV for that of Se metal than that of SeO_2 (60.8 eV). Thus, in consideration of Tanabe's results, Se appears to be combined with Zr elements as Se^{2-} in the bridging bidentate state,



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