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EMBEDDED NICKEL CATALYST IN POLYMER

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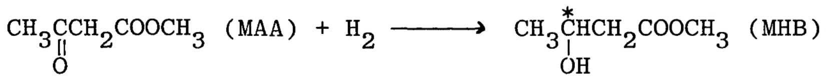
A new type embedded heterogeneous catalyst having high durability was prepared. The catalyst prepared by embedding Raney nickel catalyst modified with a mixture of NaBr and tartaric acid (TA-NaBr-MRNi) in room temperature vulcanizing silicone rubber (RTV-sillicone rubber) held its initial enantioface-differentiating ability and hydrogenation activity even after 30 times of its usage.

We wish to report a promising method for the preparation of a highly durable enantio-differentiating hydrogenation catalyst for the repeating uses.

Tartaric acid (TA) modified Raney nickel catalyst (TA-MRNi) is well documented catalyst for the enantioface-differentiating hydrogenation of methyl acetoacetate (MAA) to optically active methyl 3-hydroxybutyrate (MHB).



$$\mathrm{CH_3\underset{\underset{O}{\|}}{C}CH_2COOCH_3}\ (\mathrm{MAA}) + \mathrm{H_2} \longrightarrow \mathrm{CH_3\overset{*}{\underset{\underset{OH}{|}}{C}}HCH_2COOCH_3}\ (\mathrm{MHB})\cdots\cdots(1)$$

The recently improved catalyst, TA-NaBr-MRNi,1) showed 80% of the enantioface-differentiating ability (e.d.a.),2) while the conventional one, TA-MRNi3) showed only 34% of e.d.a. under the reaction conditions described in experimental section.

As for the durability of the e.d.a. after repeating uses, TA-MRNi was however, much better than TA-NaBr-MRNi. TA-MRNi held its original e.d.a. after five successive uses, but TA-NaBr-MRNi almost lost its e.d.a. by the twice repeating uses. The poor durability of TA-NaBr-MRNi is assumed to come from the elution of NaBr from the catalyst by the reaction media because of the weak adsorption ability of NaBr on the catalyst.4) This assumption leads us to an idea that if the catalyst is fixed into a suitable solid matrix where contacts between catalyst and reaction media are limited, the desorption of the modifying reagent from the catalyst should be prevented. Room temperature vulcanizing silicone rubber was chosen as a matrix because of its high H_2-gas permeability and moderate permeability of MAA. The TA-NaBr-MRNi embedded in silicone rubber (TA-NaBr-MRNi/SR) thus developed showed high durability of e.d.a. as shown in Fig. 1.

It is noteworthy that the silicone rubber embedded catalyst showed excellent durability with respect to the hydrogenation activity (h.a.).5) As found in Fig. 1, the h.a. of the catalyst is not significantly changed even after thirty repeating uses. The catalyst also showed good preservability. After four months of storage in air at ambient temperature, no detectable decrease of the activity was observed. These facts indicate that the silicone rubber embedding method will open the effective way to prepare the various types of highly durable metal catalyst.

The studies on the application of this method to other metal catalyst and also attempts to enhance the e.d.a. of TA-NaBr-MRNi/SR are underway.

The experimental procedures are as follows;

(1) Preparation of TA-NaBr-MRNi/SR

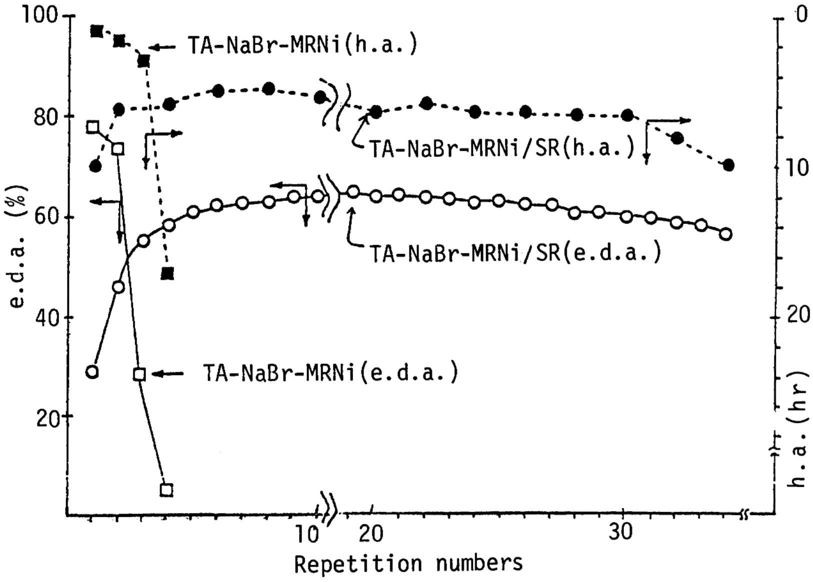
TA-NaBr-MRNi was prepared by the method reported before.$^{1)}$ Into 10 g of TA-NaBr-MRNi suspended in 3 ml of methyl propionate, 30 g of RTV-silicone rubber (KE441RTV, Shin-Etsu Chemical Co., Ltd.) was added under gentle stirring. The mixture was casted on a sheet of teflon as a film of ca. 1 mm thickness and allowed to stand for one week at room temperature to complete the curing. Thus, TA-NaBr-MRNi/SR was fabricated as flexible films containing 25% of catalyst by weight.

(2) Reaction

Into a 50 ml glass tube inserted in an autoclave, a piece of NaBr-MRNi/SR (0.8 g equivalent of TA-NaBr-MRNi, ca. 6 cm x 6 cm), 11.5 ml of MAA and 0.2 ml acetic acid were placed. The reaction was carried out under 90 kg/cm^2 initial hydrogen pressure at 100 °C. The progress of the hydrogenation was followed by the decrease of hydrogen pressure. After the reaction was completed, the reaction product was transferred into distillation flask by decantation, and then subjected to flash distillation to give pure MHB in 95% chemical yield. The optical purity of the MHB was determined by polarimetry.

The catalyst remained in the glass tube was used for the second hydrogenation without any treatment. Thus, 11.5 ml of MAA containing 0.2 ml of acetic acid was subjected to hydrogenation under the same conditions as before. The results of 30 successive runs are shown in Fig. 1.

Fig. 1 Durability of catalyst with respect to e.d.a. and h.a.



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References

1) The catalyst was prepared by soaking RNi in an aqueous solution (pH 3) containing TA and NaBr for 1 hr at 100 °C, T. Harada and Y. Izumi, Chem. Lett., 1978, 1195.

2) The e.d.a. was evaluated by the optical yield of the reaction MAA to MHB.

3) The catalyst was prepared by soaking RNi in an aqueous solution (pH 5) of TA for 1.5 hr at 0°C, S. Tatsumi, Bull. Chem. Soc. Jpn., 41, 408 (1968).

4) The h.a. was evaluated by the time required for the completion of the hydrogenation.

5) T. Harada, A. Tai, M. Yamamoto, H. Ozaki, and Y. Izumi, Proc. 7th. Int. Congr. Catal. Tokyo (1980) pp 364-375.

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