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Acceleration of the Hydrogenation of 2-Octanone with an Alkali Salt of an Organic Acid

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Synopsis. The hydrogenation of 2-octanone over various types of nickel catalysts was found to be accelerated by the addition of small amounts of carboxylates of alkali metals such as Na, K, and Li.

It is well-documented that the tartaric acid–sodium bromide-modified nickel catalyst (TA–NaBr–MNi) gives high optical yields in the enantioface-differentiating hydrogenation of 2-alkanones,[1] as well as β-keto esters,[2] β-diketones,[3] and β-keto sulfones.[4] Optical yield over this catalyst was controlled by a number of factors. For example, we have reported that the addition of small amounts of sodium ions improved the optical yield of hydrogenation of 2-alkanones over TA–MNi in a reaction media containing both pivalic acid and tetrahydrofuran (THF),[5] whereas the addition of sodium ions resulted in no improvement of the optical yield in THF.[6]

In the course of studies on the enantioface-differentiating hydrogenation of 2-alkanones over TA–MNi, it was found that the addition of a small amount of sodium pivalate to the reaction media resulted in the acceleration of the reaction as well as an increase in the optical yield. As for the acceleration of the hydrogenation over a Raney nickel (RNi) catalyst, addition of strong bases such as sodium hydroxide or potassium hydroxide have been known to be useful.[7] However these strong bases could not be applied to sensitive

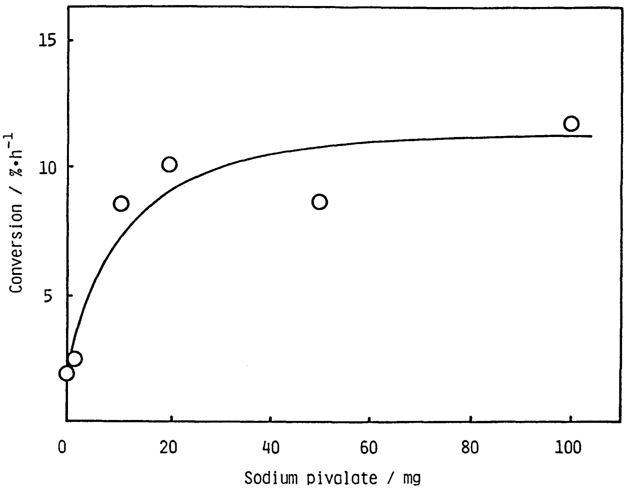

Fig. 1. Relationship between the amount of sodium pivalate in the reaction system and the rate of hydrogenation of 2-octanone.[a)]
Hydrogenation conditions: Catalyst: RNi prepared from 3.8 g of the alloy (Ni/Al=42:58) was modified with 200 ml of an aqueous solution containing TA (2 g) at 100 °C. Reaction media: a mixture of THF (20 ml) and pivalic acid (18 ml). Reaction temperature: 60 °C. Initial hydrogen pressure: 90 kg cm^{-2}.
a) The rate of the hydrogenation is represented by the conversion (%) of 2-octanone in an initial one hour.

Table 1. Effect of the Addition of an Alkali Salt on the Rate of Hydrogenation of 2-Octanone[a)]

No.	Catalyst/g	Reaction temperature/ °C	Alkali salt/mg	Hydrogenation rate[b)]
1	TA-MRNi[c)]	60	—	5
2	TA-MRNi[c)]	60	Na 2-Ethylhexanoate/20	12
3	RNi-A[d)]	60	—	11
4	RNi-A[d)]	60	Na 2-Ethylhexanoate/20	51
5	HNi/4.0[e)]	100	—	13
6	HNi/4.0[e)]	100	Na 2-Ethylhexanoate/20	31
7	Ni-FP/0.8[f)]	60	—	13
8	Ni-FP/0.8[f)]	60	Na 2-Ethylhexanoate/20	42
9	Ni-FP/0.8[f)]	60	Li 2-Ethylhexanoate/20[g)]	28
10	Ni-FP/0.8[f)]	60	K 2-Ethylhexanoate/20	30
11	Ni-FP/0.8[f)]	60	NaCl/20[h)]	17
12	MNi-FP/0.8[i)]	60	—	10

a) Hydrogenation conditions were: Substrate: 2-Octanone (10 ml), Reaction media: THF (20 ml), Initial hydrogen pressure: 90 kg cm^{-2}. b) The rate of the hydrogenation is represented by the conversion (%) of 2-octanone in an initial one hour. c) The catalyst prepared from 3.8 g of the alloy was modified with 200 ml of an aqueous solution containing TA (2 g) at 100 °C. d) The catalyst prepared from 3.8 g of the alloy was treated with 200 ml of a solution containing TA (2 g) and NaBr (12 g), at pH 3.2, 100 °C for 1h. After removal of the solution by decantation, the catalyst was treated with 1 mol dm^{-3} NaOH at 100 °C for 1 h. e) Nickel oxide was reduced at 350 °C for 1 h under a hydrogen stream. f) Nickel fine powder (mean particle size 30 nm) was reduced at 150 °C for 1 h under a hydrogen stream. g) A small amount of lithium 2-ethylhexanoate remained insoluble. h) NaCl was almost insoluble in the reaction mixture. i) Ni–FP was modified at 0 °C with 200 ml of a 0.5% aqueous solution of NaCl.

reactions such as enantioface-differentiating hydrogenation, because a small difference in reaction conditions caused great variations in the optical yield. In this paper, we shall report our findings on the effects of alkali salts on the rate of hydrogenation of 2-octanone.

Figure 1 shows the relationship between the amount of added sodium pivalate and the rate of hydrogenation of 2-octanone over the RNi catalyst modified with tartaric acid. In this experiment, the mixture of pivalic acid and THF, which was the standard reaction media for the enantioface-differentiating hydrogenation, was used as the reaction media. It was shown that the addition of the initial small amount of sodium pivalate to the reaction media resulted in a noticeable increase in the hydrogenation rate. This relationship was similar to that observed between the amount of sodium pivalate and optical yield.[8] Table 1 shows the effects of the addition of alkali ions, when THF was used as the reaction media. Hydrogenation was also accelerated by the addition of alkali ions when the reaction media did not contain pivalic acid. Among the alkali ions examined in this study, sodium ions appeared to accelerate the reaction the most. The reaction rates were enhanced approximately 5-times at maximum by the addition of sodium 2-ethylhexanoate, compared to those rates determined without sodium ions.

Potassium 2-ethylhexanoate and lithium 2-ethylhexanoate were less effective compared to sodium 2-ethylhexanoate. Lithium 2-ethylhexanoate has much less solubility in the reaction mixture than the sodium and potassium salts. When an alkali salt was almost insoluble in the reaction media (NaCl/THF), negligible acceleration effects were observed (Entry 11 in Table 1). Thus the solubility of alkali salts in the reaction mixture appeared to be one of the factors controlling the reaction rate. The cause of the difference between the reaction rate with sodium 2-ethylhexanoate and that with potassium 2-ethylhexanoate is not clear at present. The addition of sodium salts soluble in the reaction media appeared to be the most effective in promoting the reaction according to the present data.

It was found in this study that alkali carboxylates were excellent promoters for enhancing the hydrogenation of ketones over modified or unmodified Nickel catalysts. Although the mechanism of this effect is not certain, the present findings are interesting from a synthetic point of view.

Experimental

The catalysts employed in this study were prepared by the procedures reported previously.[2,8] The hydrogenation of 2-octanone was carried out in a 100-ml autoclave. The conversion (%) of 2-octanone was calculated based on the depression of hydrogen pressure and GLC analysis (5% Tween 80 on Shimalite W, 130 °C).

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6) Unpublished results; 2-octanone (10 ml) in THF (20 ml) was hydrogenated over TA–MRNi at 60 °C. The resulting optical yields were 2% without sodium salt and 6% with sodium 2- ethylhexanoate (20 mg).

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