Dehydrocyclization of Hexane to Benzene over Zirconia-supported Chromia[1]

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A dehydrogenation catalyst for alkanes was obtained by exposing $Zr(OH)_4$ to 0.05M-$(NH_4)_2CrO_4$, followed by calcination in air at 600—800 °C and reduction at 550 °C; this catalyst converted hexane into benzene with a selectivity of up to 84%.

We have reported that a solid superacid catalyst with an acid strength $H_o \leqslant -16.04$ was obtained by exposing $Zr(OH)_4$ to sulphate ion followed by calcining in air.[2a] This method of catalyst preparation was also applied to selenate and tellurate ions; the ZrO_2 catalyst thus prepared showed selective dehydrogenation activity for alcohols without any acidic action.[2b] In continuation of our studies on the catalytic ability of ZrO_2 as a support, we have found that a catalyst of chromia supported on zirconia is effective for dehydrogenation of hydrocarbons, and we report here the dehydrocyclization of hexane to benzene. This reaction is also catalysed by Cr_2O_3, MoO_3, and Pt, Pd, or Rh supported on alumina.[3]

Zirconium hydroxide was obtained by hydrolysing $ZrOCl_2 \cdot 8H_2O$ with aqueous ammonia, washing, drying at 100 °C, and powdering the precipitate (32—60 mesh). The hydroxide (2 g) was exposed to aqueous 0.05 M-$(NH_4)_2CrO_4$ (30 ml) for 30 min followed by filtering, drying, and calcining in air for 3 h. Reactions were carried out in a microcatalytic pulse reactor with a fixed-bed catalyst in the absence of hydrogen (flow rate of He carrier gas 10 ml min^{-1}; 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 550 °C before reaction. Effluent products were directly introduced into a gas chromatographic column for analysis (Bentone 34 + DIDP, 2 m, 70 °C). Conversions were taken as the average values from the 11th to the 15th pulse.

The results for the conversion of hexane into benzene are shown in Table 1. High activities were observed with catalysts calcined at 600—800 °C following treatment with chromate ion; selectivity was up to 84%. By-products were mainly cracked materials (C_1 and C_2); isomerization products (isohexanes) were negligible. It seems likely that any isohexanes formed were cracked in the absence of hydrogen.

Other metal oxides were examined, in particular γ-Al_2O_3 and SiO_2, as supports for the chromia catalyst, but they showed no increase in catalytic activity for dehydrocyclization (Table 1). The effect of modifying the proportion of chromia in the catalyst was studied. Thus, catalysts were prepared by the method of evaporation to dryness with *ca.* 0.5 wt. % Cr, but analogous results were observed. A commercial chromia catalyst supported on alumina usually contains 10—20 wt. % chromium.[4,5] In the present catalysts maximum activity was

Table 1. Reaction of hexane with various catalysts at 550 °C.

Catalyst	Calcination temp. (°C)	Products(%) Benzene	By-products[a]	Quantity of Cr (wt. %)
Cr_2O_3[b]	700	0.2	3.0	
ZrO_2[c]	650	1.6	1.5	
Cr_2O_3/ZrO_2	600	48	10	0.55
	700	52	11	
	800	41	8	0.48
	900	22	4	
Cr_2O_3/Al_2O_3	700	8	32	
Cr_2O_3/SiO_2	700	2	3	
Cr_2O_3/TiO_2	700	5	2	
Cr_2O_3/ZrO_2[d]	700	70	11	0.43
Cr_2O_3/Al_2O_3[d]	700	6	31	
Cr_2O_3/SiO_2[d]	700	14	6	
Pd/Al_2O_3[e]	700	12	45	
Pt-Re/Al_2O_3[f]	700	9	25	

[a] Mainly cracked C_1 and C_2 compounds. [b] $Cr(OH)_3$(Nakarai Chemicals, Ltd.) calcined. [c] Support only. [d] Prepared by evaporation to dryness (*ca.* 0.5 wt % Cr). [e] A reference catalyst supplied by the Catalysis Society of Japan (JRC-A4-0.5% Pd). [f] A commercial reforming catalyst, 0.27% Pt-0.27% Re/Al_2O_3, supplied by Nippon Mining Co., Ltd.

observed with 1 wt. % Cr, and activity was maintained at higher values; a small proportion of chromia is thus effective. Re-forming catalysts, Pd/Al_2O_3 and $Pt–Re/Al_2O_3$, showed much lower selectivity under the present conditions; these results probably reflect the fact that the reduction was carried out at high temperature (550 °C) and in the absence of hydrogen.

The specific surface area of catalyst treated with 0.05 M-$(NH_4)_2CrO_4$ and calcined at 700 °C was 57 $m^2 g^{-1}$; that of ZrO_2 without the chromate treatment was only 15 $m^2 g^{-1}$. This large increase in area was also observed with a solid superacid, shown to consist of bidentate sulphate ions co-ordinated to Zr metal by photoelectron spectroscopic and i.r. experiments.[2a,6,7] Photoelectron spectra of the chromate-treated ZrO_2 calcined at 700 °C showed a value of 580.8 eV for the binding energy of Cr $2p^{3/2}$, close to that (580.2 eV) for CrO_3; the value for the reduced material was estimated to be 578.3 eV, intermediate between the values of CrO_3 and Cr_2O_3 (576.8 eV). Thus, the active site for dehydrogenation appears to be Cr^{IV}, created by reduction of CrO_4^{2-}/ZrO_2.

The selectivity of the conversions of cyclohexane into benzene and ethylbenzene into styrene by the present catalyst was high. Catalyst prepared by evaporation to dryness (0.5 wt. % Cr) followed by calcination at 700 °C led to 37 and 35% conversions at 450 °C, respectively, with selectivities of 97 and 87%; yields were only 1 and 10% with Al_2O_3 as support.

The reaction of hexane was also performed in a flow system at atmospheric pressure ($W/F = 215$ g-cat h mol^{-1}, where W = catalyst amount and F = hexane flow rate; He carrier). With catalyst reduced in a reactor at 550 °C for 0.5 h in a stream of hydrogen (10 ml min^{-1}), the yield of benzene at 550 °C was steady up to 6 h (63, 60, and 60% for 2, 4, and 6 h, respectively), with 76—77% selectivity.

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