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Dehydrogenation of Cyclohexanol to Cyclohexanone Catalyzed by Tin Oxide and the Sulfated Tin Oxide

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Tin oxide prepared by hydrolysis of tin (II) octylate followed by calcination and the tin oxide sulfated by exposing to 0.5 mol/dm^3 H_2SO_4 followed by calcination in air were highly effective as catalysts for the dehydrogenation of cyclohexanol to cyclohexanone in the presence of water, a selectivity of up to 99% for 90% conversion.

Cyclohexanone, which is an important intermediate in the manufacture of nylon, is industrially produced by the catalytic dehydrogenation of cyclohexanol over Zn-Cu and ZnO;$^{1)}$ other catalysts for the reaction have been reported, CuO-CoO, $ZnO-Cr_2O_3$,$^{2)}$ CuO-ZnO,$^{3)}$ and $Cu-ZnO-Al_2O_3$.$^{4)}$ Ni supported on activated carbon was recently found to be effective.$^{5)}$ We report here that SnO_2 prepared from tin octylate is a catalyst quite suitable for the reaction.

The catalyst was prepared as follows. $Sn(OH)_4$-1 was prepared by dissolving tin (II) octylate (Nakarai Chemicals) in isopropyl alcohol, hydrolyzing with aqueous ammonium hydroxide, washing the precipitate with methanol, and drying at 100 °C. $Sn(OH)_4$-2 was obtained by hydrolyzing $SnCl_4$ with aqueous ammonia followed by washing with water and drying. The hydroxides were powdered (32-60 mesh) and calcined in air at 500 °C for

Table 1. Reaction of cyclohexanol at 330 °C

Catalyst	Products /%[a)]	
	Cyclohexene	Cyclohexanone
SnO_2-1	9	47
SnO_2-2	31	29
ZnO	20	67
Fe_2O_3	28	28
MgO	35	57
Cr_2O_3	96	4

a) The average values from the 11th to 15th pulse.

3 h. The catalysts thus prepared from $Sn(OH)_4$-1 and -2 are referred to as SnO_2-1 and -2, respectively. The sulfation of SnO_2-1 with sulfate ion was performed by exposing $Sn(OH)_4$-1 (2 g), heated at 250 °C for 1 h, to 0.5 mol/dm^3 H_2SO_4 (30 ml) for 30 min followed by filtering, drying, and calcining in air at 500 °C for 3 h.

Reactions were carried out by a conventional flow method using nitrogen as carrier gas; cyclohexanol and nitrogen were passed through the fixed-bed catalyst (1 g) at flow rates of 1.8 ml/h (liquid) and 20 ml/min, respectively. The reactions were also carried out in a microcatalytic pulse reactor (flow rate of He carrier gas 20 ml/min; pulse size 1.0 µl; catalyst 0.1 g); effluent products were directly introduced into a gas chromatographic column for analysis (PEG 20M, 2 m, 90 °C).

The results for the reaction of cyclohexanol under the pulse conditions are shown in Table 1 together with those of other metal oxides for comparison. SnO_2-1 was quite effective for the dehydrogenation, the selectivity being 83%; SnO_2-2 showed activities for both dehydration and dehydrogenation. It seems likely that acidities due to the residual chlorines on preparation of the latter catalyst were more active for the dehydration.

Other metal oxides to be expectedly efficient for the dehydrogenation

Table 2. The surface area and XRD changes of SnO_2-1 after reaction

Reaction condition	Surface area $m^2\ g^{-1}$		XRD pattern
Before use	24	41[a)]	SnO_2
360 °C, 6 h	12	24[a)]	$SnO + SnO_2$
390 °C, 6 h	7		SnO
360 °C, 6 h[b)]	24		SnO_2
390 °C, 6 h[b)]		39[a)]	SnO_2

a) The SO_4/SnO_2-1 catalyst.

b) With water (10.8% v/v).

were also examined; the catalytic action was highly dependent on metal oxides used. The catalysts were prepared from $Zn(NO_3)_2$ and $Fe(NO_3)_3$ as starting materials in the same manner as the SnO_2-2 catalyst; commercial $Mg(OH)_2$ and $Cr(OH)_3$ were also used. It is seen from Table 1 that SnO_2-1 is most effective.

The reaction was carried out under the flow conditions at 360 °C over SnO_2-1; high selectivities for the ketone were observed, 97-98% selectivity with 41, 32, 30, 25, 22, and 19% conversion for 1, 2, 3, 4, 5, and 6 h, respectively.

It was reported that SnO_2 catalysts treated with sulfate ion showed highly oxidizing action with superacidity on the surface.[6)] Thus, the SnO_2-1 catalyst was sulfated (SO_4/SnO_2-1) and examined in the reaction; the yield of cyclohexanone at 360 °C was 83, 79, 76, 71, 66, and 62% for 1, 2, 3, 4, 5, and 6 h, respectively, with 97-99 selectivity. The amount of cyclohexanone was increased by the sulfate treatment, the high selectivity being maintained.

The conversion into cyclohexanone decreased continually with time, probably owing to a decrease in the amount of oxygen of the catalyst surface; this reaction process appears to be an oxidative dehydrogenation.

In fact, by XRD analysis the conversion of SnO_2 into SnO by reaction was observed, a considerable decrease in surface area being also observed after reaction as is shown in Table 2. However, the addition of water was found to have a large effect on the structure of catalyst; both the area and the SnO_2 form were restored completely when water (2-11%) was supplied.

The reaction was performed with a mixture of cyclohexanol and water (10.8% v/v), the results being shown in Fig. 1. The yield of cyclohexanone was almost constant up to 9 h at 360-390 °C, and the selectivity was quite high, 99% in all runs.

The activity enhancement of oxidation by the sulfate addition was also observed with the Fe_2O_3 superacid; the catalyst was entirely poisoned by the addition of pyridine as a result of no catalytic oxidation.[7] Thus, the oxidation seems to be related to the surface acidity in the case of the sulfated SnO_2 and Fe_2O_3. The role of water on the catalytic action is under investigation.

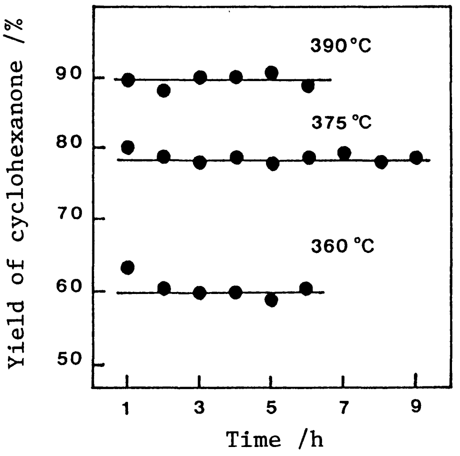

Fig. 1. Reaction of a mixture of cyclohexanol and water over SO_4/SnO_2-1.

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