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Study of the parameters controlling the enantio-differentiating ability of asymmetrically modified solid catalysts for the hydrogenation of γ-ketoesters

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Abstract

The enantio-differentiating hydrogenation of γ-ketoesters was carried out over asymmetrically modified solid catalysts. The parameters affecting the enantiomer excess (ee) were investigated and the results were compared with those of the hydrogenation of methyl acetoacetate and 2-octanone reported in the literature. The highest value of enantiomer excess of 51% was attained for the hydrogenation of methyl 4-oxopentanoate over a tartaric acid (TA)-NaBr-modified reduced nickel catalyst prepared from nickel oxide. The amount of NaBr in the modification solution needed to be optimized according to the manufacturers of the nickel oxides. The addition of an appropriate amount of carboxylic acid to the reaction media increased the enantiomer excess of the hydrogenated products.

Keywords: γ-Ketoesters; Methyl 4-oxopentanoate; Enantio-differentiating; Hydrogenation; Tartaric acid

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1. Introduction

Enantio-differentiating reactions over solid catalysts are promising for the production of optically active compounds especially for industrial production, because solid catalysts are environmentally benign, that is, they have the characteristics of easy preparation, easy separation, and easy reuse. For the enantio-differentiating hydrogenation, only two types of catalysts, a tartaric acid (TA)-NaBr-nickel catalyst and a cinchona-modified platinum catalyst, have been systematically studied and gave high enantiomer excess (ee). The combination of the type of modified catalyst and substrate producing a high ee is limited. Each modified catalyst has a narrow substrate specificity, which is a big problem for the practical syntheses of optically active compounds. The TA-NaBr-modified nickel catalyst hydrogenates β-functionalized ketones [1–3] and 2-alkanones [4] in high ee, and cinchona-modified platinum catalyst hydrogenates α-ketoesters in high ee [5–8]. Recently, it was demonstrated that simple ketones and β-ketoesters containing fluorine were hydrogenated in moderate ee over a cinchona-modified platinum catalyst [9]. However, the study of the enantio-differentiating catalysts for increasing the substrate specificity is still a challenging subject.

In the case of the hydrogenation of γ-ketoesters, no systematic studies for the parameters relating to the ee have been reported. Tai et al. reported that the hydrogenation of methyl 4-oxopentanoate gave 38% ee over

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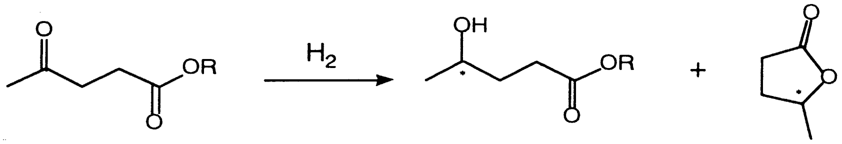
a TA-NaBr-modified Raney nickel (RNi) [10]. Sugimura et al. reported that the addition of a large amount of pivalic acid to the reaction media decreased the ee for the hydrogenation of methyl 4-oxopentanotate over the TA-NaBr-modified RNi [11]. These studies were carried out only at the optimum conditions for methyl acetoacetate (MAA) or 2-octanone, and the detailed studies of the effect of the parameters on the ee have not been carried out.



In this study, the effects of the various catalyst preparation conditions and hydrogenation conditions on the ee were systematically investigated for the hydrogenation of γ-ketoesters.

2. Experimental

All chemicals except the substrates were used as received. The 4-oxopentanoic acid esters were synthesized by refluxing the mixture of 4-oxopentanoic acid and the corresponding alcohol over an ion exchange resin (Amberlyst 15). The GLC measurements of the products were carried out using Hitachi 263-30 and Shimadzu GC18A gas chromatographs.

2.1. Catalyst

2.1.1. RNi catalyst

A nickel–aluminum alloy (Ni/Al = 42/58) (0.6 g) was digested with a 20% NaOH solution at 373 K for 1 h. The catalyst is then washed with 160 ml (20 times of 8 ml of water) of water.

2.1.2. Fine nickel powder catalyst (FNiP)

Commercially available FNiP (Vacuum Metallurgical Co. Ltd., mean particle diameter: 20 nm; 0.25 g) was treated in a hydrogen stream at 553 K for 0.5 h before use.

2.1.3. Reduced nickel catalyst (HNi)

Commercially available NiO (0.94 g) was reduced in a hydrogen stream at 623 K for 1 h before use. HNi is designated according to the NiO source as follows; HNi-1 (prepared from NiO manufactured by Nacalai Tesque Inc., lot. M3F8679), HNi-2 (prepared from NiO manufactured by Kanto Chemical Co. Inc., lot. 503E1668), HNi-3 (prepared from NiO(II) 99.9% manufactured by Wako Pure Chemical Industries Ltd., lot. DSG7505), HNi-4 (prepared from NiO(II) + (III) manufactured by Wako Pure Chemical Industries Ltd., lot. WTK2598), HNi-5 (prepared from NiO(II) manufactured by Wako Pure Chemical Industries Ltd., lot. WDG3108).

2.1.4. Noble metal catalyst

Pt/Al_2O_3, Pd/Al_2O_3, Rh/Al_2O_3, and Ru/Al_2O_3 were supplied by Kawaken Fine Chemicals Co. Ltd., Pt/Al_2O_3, Rh/Al_2O_3, and Ru/Al_2O_3 were activated in a hydrogen stream at 573 K for 1 h. Pd/Al_2O_3 was used without treatment in a hydrogen stream.

2.2. Modification of Ni catalysts

The activated Ni catalyst was soaked in a solution containing (*R*,*R*)-TA and NaBr (the amount of them are stated in the text) at 373 K for 1 h. This modification solution was adjusted in advance to pH 3.2 with NaOH solution. The catalyst was then washed with water, methanol and the reaction solvent.

2.3. Enantio-differentiating hydrogenation of γ-ketoesters

2.3.1. Hydrogenation over modified Ni catalysts

The mixture of 4-oxopentanoic acid ester, solvent (methyl propionate or THF), and the carboxylic acid (their amounts are stated in the text) were subjected to hydrogenation. The initial hydrogen pressure was 9 MPa and the hydrogenation temperature was 333–393 K.

2.3.2. Hydrogenation over modified noble metal catalysts

The mixture of methyl 4-oxopentanoate (1.04 g), THF (15 ml), and cinchonidine (2.4 mg) was subjected to hydrogenation over 0.2 g of the catalyst. The initial hydrogen pressure was 9 MPa and the hydrogenation temperature was 373 K.

2.4. *Determination of enantiomer excess (ee)*

A portion of the reaction mixture was subjected to the analysis of a chiral capillary gas chromatograph equipped with CP Chirasil DEX-CB (0.25 mm × 25 m). The ee was calculated from the peak integration of the corresponding enantiomers of 4-pentanolide.

3. Results and discussion

3.1. *Enantio-differentiating hydrogenation of methyl 4-oxopentanoate*

3.1.1. *Effect of catalyst type on ee*

Among the modified solid catalysts for the enantio-differentiating hydrogenation reported so far, a TA-NaBr-modified Ni for β-ketoesters and a cinchonidine modified Pt for α-ketoesters showed high enantio-differentiating abilities for each substrate. In this study, the enantio-differentiating hydrogenation of methyl 4-oxopentanoate was surveyed over various cinchonidine modified noble metal catalysts and TA modified Ni catalysts. The obtained results are shown in Table 1. The TA modified Ni catalysts had a higher ee than the cinchonidine modified noble metal catalysts for the enantio-differentiating hydrogenation of methyl 4-oxopentanoate. With regard to the TA modified Ni catalysts, the ee varied with the Ni source materials. RNi, which was reported as the standard starting material for the TA modified Ni for the hydrogenation of MAA [2], gave a lower ee than HNi and FNiP for the hydrogenation of methyl 4-oxopentanoate. In the case of the TA-modified HNi catalysts, the manufacturers of the NiO also affected the ee. The dependency of the ee on the NiO manufacturers was also reported for the hydrogenation of MAA [12,13] and alkanones [14]. The configuration of the products obtained by using the (*R*,*R*)-TA modified Ni was (*R*), which was the same configuration obtained for the hydrogenation of MAA over the TA modified Ni, in contrast to the fact that the hydrogenation of 2-alkanones gave the (*S*)-forms. This indicates that methyl 4-oxopentanoate would have an interaction with TA through two hydrogen bonds as well as MAA. The TA modified Ni was used for the remainder of this study.

Table 1
Enantio-differentiating hydrogenation of methyl 4-oxopentanoate

Catalysts	ee (%)
Cinchonidine-modified Pt/Al_2O_3[a]	2 (*S*)
Cinchonidine-modified Pd/Al_2O_3[a]	–[b]
Cinchonidine-modified Rh/Al_2O_3[a]	1 (*S*)
Cinchonidine-modified Ru/C[a]	1 (*S*)
TA-modified RNi[c,d]	1 (*R*)
TA-modified HNi-1[c,d]	19 (*R*)
TA-modified HNi-2[c,d]	2 (*R*)
TA-modified HNi-3[c,d]	1 (*R*)
TA-modified HNi-4[c,d]	4 (*R*)
TA-modified HNi-5[c,d]	3 (*R*)
TA-modified FNiP[c,d]	12 (*R*)

Hydrogenation temperature: 373 K.

[a] Reaction mixture: 1.04 g methyl 4-oxopentanoate, 2.4 mg cinchonidine, and 15 ml THF.

[b] 4% conversion after 24 h.

[c] Modification solution: 0.3 g TA in 30 ml H_2O.

[d] Reaction mixture: 3.82 g methyl 4-oxopentanoate, 0.065 g acetic acid, and 7 ml methyl propionate.

3.1.2. *Effect of the inorganic salts in the modification solution on ee*

Table 2 shows the effects of the inorganic salts in the modification solution on ee over the modified HNi. The added amounts of NaF and NaI were those reported in the literature [15]. The added amounts

Table 2
Effects of the inorganic salts on ee

Inorganic salts (mol)	ee (%)
–	19 (*R*)
NaF (0.039)[a]	9 (*R*)
LiCl (0.053)	12 (*R*)
NaCl (0.053)	40 (*R*)
LiBr (0.053)	20 (*R*)
NaBr (0.053)	37 (*R*)
KBr (0.053)	23 (*R*)
NaI (1.8×10^{-6})	3 (*R*)

Catalyst: TA-inorganic salt-modified HNi-1; modification: 0.9 g TA and inorganic salts in 90 ml H_2O; reaction mixture: 3.82 g methyl 4-oxopentanoate, 0.065 g acetic acid and 7 ml methyl propionate; hydrogenation temperature: 373 K.

[a] Modification pH: 5.5.

of other inorganic salts were the optimum amounts of NaBr for the HNi-1 catalyst. The tendency of the effects of the cations and the anions on the ee was similar to those for the hydrogenation of MAA [16] and 2-octanone [17]. Fluoride and iodide gave low ee values. Chloride and bromide gave moderate ee values. The order of cations giving a higher ee is as follows: Na$^+$ > K$^+$ > Li$^+ \geqq$none. The importance of sodium ions for attaining a high ee value was confirmed for the hydrogenation of methyl 4-oxopentanoate. The importance of sodium ions in the reaction system has also been reported for the hydrogenation of MAA and 2-octanone. Recently, we proposed a new enantio-differentiation mode, where the substrate would effectively interact with TA through the sodium ions [18]. The effectiveness of the sodium ions and (*R*) configuration of the product in the hydrogenation of γ-ketoesters suggested that the enantio-differentiating mode of the γ-ketoesters would be similar to that of MAA.

3.1.3. Effect of the amount of NaBr in the modification solution on ee

The results shown in Table 1 were obtained over the catalysts modified with only TA. The effect of the amount of NaBr in the modification solution on ee was investigated using the Ni catalysts prepared from various Ni sources. NaBr was the most studied co-modifier for the hydrogenation of MAA and 2-octanone [16,17,19–22]. Fig. 1 shows the results. In all cases, it can be recognized that the ee increased with the addition of an appropriate amount of NaBr to the modification solution, but that excess amounts of NaBr decreased the ee. The modified HNi generally gave a higher ee value than the modified FNiP and modified RNi. The ee value of 51% was the highest so far for the hydrogenation of methyl 4-oxopentanoate over the solid catalysts. This was obtained over the HNi-2 catalyst modified by using the solution containing 0.9 g of TA and 13.5 g of NaBr in 90 ml of water. The maximum ee values and the required amounts of NaBr for attaining these values depended on the type of Ni catalyst (RNi, HNi, or FNiP) and also on the NiO manufacturers (in the case of HNi). These results revealed that the dependency of the ee values on the Ni source reported so far [12–14] is partly attributed to the non-optimization of the amount of NaBr in the modification solution. Fig. 1 shows ee dependency on the amount of NaBr (g/g Ni catalyst) from a practical point of view. When the relation between the ee and the amount of NaBr per catalyst surface area (g/(m^2 g^{-1})) was drawn (Fig. 2), the maximum ee and the optimum amount of NaBr also depended on the NiO manufacturers. This means that the structure of the Ni surface could be also important for determining the ee value. The amount of NaBr necessary for the maximum ee for HNi was greater than that of RNi. This was different from the results for the hydrogenation of MAA and alkanones, that is, a smaller amount of NaBr was enough for attaining a high ee for the HNi catalysts than RNi. It was demonstrated that Br$^-$ deactivated the nonenantio-differentiating sites to increase the ee and that the area of the nonenantio-differentiating sites of HNi was smaller than that of RNi [23]. This was based on the fact that HNi had a larger Ni crystallite size and had more arranged Ni atoms on the surface than RNi [24]. The present results could suggest that the area of the nonenantio-differentiating sites varied according to the substrates or that Br$^-$ had other role(s) in addition to the deactivation of the nonenantio-differentiating sites.

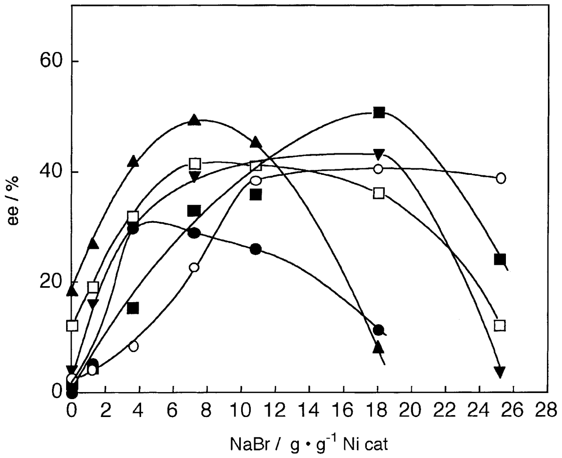


Fig. 1. Effect of the amount of NaBr in the modification solution on ee. (●): TA-NaBr-modified RNi (a); (▲): TA-NaBr-modified HNi-1 (b); (■): TA-NaBr-modified HNi-2 (b); (▼): TA-NaBr-modified HNi-4 (b); (○): TA-NaBr-modified HNi-5 (b); (□): TA-NaBr-modified FNiP (a). (a) Modification solution: 0.3 g TA and NaBr in 30 ml of H_2O; (b) modification solution: 0.9 g TA and NaBr in 90 ml of H_2; reaction mixture: 3.82 g methyl 4-oxopentanoate, 0.065 g acetic acid, and 7 ml methyl propionate; hydrogenation temperature: 373 K.

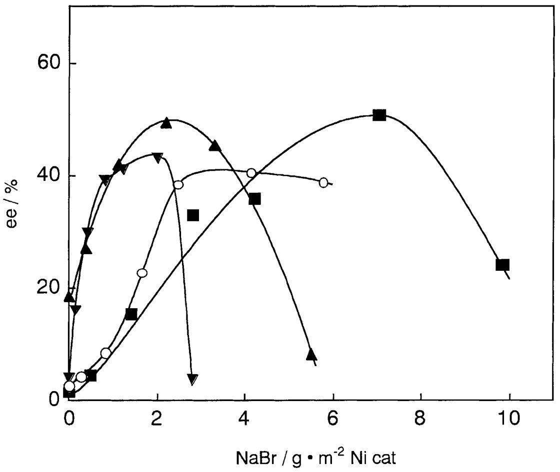


Fig. 2. Effect of the amount of NaBr in the modification solution on ee. (▲): TA-NaBr-modified HNi-1; (■): TA-NaBr-modified HNi-2; (▼): TA-NaBr-modified HNi-4; (○): TA-NaBr-modified HNi-5.

3.1.4. Effect of the carboxylic acids added to the reaction media on ee

The addition of a carboxylic acid to the reaction media was one of the important factors for attaining a high ee for the hydrogenation of MAA and the 2-alkanones. Especially, in the case of the 2-alkanones, the addition of a carboxylic acid was indispensable for the enantio-differentiation of the substrate. The bulkiness of the alkyl group of the acid changes the degree of the enantio-differentiating ability of the catalytic system [17]. On the other hand, for the hydrogenation of MAA, the structure of the carboxylic acid did not significantly affect the degree of the enhancement of ee, but the required amount of the acid for attaining a high ee depended on the strength of the acidity [25]. Fig. 3 shows the relation between the added carboxylic acid to the reaction media and the ee of the product for the hydrogenation of methyl 4-oxopentanoate. The ee increased with the addition of the acid and reached the maximum ee, but the addition of excess acids decreased the ee. The required amount of the acid for attaining the maximum ee in each acid depended on the p*K*a value of the acid. When the acid had a smaller p*K*a value, the optimum amount of the acid was lower (acetic acid; $pK_a = 4.76$, pivalic acid; $pK_a = 5.03$). This tendency is the same as that for the hydrogenation of MAA [25]. The effect of the addition of the acid on ee for the hydrogenation of γ-ketoesters has been only slightly reported so far. The ee values for the optimum conditions for the hydrogenation of MAA and 2-octanone were reported for the discussion of the effects of the acids for the hydrogenation of various ketoesters

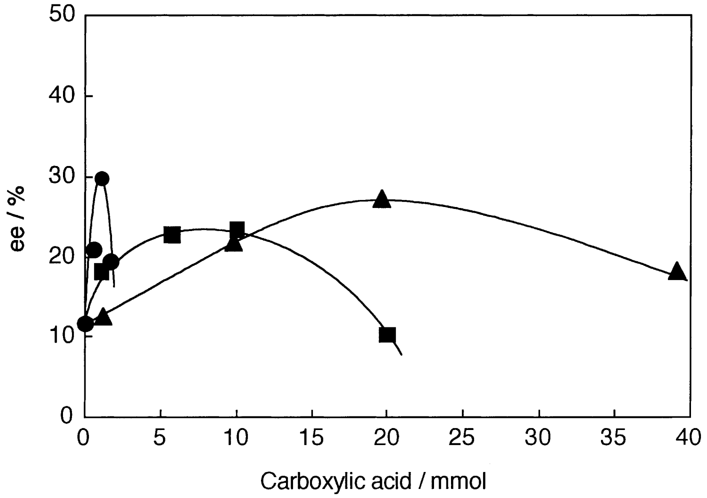


Fig. 3. Effects of the amount of carboxylic acid on ee. (●): acetic acid; (■): isobutyric acid; (▲): pivalic acid. Catalyst: TA-NaBr-modified RNi; modification: 0.3 g TA and 0.9 g NaBr in 30 ml H_2O; reaction mixture: 3.82 g methyl 4-oxopentanoate, 7 ml methyl propionate, and carboxylic acid; hydrogenation temperature: 373 K.

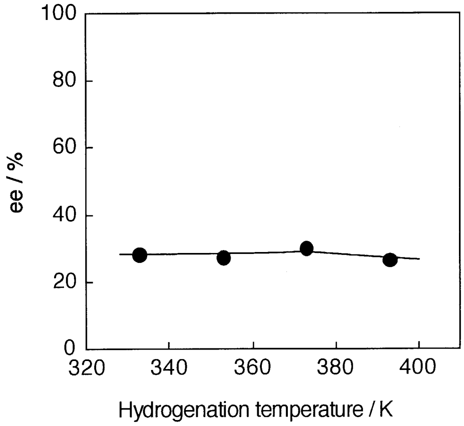


Fig. 4. Effects of the hydrogenation temperature on ee. Catalyst: TA-NaBr-modified RNi; modification: 0.3 g TA and 0.9 g NaBr in 30 ml H_2O; reaction mixture: 3.82 g methyl 4-oxopentanoate, 0.065 g acetic acid, and 7 ml methyl propionate; hydrogenation temperature: 373 K.

[11]. The present study revealed that the features of the effects of the acids for the hydrogenation of γ-ketoesters were similar to that of MAA. This also suggests that the mode of the enantio-differentiation of the γ-ketoesters could be similar to that of MAA.

3.1.5. Effect of the hydrogenation temperature on ee

Fig. 4 shows the effect of the hydrogenation temperature on ee. In the temperature range of 333–393 K, the ee did not depend on the hydrogenation temperature. This tendency was also the same as that for the hydrogenation of MAA, in contrast to the fact that the ee increased with the decrease in the hydrogenation temperature for the 2-alkanones. These results could support the fact that the mode of enantio-differentiation of the γ-ketoesters is similar to that of MAA.

3.2. Enantio-differentiating hydrogenation of various γ-ketoacid derivatives

The effects of the substrate structures on the ee varied with the combination of the types of modifiers, metals, and substrates. The cinchonidine-modified platinum catalyst hydrogenates an α-ketoacid in high ee as well as α-ketoesters [26]. In this case, the carbonyl group to be hydrogenated would have an interaction with the protonated nitrogen in the quinuclidine group of cinchonidine and the carboxyl group in the substrate would not interfere with the interaction between the substrate and the modifier. For the cinchonidine-modified palladium catalyst used for the hydrogenation of (*E*)-α-phenylcinnamic acid, a carboxyl group was mandatory for attaining a high ee, and the conversion of the acid to ester completely lost its enantio-selectivity. In this case, (*E*)-α-phenylcinnamic acid would have a two-point interaction with cinchonidine through the carboxyl group [27,28]. Table 3 shows the results of the enantio-differentiating hydrogenation of various γ-ketoesters, γ-ketoacid, and the sodium salt of γ-ketoacid. The hydrogenation of the acid gave almost a racemic product. However, its sodium salt provided a 13% ee. Bartók et al. demonstrated that sodium (*E*)-α-phenylcinnamate was hydrogenated in 17% ee, while (*E*)-α-phenylcinnamic acid gave almost a racemic compound over the TA-NaBr-modified RNi [29]. For the enantio-differentiating hydrogenation of C=O as well as C=C over TA-modified Ni, the carboxylic acid moiety in the substrate would hinder the appropriate orientation of the substrate to TA, which was effective for the enantio-differentiation of the substrate. The conversion of the acid to the sodium salt would reduce the inappropriate interaction. The present study indicated that the carbonyl groups of the γ-ketoesters would be important for the interaction with TA, and the carboxyl group in the substrate changed the appropriate orientation of the substrate to TA.

The ester with the smaller alkyl group (methyl) gave a little higher ee than those with the bulky ones for

Table 3
Enantio-differentiating hydrogenation of various γ-ketoacid derivatives

Substrates ($CH_3COCH_2CH_2COO$-R)	ee (%)
–H[a]	0.2 (*S*)
–Na[b]	13 (*S*)
$-CH_3$[a]	25 (*R*)
$-CH_2CH_2CH_2CH_3$[a]	22 (*R*)
$-CH_2CH(CH_3)_2$[a]	14 (*R*)
–Cyclohexyl[a]	16 (*R*)

Catalyst: TA-NaBr-modified RNi; modification: 0.3 g TA and 0.9 g NaBr in 30 ml H_2O; hydrogenation temperature: 373 K.

[a] Reaction mixture: 29 mmol substrate, 0.065 g acetic acid, and 7 ml THF.

[b] Reaction mixture: 29 mmol substrate and 2.4 ml H_2O+4.8 ml ethanol.

the hydrogenation of γ-ketoesters, while the type of the ester moieties did not affect the ee in the case of the hydrogenation of MAA at 373 K [11].

4. Conclusions

The following new results were revealed from the detailed systematic investigation of the parameters affecting the ee: (i) the TA-NaBr-modified HNi catalyst produced a 51% ee for the enantio-differentiating hydrogenation of methyl 4-oxopentanoate; (ii) the optimal amount of NaBr in the modification solution strongly depended on the manufacturers of the nickel oxide precursor. This finding means that the dependency of the ee values on the Ni source reported so far is partly attributed to the non-optimization of the amount of NaBr in the modification solution; (iii) the addition of the appropriate amount of the carboxylic acid to the reaction media increased the ee of the hydrogenated products.

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