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Effects of Sodium Acetate and Residual Aluminum on the Hydrogenation Rate, Optical Yield and Catalyst Durability for the Enantio-Differentiating Hydrogenation of Methyl Acetoacetate Over Tartaric Acid-Modified Raney Nickel Catalysts

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Abstract The effects of Na acetate and residual aluminum on the hydrogenation rate, optical yield and catalyst durability for the enantio-differentiating hydrogenation of methyl acetoacetate were studied over tartaric acid-modified Raney nickel catalysts with the in situ modification. There was an optimal Na acetate amount at which the highest optical yield and high hydrogenation rate were achieved. The addition of Na acetate in the repeat use could improve the catalyst durability significantly. The amount of the residual aluminum in Raney nickel catalysts also played an important role in this catalyst system. The highest optical yield of 61.6% was achieved over the improved T-1 RNi catalyst. Compared with previous literatures, this is the best result for the enantio-differentiating hydrogenation of methyl acetoacetate over in situ modified Raney nickel catalysts.

Keywords Na acetate · In situ modification · Enantio-differentiating · Raney nickel · Tartaric acid · Methyl acetoacetate

1 Introduction

At present, the synthesis of optically pure substances has gained great importance, particularly in the production of pharmaceuticals, agrochemicals and, fragrant/flavour substances [1]. And the effective way to produce the optically pure substance is via the asymmetric catalysis. Much attention has been paid to the chirally heterogeneous catalyst due to its special advantage in separation, stability, and recovery [2, 3]. Tartaric acid (TA) modified nickel catalyst is one of the most successful enantio-selective heterogeneous catalysts and high optical yields can be obtained in hydrogenation of various β-ketoesters (80–98% ee) [4–7] and β-diketones (72–85% ee) [8, 9] with this catalyst system. The catalyst system can be prepared by two methods, one is a pre-modification and the other is an in situ modification. There have been lots of general researches with the former method for it has been typically studied for many years [10–14]. In this method, the activated nickel is immersed into an aqueous solution of TA (and if necessary, NaBr) at the optimal pH value and temperature for modification before immersed into the reaction mixture. Instead, TA and NaBr are directly added to the reaction mixture in the latter method.

For the enantio-differentiating hydrogenation over the TA–NaBr-modified nickel, it has been reported that the addition of carboxylic acid to the reaction mixture increased the optical yield [15, 16]. Recently, Osawa et al. [17, 18] reported their investigations about that with the in situ modification over the reduced nickel catalyst. They applied acetic acid and pivalic acid in the hydrogenation of MAA and 2-octanone, respectively. For the easy preparation from a Ni–Al alloy, high hydrogenation activity and high optical yield, Raney nickel is more suitable than other active nickels (reduced nickel, fine nickel powder and supported nickel) in the pre-modification method. Court and co-workers [19] reported that the starting Ni–Al phases had a significant effect on the enantio-differentiating properties with the pre-modification method. In addition, Na^+ has been reported to increase both the optical yield and hydrogenation rate [20]. However, there are a few reports about the role of sodium acetate (Na acetate) and residual aluminum over Raney nickel with the in situ modification method published, though this method is a

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powerful method for kinetic investigations [18]. It should be noted that the optical yield on the in situ modified Raney nickel is still low (36% [21]) while the best in situ modification variables for the reduced nickel are employed. This may be the reason why few researchers paid their attentions to that.

In this paper, the aim of our investigation is to describe the role of Na acetate and residual aluminum in the catalyst for the enantio-differentiating hydrogenation of MAA over Raney nickel. The effects of Na acetate and residual aluminum in the catalyst on the hydrogenation rate, optical yield and the durability of the catalysts were examined using the in situ modification method. In addition, in order to gain a deeper understanding of the effects of Na acetate and residual aluminum, the catalysts were characterized using various physico-chemical methods: infra-red spectroscopy (FTIR), inductive coupled high frequency plasma source (ICP), organic elemental analysis (OEA), ion chromatography (IC), scanning electron microscopy (SEM), BET, X-ray diffractometry (XRD).

2 Experimental

2.1 Chemicals

Al–Ni alloy of 42/58 and methyl acetoacetate ($\geq$98.0%) were supplied by Sinopharm Chemical Reagent Co., China; (2R, 3R)-(+)-tartaric acid (99 + %) was supplied by Acros, USA. All the chemicals were used as-received.

2.2 Catalyst Preparation

2.2.1 T-1 Types of Raney Nickel

Following the method reported by Dominguez et al. [22], 6 g Al–Ni alloy was added in small portions to 90 mL stirred 20% sodium hydroxide (NaOH) aqueous solution kept between 90 and 95 °C. After completion of the addition, the temperature was maintained at 90 °C for a further 1 h.

2.2.2 The Improved T-1 Raney Nickel (improved T-1 RNi)

Raney nickel was prepared according to the procedure mentioned in Sect. 2.2.1. Then, the catalyst was washed 5 times with 50 mL portion of distilled water. After that, Raney nickel was introduced into the NaOH aqueous solution (94 °C, 100 mL, 20 wt.%) under magnetic stirring for 1 h.

2.2.3 W-4 Types of Raney Nickel

W-4 types of Raney nickel were freshly prepared with the conventional method [23]. About 6 g Al–Ni alloy was added in portions into an alkaline solution (15 g NaOH dissolved in 50 mL distilled water), which was cooled below 20 °C in an ice bath. The temperature of the mixture was kept around 20 °C with constant stirring by controlling the addition rate of the Al–Ni alloy. The resulting suspension of Raney nickel was kept at 50 °C for 1 h.

2.2.4 Alkaline Raney Nickel

Different from the formers, 9.6 g NaOH was added in portions into a mixture of 6 g Al–Ni alloy and 60 mL distilled water with constant stirring. The addition rate was controlled to keep the mixture boiling and prevent it from spilling over the glass flask. After standing for 10 min, the resulting Raney nickel was maintained at 70 °C for a further 30 min.

2.3 Enantio-Differentiating Hydrogenation Using the In Situ Modification Method

A stainless steel autoclave (100 mL) with a magnetic stirrer was used for high-pressure hydrogenation reactions. The Raney nickel catalyst (usually 3 g) was washed 15 times with 50 mL portion of distilled water and then 5 times with 30 mL reaction solvent. After that, the catalyst (0.2 g) was quickly immersed into a mixture of MAA (2 mL), MeOH (4 mL), sodium bromide (NaBr, 15 mg), tartaric acid (TA, 50 mg), and an appropriate amount of anhydrous sodium acetate (Na acetate). The reaction was carried out at 60 °C and under the initial hydrogen pressure of 6 MPa. After the reaction was completed, the reaction medium was separated by decantation from the catalyst and subjected to distillation. The catalyst remaining in the glass tube after decantation was washed three times with 4 mL MeOH and then subjected to the next run under the same reaction temperature and hydrogen pressure during the repeated use.

2.4 Catalyst Characterization

The presence of individual elements in the catalyst was determined by ICP (IRIS/ES TJA), IC (861 Advanced Compact IC, Metrohm) and OEA (Elementar Analysensysteme GmbH VarioEL). Prior to measurement by ICP and IC, it was necessary to dissolve the samples. Since each sample had a high chemical activity and could be easily oxidized in the air, they were weighed in ethanol firstly. After dried in vacuum, the samples were dissolved in a solution of about 95 mL double-distilled water and 5 mL concentrated nitric acid. The content of aluminum (Al), nickel (Ni), and sodium (Na) present in samples was determined in the acquired solutions using ICP, and the bromine (Br) was measured by IC with a Metrosep A Supp

4–250 column and 1.8 mmol/L Na_2CO_3 + 1.7 mmol/L $NaHCO_3$ mixed solution in anion system. The content of carbon (C) and hydrogen (H) in the samples, which were spread out in an agate mortar before analysis, were determined using OEA.

FTIR spectra were recorded with a Nicolet NEXUS 670 FT-IR instrument with a DTGS detector. The samples were measured with KBr pellets. The preparations of the samples were carried out under the protection of argon gas after dried at 100 °C by blowing argon for 4 h in a quartz tube furnace.

The BET surface area of each sample was determined by the physical adsorption of nitrogen at −195 °C with a ChemiSorb2750 instrument of the Micromeritics Co. (USA). In order to accurately weigh each sample and prevent its oxidation, the samples were stored in EtOH, and then transferred with the medium to the quartz tube which had been weighed first. The resulting wet catalysts were dried at 120 °C by blowing argon for 2 h and weighed with the quartz tube before adsorption analysis.

X-ray powder analysis was recorded on a Rigaku D/Max-2400 diffractometer, using CuK_α radiation as the X-ray source in the 2θ range of 10°–90°. The samples were prepared as reported in the literature [24]. They were transferred from EtOH to a 2% solution of cellulose nitrate in isoamyl acetate before analysis. For this, a suspension of the samples was then dispersed over a clean glass slide and the plastic film formed on drying prevented air oxidation of the specimen.

Scanning electron microscopy (SEM) images were detected with a JEOL JSM-6380LV microscope.

2.5 Product Analysis

Samples of the reaction mixture were withdraw during the reactions and analyzed using a gas chromatograph HP 5890 Series II, which was equipped with an FID detector and an FFAP capillary column (30 m × 0.32 mm × 0.32 μm). Nitrogen was used as a carrier gas and the oven temperature was programmed from 80 to 160 °C at the ramping rate of 8 °C/min. when the total conversion of MAA was achieved, the catalyst and the reaction medium were removed from the reaction mixture by filtration and distillation in vacuum. The hydrogenation product with a chemical purity of more than 99% (GC analysis) was obtained.

The ee of the product was also measured by the gas chromatograph mentioned above with an enantioselective capillary column β-DEX-225 (30 m × 0.25 mm × 0.25 μm) instead. The oven temperature program of 80–160 °C was used during the analysis with a starting constant temperature maintained for 3 min, up to the temperature of 95 °C at the ramping rate of 10 °C/min firstly and to the end temperature of 160 °C at the ramping rate of 3 °C/min. Thus, a separation of the hydrogenation product, (R)- and (S)-enantiomers of methyl-3-hydroxybutyrate was achieved. The ee was then calculated in accordance with the following equation:

$$\begin{aligned}\text{e.e.} &= \text{optimal yield}(\%)\\ &= \frac{[(\mathrm{R})-\mathrm{MHB}]-[(\mathrm{S})-\mathrm{MHB}]}{[(\mathrm{R})-\mathrm{MHB}]+[(\mathrm{S})-\mathrm{MHB}]}\times 100\end{aligned}$$

2.6 Determination of Hydrogenation Rate

The hydrogenation rate was obtained from the amount of hydrogen consumption during the MAA hydrogenation reaction [20]. As soon as the autoclave reached the fixed reaction temperature, the stirring was started and the reaction time was calculated.

3 Results and Discussion

3.1 Enantio-Differentiating Hydrogenation Over T-1 Raney Nickel

3.1.1 The Effect of the Amount of Na Acetate

Figure 1 shows the dependence of the optical yield and hydrogenation rate on the amount of Na acetate. The optical yield dependence passes through a maximum. When the addition of Na acetate was in the region of about 10 mg, the highest optical yield was achieved. At higher amounts of Na acetate, the optical yield decreased. On the other hand, as seen clearly, the hydrogenation rate dependence had a different tendency from the former which always increased with an increasing of the amount of Na acetate. However, the discussion should be begun with the influence of modifying pH value in the asymmetry catalyst system prepared by the conventional modification procedure. It has been demonstrated elsewhere [9, 12, 14, 25] that the modification pH had a significant effect on the optical yield and there was an optimal value for achieving the highest optical though the specific optimal value was different in these papers. Such a tendency is explained by the overlap of the two factors [9, 25], that is, surface conditioning and the adsorption of suitable species for enantio-differentiation. Below about pH 4.5, TA corrodes the Ni surface to provide a suitable surface for enantio-differentiation. On the other hand, above pH 3, TA adsorbs on the Ni surface as an appropriate species (sodium tartrate) for enantio-differentiation. In order to attain a high optical yield, both the conditioned surface and the adsorption of the sodium tartrate are needed [9]. It is known that, with the in situ modification, the reaction medium can not be adjusted pH using NaOH for some H_2O

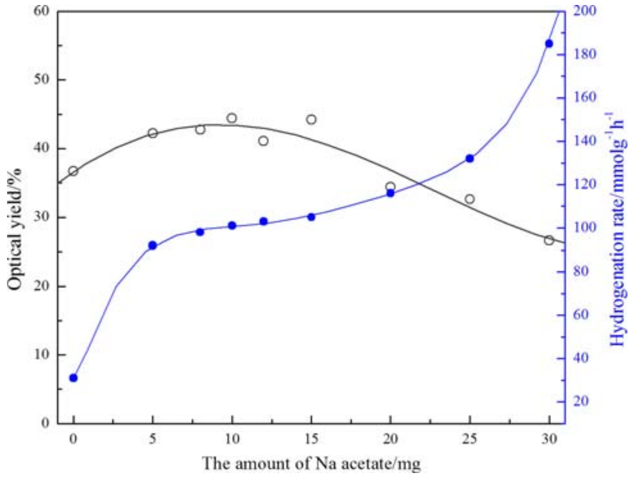


Fig. 1 Effect of Na acetate on the optical yield and hydrogenation rate, reaction conditions: MeOH (4 ml), MAA (2 ml), catalyst (0.2 g), TA (50 mg), NaBr (15 mg), H_2 (6 MPa), 60 °C. (●) hydrogenation rate; (○) optical yield

will be made in the reaction medium and this will decrease the optical yield. On the other hand, our result, adding only TA (50 mg) and NaBr (15 mg) to the reaction medium gave low optical yield and hydrogenation rate, as shown in Fig. 1, indicates that the addition of only NaBr is more than enough neither for a high optical yield nor especially for a high hydrogenation rate in the in situ modified Raney nickel catalyst system. Other additive such as Na acetate is also necessary for a high optical yield. And the addition of Na acetate increased both the optical yield and hydrogenation rate at its optimal amount. Na acetate may play two roles as followed: one is for Na^+ to form sodium tartrate and play an important role in determining the hydrogenation rate [20]; the other is for CH_3COO^- to form acetic acid which has been reported to affect the enantioselectivity significantly [17]. The inference bases on the fact that the pK_{a1} (3.04, estimated in aqueous solutions [26]) of TA is lower than the pK_a (4.75, estimated in aqueous solutions [26]) of acetic acid.

3.1.2 *The Influence of Na Acetate on the Enantio-Differentiating Durability*

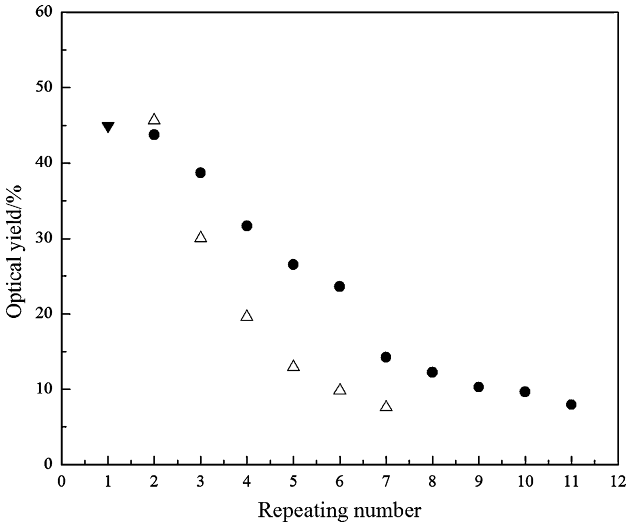


Fig. 2 Variation of the optical yield with run number, reaction conditions: solvent (4 ml), MAA (2 ml), catalyst (0.2 g), H_2 (6 MPa), 60 °C, (▼) addition of 50 mg TA, 0.05 ml acetic acid and 15 mg NaBr and using MeOH as solvent; (●) using MeOH as solvent; (△) using THF as solvent

The durability of the enantio-differentiating ability (e.d.a.) is viewed as one of the most important indications to decide whether the catalyst system is excellent. As shown in Fig. 2, the optical yield decreased gradually from 44.9% to 8.0% from the 1st to 11th runs when MeOH was used as a reaction solvent. Although the durability of the catalyst with repeated use is not significantly improved as reported by Osawa et al. [27], it still performed its higher durability than the conventional modified catalyst which has been claimed that the optical yield decreased to almost zero after three successive runs [28]. Likewise, the recycling tests, as given in Fig. 2, too, were carried out in THF after the 1st run for comparison. But the tendency was not changed except that a little higher optical yield was attained in the second run and then decreased more significantly in the following runs. The results should be caused mostly by the instability of the TA–NaBr–RNi catalyst system. As reported by Keane et al. [29, 30], a proportion of the surface enantioselective nickel sites were leached into solution during the hydrogenation step. And in the experiment, we noted that nickel tartrate from the catalyst started to leach into the reaction medium after the second run which could be examined visually as the color of the reaction medium was changed from clear to light green. Thereafter, more and more nickel tartrate leaching to the reaction medium in the following runs brought about a successive decrease in the optical yield. As well known, the hydrogenation rate in THF is lower than in MeOH with this catalyst system for the former polarity is lower [13]. And more nickel tartrate leach to the reaction medium during the longer reaction time. As seen clearly in Fig. 2, both the two curve decrease sharply first and then the decrease become slight. From these results, we assume that the TA complex exists in the main form of monotartrate (one of the carboxylic acid groups is deprotonated) in former runs and this form has been reported to be weak in stability [31]. And with the repeated tests continuing, the coverage of the catalyst surface by TA decreases and the TA complex will exist in the main form of bitartrate (both acid groups are deprotonated producing two carboxylate functionalities) instead.

In order to confirm our assumption, the FT-IR spectra analysis of the catalysts from the 2nd run and 10th run with

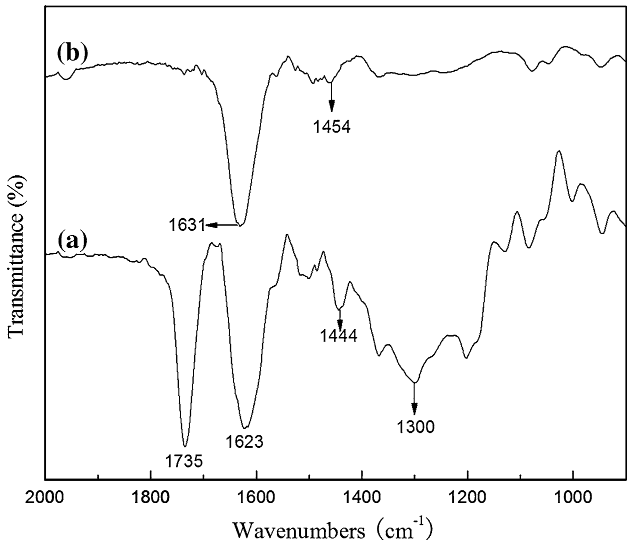


Fig. 3 FT-IR spectra of the catalysts: **a** T-1 Raney nickel catalyst after the 1st run; **b** T-1 Raney nickel catalyst after the 10th run

using MeOH as a reaction solvent were also carried out. As shown in Fig. 3, it can be seen that for the spectrum of the catalyst after the first run (Fig. 3a), the bands emerging at 1,735 and 1,300 cm^{-1} can be assigned to the COOH group. Thus, we can infer that there are still carboxylic acid group on the catalyst system. In addition, the presence of the COO^- group is also signaled by the appearance of the ν_{as}(OCO) and ν_{s}(OCO) vibrations at 1,623 and 1,444 cm^{-1}, respectively [32, 33]. On the contrary, for the catalyst after the 10th run, the bands at 1,631 and 1,454 cm^{-1} of the COO^- group are observed only, as shown in Fig. 3b. These results do have a good agreement with the assumption described above.

We reported that the durability of the enantio-differentiating ability could be amended when 15 mg NaBr was added in every run with the conventional modification method [14]. Figure 4 shows the effect of NaBr on the durability of the in situ modified Raney nickel. Though it has a slight effect on the durability, some other important information can be seen from the result, too. The optical yield increased in the second run and then decreased sharply, like the result attained in THF (Fig. 2), which should be attributed to the presence of NaBr (especially Br^-) in reaction medium. Beacause two kinds of sites, enantio-differentiating (e.d.) sites and non-enantio-differentiating (n.e.d.) sites, are present on the catalyst surface and the Br^- would prefer to adsorb on the n.e.d. sites, block their activity [9]. In runs 7–12, about 15% optical yields were attained. In the 13th runs, two different pulse tests were carried out, respectively. For one sample, 15 mg TA and 15 mg NaBr were added into the reaction medium and the optical yield increased sharply from 15% to 46%, but decreased quickly to 15% in the following three runs; for the other sample, 10 mg Na acetate and 15 mg NaBr were added and an increase of the optical yield was also achieved but slighter than the former and the higher optical yield was almost maintained in later repeated tests. The pulse tests suggest an inherent problem in the instability of the catalyst system during the repeated runs. Two main factors, both the instability of TA and NaBr which are absorbed on the catalyst surface, act together. And the addition of Na acetate can enhance the stability of TA. With a comparison between Fig. 2 and Fig. 4, it seems reasonable to assume that NaBr, especially Br^-, adsorbs on the catalyst surface more stably than TA in the in situ modification method. The conclusion is also in accordance with the result reported in the literature [34].

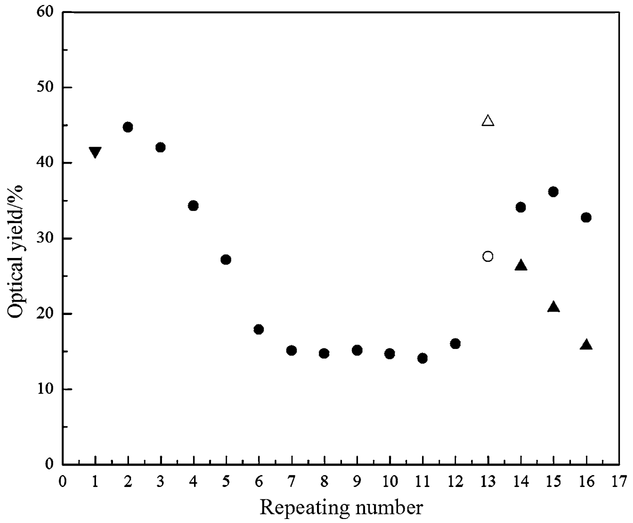


Fig. 4 Variation of the optical yield with run number, Reaction conditions: MeOH (4 ml), MAA (2 ml), catalyst (0.2 g), H_2 (6 MPa), 60 °C, (▼) addition of 50 mg TA, 0.05 ml acetic acid and 15 mg NaBr; (●) addition of 15 mg NaBr; (△) addition of 15 mg TA and 15 mg NaBr; (○) addition of 10 mg Na acetate and 15 mg NaBr; (▲) addition of 15 mg NaBr

In order to investigate it in more details, the quantitative analysis of Al, Ni, C, H, Na^+ and Br^- in the catalyst system after the 1st run and 12th run were carried out compared with the fresh catalyst. The results are shown in Table 1. We can see that both the amount of TA (C, H) and Al decreased from the 1st to the 12th runs. After the 12th run, the amount of C was a little higher than in the fresh catalyst, which was with respect to the low amount of TA. The results indicate that the instability of TA absorbed on the catalyst surface, at least in part, is due to the residual Al. On the contrary, that the amount of Na^+ and Br^- increased from the 1st to the 12th runs should be attributed to the absorption of these two kinds of ions on the area of the catalyst surface where TA was desorbed.

In this way, the key way to improve the durability of the catalyst is to enhance the stability of TA absorbed on the catalyst surface. Adding additive, such as Na acetate, which can form compound with TA may meet that. As

Table 1 Elemental composition of the catalyst measured by ICP (Al, Ni, Na), IC (Br) and OEA (C, H)

Entry	Catalyst	Al (wt.%)	Ni (wt.%)	Na (wt.%)	Br (wt.%)	C (wt.%)	H (wt.%)
1	T-1 Raney nickel	7.5	91.9	0.1	–	0.4	0.1
2	Catalyst after the 1st run	7.0	91.2	0.3	0.5	0.9	0.1
3	Catalyst after the 12th run	6.4	91.9	0.4	0.6	0.6	0.1

shown in Fig. 5, the decrease of the optical yield became slight when 10 mg Na acetate was added in every run. It should be noted that there was not a slight increase in the second run any more. This supports our conclusion that the slight increase in the second run is caused by NaBr, especially Br^-, as described above. In 11th run, when 10 mg Na acetate and 15 mg NaBr were added to the reaction medium, the optical yield nearly maintained at the same value. This is also in good agreement with our discussion that the absorbed Br^- on the catalyst surface is more stable with the in situ modification method.

3.2 The Influence of the Residual Aluminum on the Enantio-Differentiating Ability

Various Raney nickels were employed in our experiment. As reported by Osawa et al. [17], the enantio-differentiating ability of the catalyst was increased when added acetic acid to the reaction media. Thus, acetic acid was used as an additive in the experiment. The result is shown in Table 2. The amount of the residual aluminum in Raney nickel has a significant effect on the optical yield though the dependence of the hydrogenation rate is nearly negligible. And when the Improved T-1 RNi was used, the highest optical yield of 61.6% was achieved with an addition of 0.05 ml acetic acid. This is also the highest value reported so far for the hydrogenation of MAA using the in situ modified Raney nickel. When Na acetate was used as an additive, on the premise of maintaining the optical yield at the same value nearly, it significantly enhanced the hydrogenation activity, which was in accordance with our discussion in Sect. 3.1.1. We can infer from the result that the decrease of residual aluminum, known to be detrimental to the asymmetric process [25], may account for the greater improvement in the optical yield. The inference is also supported by the fact that the optical yield increases with the decrease of Al content in various Raney nickels with a comparison between the data presented in Table 2 and Table 3.

Nevertheless, how the residual aluminum acts on the optical yield is not clear enough yet. Hence, XRD, as shown in Fig. 6, was applied to describe it in more details. Following the explanation proposed by Robertson and Anderson [24], it can be seen clearly that with decreasing residual aluminum content in catalyst or with increasing extraction temperature of catalyst, the diffraction peaks of

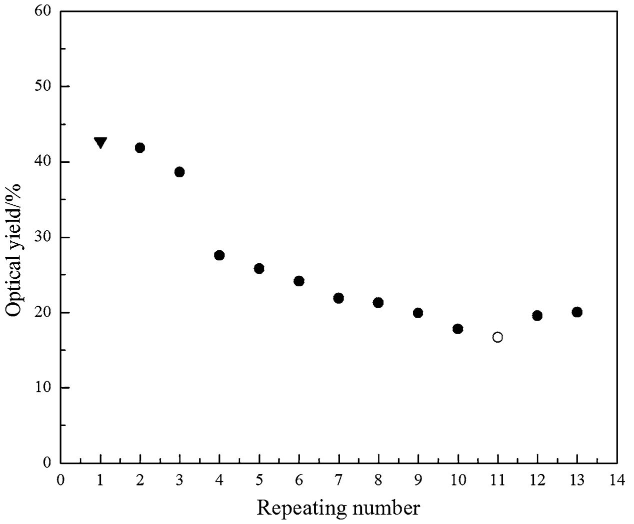


Fig. 5 Variation of the optical yield with run number, Reaction conditions: MeOH (4 ml), MAA (2 ml), catalyst (0.2 g), H_2 (6 MPa), 60 °C, (▼) addition of 50 mg TA, 0.05 ml acetic acid and 15 mg NaBr; (●) addition of 10 mg Na acetate; (○) addition of 10 mg Na acetate and 15 mg NaBr

Table 2 Dependence of the optical yield and hydrogenation rate on various Raney nickels

Entry	Catalyst	Hydrogenation rate (mmolg^{-1} h^{-1})	Optical yield (%)
1	W-4 Raney nickel[a]	12	11.3
2	Alkaline Raney nickel[a]	20	14.4
3	T-1 Raney nickel[a]	23	44.9
4	Improved T-1 RNi[a]	26	61.6
5	Improved T-1 RNi[b]	93	59.6

[a] Reaction conditions: solvent (4 ml), MAA (2 ml), catalyst (0.2 g), TA (50 mg), NaBr (15 mg), acetic acid (0.05 ml), H2 (6 MPa), 60 °c

[b] Reaction conditions: solvent (4 ml), MAA (2 ml), catalyst (0.2 g), TA (50 mg), NaBr (15 mg), Na acetate (10 mg), H2 (6 MPa), 60 °c

Table 3 Textural properties of the catalysts

Entry	Catalyst	Weight ratio Al–Ni[a]	BET surface (m^2 g^{-1})
1	W-4 Raney nickel	0.159	105.8
2	Alkaline Raney nickel	0.093	99.0
3	T-1 Raney nickel	0.081	79.5
4	Improved T-1 RNi	0.066	70.7

[a] Measured by ICP

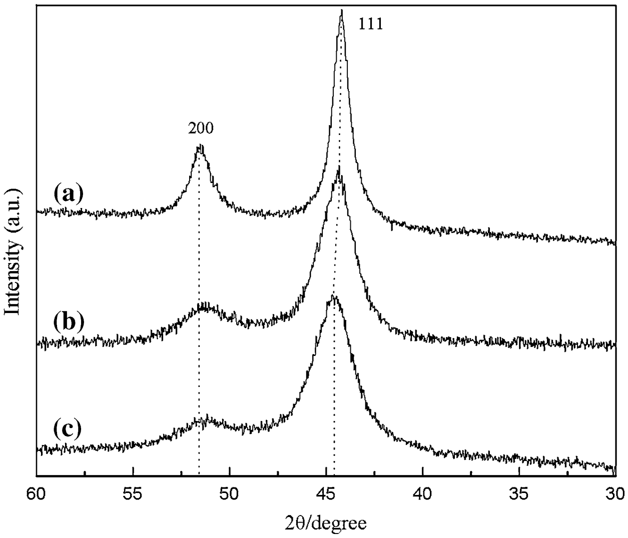


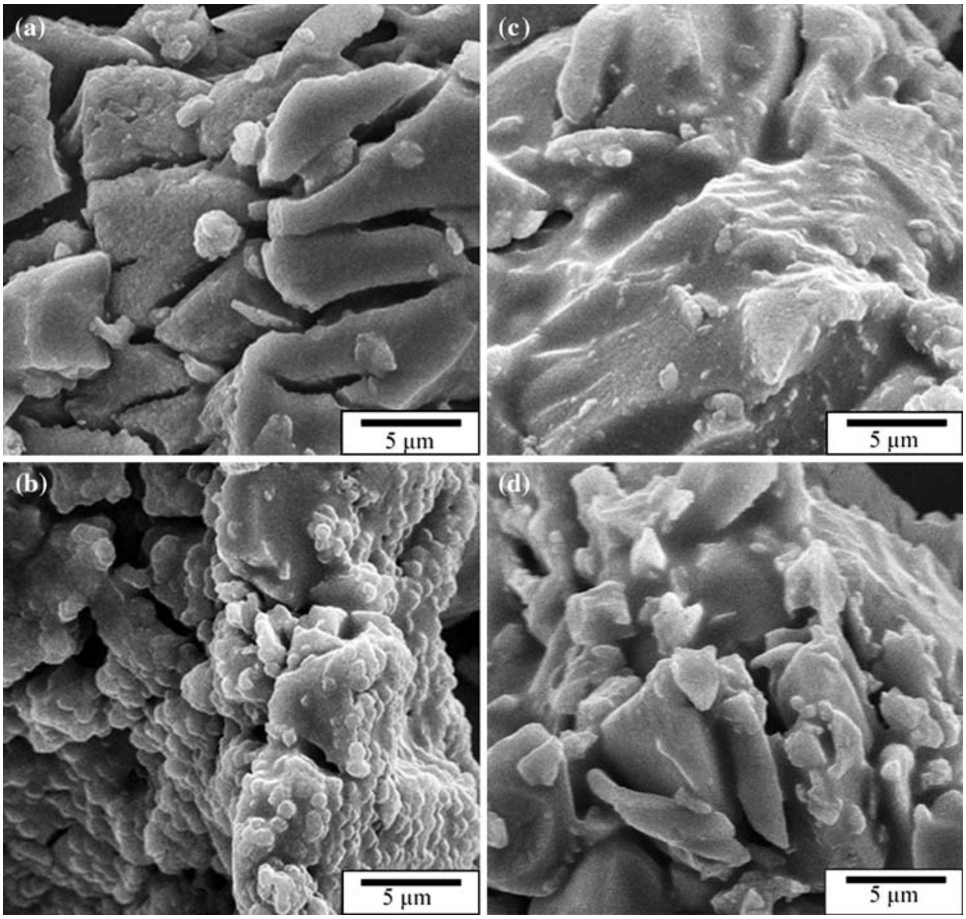
Fig. 6 XRD pattern of the catalysts: **a** T-1 Raney nickel (extraction temperature: 94 °C); **b** alkaline Raney nickel (extraction temperature: 70 °C); (c) W-4 Raney nickel (extraction temperature: 50 °C)

the (111) and (200) became more and more sharp, which suggested the larger crystallites. The BET surface area, shown in Table 3, where it decreased with increasing extraction temperature of catalyst, also implied the same information. This may be the other main aspect of the residual aluminum influence on the optical yield that the higher content of the residual aluminum exists in the Raney nickel, the smaller the crystallites are, the higher the BET surface is and the lower the optical yield is achieved. The result is in accord with the findings of Wolfson et al. who used the supported nickel in the conventional modification [35, 36].

On the other hand, the negligible effect on the hydrogenation rate, different from the reported result with the conventional method [35, 36], may be because the residual aluminum plays a negligible role in the kinetic control compared with the reaction medium pH using the in situ modification.

SEM images of the catalysts are shown in Fig. 7. It can be seen that the samples formed larger compact particles in the improved T-1 RNi before used in reaction. And for both Raney nickel catalysts; the particles became smaller and far less compact after the first run, which was consistent with the findings of Kukula and Červený [37]. The result indicates that the catalyst surface is changed to be more favorable for its high enantio-differentiating ability when TA absorbs on it during the reaction.

Fig. 7 SEM images of the catalysts: **a** T-1 Raney nickel; **b** T-1 Raney nickel catalyst after the first run; **c** improved T-1 RNi; **d** improved T-1 RNi catalyst after the first run



4 Conclusions

The effects of Na acetate in the reaction media and residual aluminum in catalyst were investigated for the enantio-differentiating hydrogenation of MAA over TA-in situ-modified Raney nickels. When Na acetate was added in the reaction media, not only the hydrogenation rate but also the optical yield was increased significantly. Moreover, the addition of Na acetate every run could also improve the catalyst durability during the repeated use. Na acetate may play two roles as followed: one is for Na^+ to form mono-sodium tartrate and play an important role in determining the hydrogenation rate; the other is for CH_3COO^- to form acetic acid and affect the enantioselectivity significantly. The highest optical yield of 61.6% was achieved over the improved T-1 RNi catalyst, which included less residual aluminum, with an addition of 0.05 mL acetic acid.

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