Dehydrogenation of Propan-2-ol to Acetone catalysed by Zirconium Oxide treated with Selenate and Tellurate Ions[1]

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A dehydrogenation catalyst was obtained by exposing $Zr(OH)_4$ to 0.05 M H_2SeO_4 or H_2TeO_4 and followed by calcination in air at 600—800 °C; this catalyst converted propan-2-ol into acetone with 100% selectivity.

We have previously reported[2] that a solid superacid catalyst with an acid strength of $H_0 \leqslant -16.04$ was obtained by exposing $Zr(OH)_4$ to sulphate ion followed by calcining in air. Following the same procedures with selenate and tellurate ions, the catalyst showed high dehydrogenation activity for alcohols, without any acidic action.

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 a 0.05 M aqueous solution (30 ml) of selenic (H_2SeO_4) or telluric (H_6TeO_6) acid for 20 min followed by drying, and calcining in air for 3 h. Reactions were carried out in a microcatalytic pulse reactor with a fixed-bed catalyst (flow rate of He carrier gas 30 ml min^{-1}; pulse size 0.4 µl; catalyst 50 mg). The catalyst was heated at 400 °C for 1 h in the He flow before reaction. Effluent

Table 1. Reactions of propan-2-ol on the oxide catalysts.

Metal oxide	Treatment	Calcination temp./°C	Reaction temp./°C	Products/% Propene	Products/% Acetone
ZrO_2	None	500	300	43	2
		600	300	23	2
		700	300	18	2
	H_2SeO_4	600	220	0	28
		600	250	2	45
		650	220	0	31
		650	250	2	49
		700	220	0	27
		700	250	3	41
		800	250	1	18
	H_2TeO_4	600	250	1	16
		650	250	2	27
		700	250	0	17
Al_2O_3 (10 mg)	None	500	280	60	4
		650	280	45	5
	H_2SeO_4	500	280	67	4
		650	280	72	4
TiO_2	None	500	300	5	10
	H_2SeO_4	500	250	69	6

products were directly introduced into a gas chromatographic column for analysis (Porapak R, 2 m, 120 °C). Conversions were taken as the average of the first to the fifth pulse value.

The results for the reaction of propan-2-ol catalysed by zirconium oxide with or without selenate and tellurate ions are shown in Table 1. Dehydration took place predominantly to form propene over ZrO_2 prepared by calcining $Zr(OH)_4$. However, the ZrO_2 catalyst treated with selenic acid exhibited a high selectivity for the dehydrogenation of propan-2-ol to acetone, the selectivity being >93% at 250 °C and 100% at 220 °C. The analogous treatment with telluric acid also enhanced the activity of ZrO_2 for the dehydrogenation but its promoting effect was smaller than that of selenic acid. The activity was found to depend on the concentration of selenic acid. Namely, the catalysts prepared by treatment with 0.01, 0.05, 0.10, 0.25, and 1.00 M H_2SeO_4, then calcining at 650 °C, led to 12, 31, 27, 19, and 14% conversions for the dehydrogenation at 220 °C, respectively, the maximum activity being for 0.05 M concentration.

As shown in Table 1 maximum activity was observed on calcination at 650 °C following treatment with both selenic and telluric acids. The ZrO_2 catalyst treated with H_2SeO_4 and calcined at 650 °C also converted ethanol into 1% CO_2 and 9% CH_3CHO at 250 °C and butan-2-ol into 5% but-2-ene and 43% methyl ethyl ketone at 220 °C under the same conditions.

In a typical reaction of propan-2-ol, the conversion into acetone decreased continually after the third pulse, probably owing to a decrease in the amount of oxygen of the catalyst surface; the activity was restored completely if O_2 was supplied following the third pulse. The dehydrogenation activity is thus related to surface oxygen. Solid base catalysts such as MgO and CaO are also effective for dehydrogenation of propan-2-ol.[3] Poisoning experiments with injection of CO_2, H_2O, or n-butylamine at 250 °C before reaction had no effect on the yield of acetone. Consequently, this dehydrogenation process appears to be an oxidative dehydrogenation. The catalysts treated with 0.05 M H_2SeO_4 and heated at 500, 650, and 750 °C converted CO into CO_2 in 61, 88, and 19% yields at 400 °C, respectively, while yields were only 2—3% without the selenate treatment (pulse size, 0.05 ml; He carrier, 30 ml min^{-1}; catalyst, 50 mg).

Other metal oxides (Al_2O_3 and TiO_2) were also examined, but they showed no increase in catalytic activity for dehydrogenation (Table 1). Thermogravimetric data for the ZrO_2 catalyst treated with 0.05 M H_2SeO_4 showed a weight decrease of 4.5 wt% at 600—900 °C, probably caused by the decomposition of selenate to form SeO_2. In general, H_2SeO_4 is known to be decomposed to form SeO_2 below 300 °C.

It is of interest that the treatment with sulphate ions followed by calcination creates superacid sites on the ZrO_2 surface, whereas treatment with selenate or tellurate ions produces dehydrogenation catalysts without any acidic action.

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References

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