

# Highly efficient enantio-selective hydrogenation of methyl acetoacetate over chirally modified Raney nickel catalytic system

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## Abstract

A new method of preparing a tartaric acid modified Raney nickel (TA-MRNi-NaBr) catalytic system has been studied. Raney nickel was modified with (*R,R*)-tartaric acid. Then, methanol, in which an appropriate amount of NaBr dissolved, was used as the hydrogenation reaction medium. This new catalytic system showed high efficiency and high durability in enantio-selective hydrogenation of methyl acetoacetate (MAA). The influence of the important modifying parameter (modifying pH) and reaction variables (solvent type, the types of inorganic salts and their amount, reaction temperature and hydrogen initial pressure) on the hydrogenation rate and optical yield were systematically investigated. The high optical yield of 85% was achieved at pressure (0.6 MPa) nearly 17-fold lower than those previously used to achieve such results, and the hydrogenation rate was enhanced significantly. For comparison, the conventional TA-NaBr-MRNi catalyst was also prepared. Characterization data confirmed that compared with the conventional TA-NaBr-MRNi catalyst, the improved TA-MRNi-NaBr catalyst had lower weight ratio of Al-Ni, higher total surface area and more acid-corrosion on its surface, which could lead to the high efficiency of the TA-MRNi-NaBr catalytic system.

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**Keywords:** Enantio-selective hydrogenation; Modified Raney nickel; Tartaric acid; Methyl acetoacetate

## 1. Introduction

Nowadays, people have gradually recognized the importance of the optical pure substances, particularly in the production of pharmaceutical, agrochemical and fragrant/flavour substances [1]. One of the most efficient strategies for producing the optical pure substances is the asymmetric catalysis. Chirally heterogeneous catalyst systems are preferred over homogeneous system due to easy recyclability and separability [2,3]. Tartaric acid modified Raney nickel catalyst is among the most successful enantio-selective heterogeneous catalysts, which can be easily prepared from Raney nickel [4–11], supported nickel [12–21] and nickel powder [22–25]. High optical yields can be obtained in hydrogenation of various  $\beta$ -ketoesters (80–98%) [9,26–28] and  $\beta$ -diketones (72–85%) [29,30] over the TA-NaBr-MRNi catalyst.

Many investigations have indicated that the hydrogenation active sites of the TA-NaBr-MRNi catalyst consisted

of the enantio-differentiating (e.d.) sites and non-enantio-differentiating (n.e.d.) sites. It has also been predicated that pure crystalline nickel surfaces could provide e.d. sites and that disordered nickel surfaces containing residual aluminum compounds served as n.e.d. sites [9,15,31,32]. In the 1990s, Tai proposed the ultrasonic-irradiation method for washing Raney nickel, aiming at removing the most of aluminum on the Raney nickel surface and producing a highly efficient TA-NaBr-MRNi catalyst [26,33]. As expected, the improved TA-NaBr-MRNi-U catalyst showed comparatively higher enantio-differentiating ability (e.d.a.) and activity in the hydrogenation of a series of  $\beta$ -ketoesters and 1,3-diketones than the conventional TA-NaBr-MRNi catalyst. The optical yield of 86% was achieved in the hydrogenation of MAA. The results, however, were achieved still under high initial hydrogen pressure (9–10 MPa) and long reaction time (2.5 h) as was the case of the previous reports [4,6,7], which revealed low hydrogenation activity of the TA-NaBr-MRNi catalytic system.

One of the important impacts leading to low hydrogenation activity is the modifying method. In the traditional modification method, the TA-NaBr-MRNi catalyst was prepared by soaking the Raney nickel catalyst in a slightly acidic hot aqueous solution

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of tartaric acid (1 wt.%) and NaBr (10 wt.%) [29,33], based on the idea that the n.e.d. sites could be removed at least in part by acid-corrosion and the rest could be deactivated by poisoning with the NaBr adsorbed [34]. Yet, NaBr would compete with tartaric acid for adsorbing on the Raney nickel surface. NaBr adsorbed on the Raney Ni surface, on the one hand, could retard the hydrogenation activity of the TA-NaBr-MRNi catalyst [35]. On the other hand, the introduction of a large amount of NaBr in modifying solution, as demonstrated by Kukula, could result in a lower degree of nickel leaching [36] and reduce the chance that the Raney nickel was corroded by the tartaric acid.

The type of the hydrogenation reaction solvents is another important factor. Although nowadays it is generally agreed that higher optical yields can be obtained when aprotic semi-polar solvents are used, the disagreement arises from the influence of the solvent types on the e.d.a. and the hydrogenation activity, especially for modified Raney nickel catalysts [19,37,38].

Numerous investigations on the TA-NaBr-MRNi catalytic system were carried out. However, no significant improvement has been achieved in relation to improving its hydrogenation activity. The aim of our present investigation is to enhance the hydrogenating activity and maintain the high e.d.a. of the TA-MRNi catalyst, based on the idea that NaBr was directly added to the hydrogenation solvents as a “promoter” [39]. As expected, the improved TA-MRNi-NaBr catalytic system showed excellent e.d.a. and hydrogenating activity in the hydrogenation of MAA. The optical yield of over 85% was achieved at the H<sub>2</sub> initial pressure of 0.6 MPa, and the hydrogenation rate was enhanced significantly. In addition, the TA-MRNi-NaBr catalyst was repeatedly used in our research.

## 2. Experimental

### 2.1. Chemicals

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

### 2.2. Catalyst preparation

#### 2.2.1. Raney nickel

W-4 types of Raney nickel were freshly prepared with the conventional method [40]. Six grams of the Al–Ni alloy was added in portions into an alkaline solution (15 g sodium hydroxide 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.

#### 2.2.2. The improved TA-MRNi catalyst

First, the Raney Ni catalyst (usually 3 g) was washed 10 times with 250 mL distilled water, and then put into 400 mL 1 wt.% aqueous solution of (*R,R*)-(+)-tartaric acid. This washing procedure was carried out under stirring with a magnetic stirrer for a

period of 10 min. The catalyst was then washed with 250 mL distilled water and introduced into the aqueous solution of tartaric acid (94 °C, 250 mL, *c* = 0.2 mol/L) and modified twice. The pH of the modifying solution (adjusted with 1 mol/L NaOH) was measured by a digital pH meter (Hanna pH 211 with a combined electrode HI 1131B, Portugal). Then, the catalyst was washed 10 times with 250 mL distilled water and then 5 times with 100 mL methanol. In this step, no NaBr was added into the modifying solution.

#### 2.2.3. The conventional TA-NaBr-MRNi catalyst

The conventional TA-NaBr-MRNi catalyst was prepared according to Ref. [33]. (*R,R*)-Tartaric acid (3.8 g) and NaBr (38 g) dissolved in distilled water (380 mL), the pH of which was adjusted to 3.2 by adding 1 M NaOH. The resulting solution worked as the modifying solution. Raney nickel (usually 3 g) was modified twice with a half portion of the hot modifying solution at 94 °C, each time for 30 min. The supernatant solution was removed by decantation. Then, the catalyst was successively washed five times with 200 mL portions of distilled water and five times with 100 mL methanol.

#### 2.2.4. The TA-NaBr-MRNi-U catalyst

The TA-NaBr-MRNi-U catalyst was prepared by the same procedure as the TA-NaBr-MRNi catalyst, except for introducing the ultrasonic-irradiation method in the process of washing Raney nickel. The freshly prepared Raney nickel was freed from NaOH, and immersed into 100 mL distilled water. Then, it was subjected to ultrasonic irradiation in a bath type ultrasound generator and the supernatant suspension was removed by decantation. The same operation was repeated two more times to afford the RNi-U catalyst.

### 2.3. Catalyst characterization

The following physical–chemical methods were applied: ICP (IRIS/ES TJA), total surface area determination using the BET method (Micromeritics ASAP 2010), scanning electron microscopy with an X-ray microanalyzer (SEM–EDAX) (Hitachi S-4800 microscope) and transmission electron microscopy (TEM) (Hitachi-600 microscope).

### 2.4. Enantio-selective hydrogenation of methyl acetoacetate

A stainless steel autoclave (100 mL) with a magnetic stirrer was used for high-pressure hydrogenation reactions. The modified TA-MRNi catalyst (0.2 g) was quickly immersed into 4 mL reaction solvent, into which an appropriate amount of NaBr was directly added, and then 2 mL MAA was introduced into it. The reaction temperature was varied between 60 and 100 °C and the initial hydrogen pressure from 0.6 to 9 MPa. Samples of the reaction mixture were withdrawn 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. Thus, the hydrogenation products with a chemical purity of more than 99% (GC analysis) were obtained.

### 2.5. Determination of optical yield

The optical yield was determined polarimetrically by means of the optical activity measurement of the product in its pure state. Digital polarimeter PerkinElmer polarimeter-341 (USA) was used for measurement. The optical yield was then calculated in accordance with the following equation:

$$\text{optical yield (\%)} = \frac{[\alpha]_{\text{D}}^{20} \text{ product}}{[\alpha]_{\text{D}}^{20} \text{ of optically pure methyl 3-hydroxybutyrate}} \times 100$$

The specific optical rotation of the optically pure (*R*)-methyl-3-hydroxybutyrate ( $d = 1.055 \text{ g cm}^{-3}$ ) is  $-22.95^\circ$  (neat) [6].

### 2.6. Determination of hydrogenation rate

The hydrogenation rate was obtained from the amount of hydrogen consumption during the MAA hydrogenation reaction [23]. Just after the autoclave reached the fixed reaction temperature, the stirring was started and the reaction time was calculated.

## 3. Results and discussion

### 3.1. The characterization of the chirally modified Raney nickel catalyst

It is worth noting that the textural properties of the tartaric acid modified Raney nickel catalyst are evidently dependent on the pH of the modifying solution. In the whole characterization process, the improved TA-MRNi catalyst was prepared by immersing the Raney nickel into a tartaric acid solution, of which the pH was adjusted to 4.4, because the highest optical yield was attained as will be described in Section 3.2.3.

The ratio of Al–Ni in each sample was determined by ICP, and the results are shown in Table 1. Since each sample had the high chemical activities and can easily be oxidized in the air, they were weighed in methanol before analysis. After dried in vacuo, the samples were dissolved in a solution of about 95 mL distilled water and 5 mL concentrated hydrochloric acid. Tai et al. demonstrated that the content of Al had important influence on the efficiency of the enantio-selective hydrogenation

Table 1  
The element weight ratio Al–Ni measured by ICP

Entry	Catalyst	Weight ratio Al–Ni
1	TA-MRNi	0.071
2	TA-NaBr-MRNi	0.118
3	TA-NaBr-MRNi-U	0.104
4	RNi	0.159
5	RNi-U	0.129

of MAA [26,33]. In order to enhance the hydrogenation activity of the TA-NaBr-MRNi catalyst, they introduced ultrasound irradiation in the preparation of Raney nickel. This treatment was based on the idea that most of Al could be removed from the surface of the catalysts, thus increasing finely pulverized pure nickel. According to the idea of Tai et al., our investigation was engaged in preparing the chirally modified Raney Ni catalysts with high Ni contents, aiming at achieving highly efficient enantio-selective hydrogenation of MAA. From the characterization data obtained, it was evident that the improved TA-MRNi catalyst had the lowest weight ratio of Al–Ni, compared with the conventional TA-NaBr-MRNi and TA-NaBr-MRNi-U catalysts.

The BET surface area and the pore volume of each sample were determined by the physical adsorption of nitrogen at  $-195^\circ\text{C}$ . In order to accurately weigh each sample and prevent its oxidation, the fresh catalysts were firstly washed five times with methanol, and then five times with diethyl ether. The resulting wet catalysts were dried at  $40^\circ\text{C}$  by blowing argon for 2 h. Before analysis, the samples were degassed at  $60^\circ\text{C}$  and  $1.07 \times 10^{-3} \text{ kPa}$  for 12 h. The results of the properties of the different chirally modified catalysts are shown in Table 2. It was found that the TA-NaBr-MRNi catalyst and TA-NaBr-MRNi-U catalyst had almost the same structure. The improved TA-MRNi catalyst had the largest surface area and smallest pore diameter.

SEM images of the chirally modified Raney Ni catalysts are shown in Fig. 1. It could be seen that Raney nickel had a flat surface before acid-corrosion, and due to more extensive acid-corrosion, there existed densely spread hollows on the surface of the improved TA-MRNi catalyst, the amount of which was far more than that on the surface of the conventional TA-NaBr-MRNi. EDAX is used to determine the rough weight ratio of Al–Ni, as shown in Table 3. It was found that the improved TA-MRNi catalyst contained the lowest Al content, which was in accordance with the results obtained from ICP.

TEM images of the Raney nickel, TA-NaBr-MRNi and improved TA-MRNi catalysts are shown in Fig. 2. It was clear that Raney nickel catalyst formed larger compact particles. The particles of the modified catalyst were more dispersed, and the improved TA-MRNi catalyst was the most dispersed. These

Table 2  
Textural properties of the modified catalysts

Entry	Catalyst	BET surface ( $\text{m}^2 \text{g}^{-1}$ )	Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Average pore diameter (nm)
1	TA-MRNi	20.1	0.075	12.01
2	TA-NaBr-MRNi	12.4	0.081	22.13
3	TA-NaBr-MRNi-U	12.3	0.059	15.69

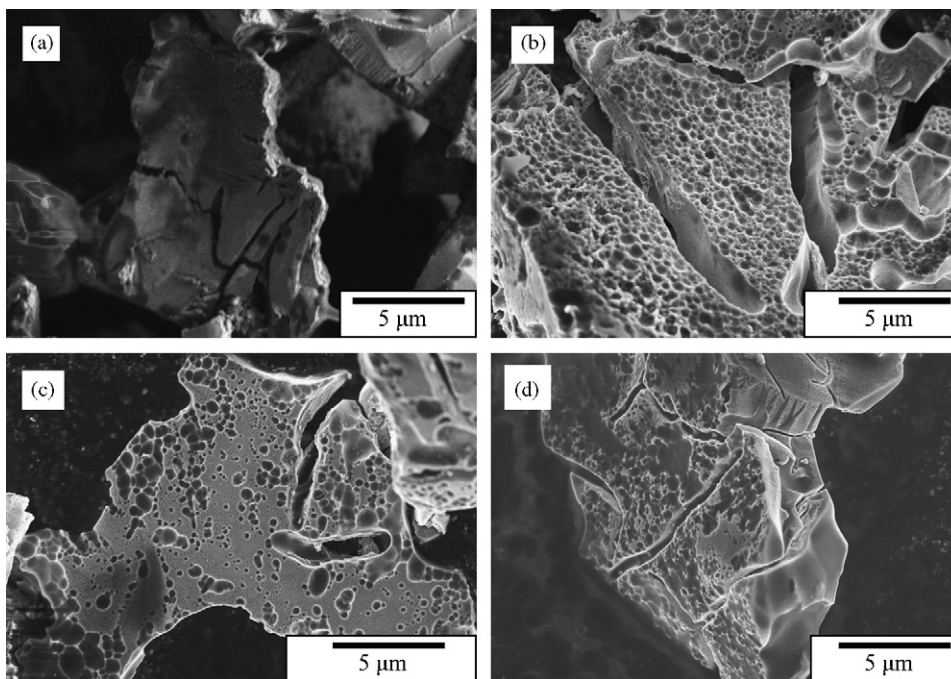


Fig. 1. SEM images of Raney nickel (a), TA-MRNi (b), TA-NaBr-MRNi (c) and TA-NaBr-MRNi-U (d).

phenomena indicated that the Raney nickel catalyst could be corroded more completely while modified only with tartaric acid. Meanwhile, it was in accordance with the idea of Kukula and Červený, who demonstrated that the presence of NaBr in the modifying solution resulted in a lower degree of nickel leaching [36].

From the data obtained, the properties of the improved TA-MRNi catalyst were much different from the conventional chirally modified Raney nickel catalyst. The method of modifying Raney nickel only with tartaric acid could increase the chance of Al and Ni being corroded from the Raney nickel surface, thus leading to higher contents of Ni, larger surface area, more acid-corrosion and more dispersed particles of the TA-MRNi catalyst.

### 3.2. Influence of the modifying parameter and reaction variables on hydrogenation rate and optical yield

#### 3.2.1. The influence of solvent

Hydrogenation activities as well as e.d.a. of the tartaric acid modified Raney nickel catalyst are clearly dependent on the reaction solvents. Recently, Kukula and Červený have reported that

Table 3  
Al and Ni content in modified nickel catalysts measured by EDAX

Entry	Catalyst	Al (wt.%)	Ni (wt.%)	Al–Ni
1	Raney Ni	19.9	80.1	0.248
2	TA-MRNi	1.36	98.6	0.014
3	TA-NaBr-MRNi	4.24	95.8	0.044
4	TA-NaBr-MRNi-U	1.90	98.1	0.019

the reaction performed in methanol was five times as fast as in THF, but that the optical yield was significantly lower. When methanol was used as the reaction medium, the highest optical yield of 37.3% was attained [37]. On the contrary, Lipgart et al. claimed the higher optical yield in MeOH than in THF over modified Raney nickel [38]. Keane also reported higher optical yield for BuOH over Ni/SiO<sub>2</sub> [19]. However, their optical yield attained were 19 and 27%, respectively [38,19]. The dependence of the optical yield and the hydrogenation activity on the solvent types indicated that it was necessary to further investigate the influence of solvent types on hydrogenation rate and optical yield.

The influence of the selected solvents on the hydrogenation activities and e.d.a. can be seen from Table 4. In contrast to the findings of Kukula and Červený, the hydrogenation activity and the e.d.a. increased as follows, THF < BuOH < EtOH < MeOH. In MeOH the reaction was 7.5 times as fast as in THF, and the optical yield was 3 times as high. It showed that high hydrogenation rate and optical yield could be achieved when methanol served as the reaction medium.

Table 4  
Dependence of optical yield and hydrogenation rate on different solvents

Entry	Solvent	Hydrogenation rate (mmol g <sup>-1</sup> h <sup>-1</sup> )	Optical yield (%)
1	THF	31	24
2	BuOH	46	64
3	EtOH	92	71
4	MeOH	230	75

Modifying conditions:  $c_{TA} = 0.2$  mol/L, pH 4.0,  $T = 94$  °C,  $t = 60$  min; reaction conditions: solvent (4 mL), MAA (2 mL), catalyst (0.2 g), NaBr (10 mg), H<sub>2</sub> (6 MPa), 60 °C.



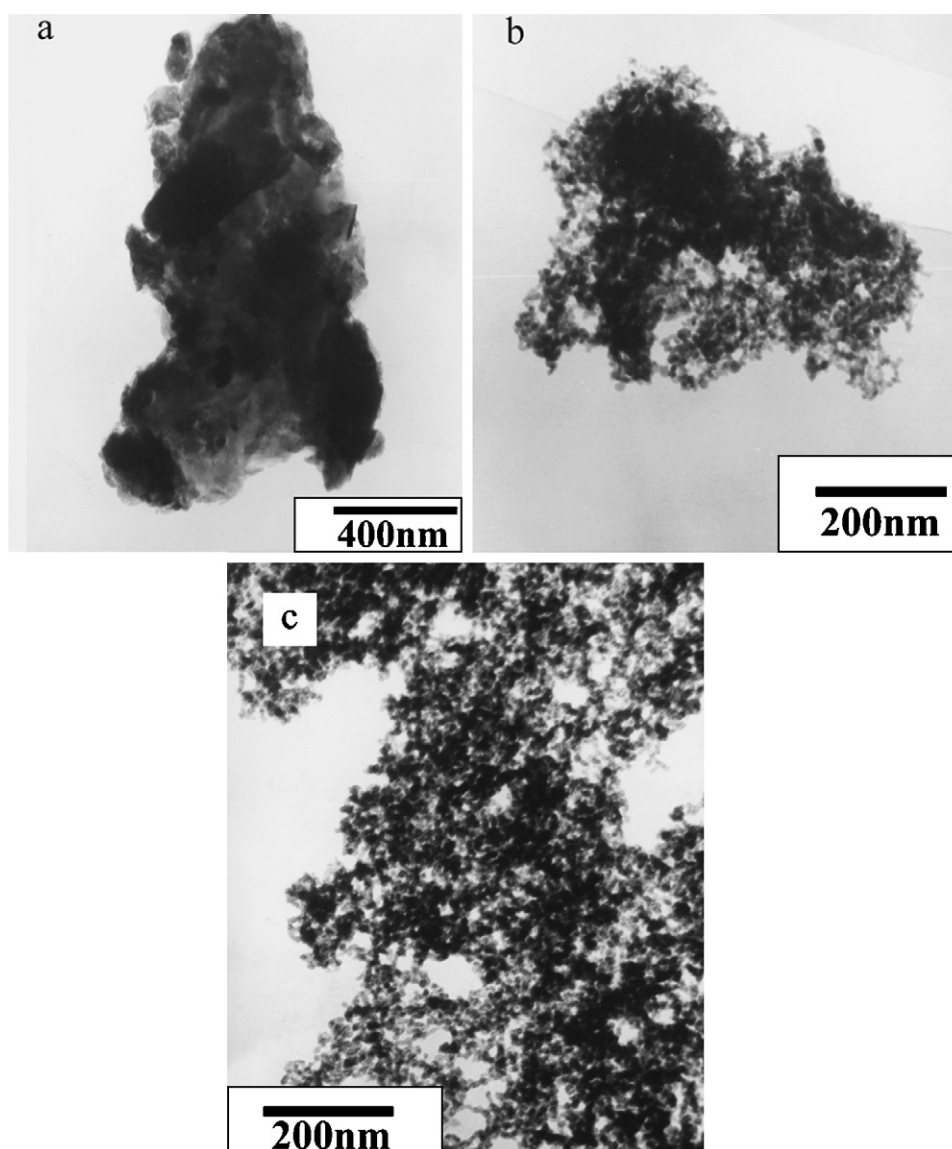


Fig. 2. TEM images of Raney nickel (a), TA-NaBr-MRNi (b) and TA-MRNi (c).

### 3.2.2. The influence of types of the inorganic salts added to the reaction medium

Table 5 shows the effects of the inorganic salts dissolved in the solvent on the hydrogenation rates and e.d.a. Except for NaI and  $(C_4H_9)_4NBr$ , the addition of inorganic salts could clearly enhance the hydrogenation activities. The order of ions giving a higher optical yield was as follows,  $Br^- > Cl^- > F^- > I^-$ . In addition, the highest optical yield of 76% and the hydrogenation rate of  $230 \text{ mmol g}^{-1} \text{ h}^{-1}$  were achieved, when NaBr was added to methanol. However, the addition of  $(C_4H_9)_4NBr$  had no effect on the hydrogenation rate. Obviously,  $Na^+$  was an important ingredient for attaining a high optical yield and a high hydrogenation rate. The results were generally in accord with the findings of Osawa et al., who reported that NaBr added to the reaction medium had the following roles: (i)  $Na^+$  increased the optical yield and the hydrogenation rate and (ii)  $Br^-$  increased the optical yield and decreased the hydrogenation rates [23].

### 3.2.3. The influence of modifying pH

It has been well known that the e.d.a. of the tartaric acid modified Raney nickel catalyst was strongly affected by the modifying

Table 5  
Dependence of optical yield and hydrogenation rate on inorganic salts

Entry	Inorganic salt (mmol)	Hydrogenation rate ( $\text{mmol g}^{-1} \text{ h}^{-1}$ )	Optical yield (%)
1	NaF (0.238)	92	48
2	NaCl (0.238)	92	67
3	NaBr (0.238)	230	76
4	NaI (0.119)	12	15
5	KCl (0.238)	31	27
6	KBr (0.238)	46	44
7	LiBr (0.238)	46	23
8	$(C_4H_9)_4NBr$ (0.0793)	23	28
9	–	23	13

Modifying conditions:  $c_{TA} = 0.2 \text{ mol/L}$ , pH 4.0,  $T = 94^\circ\text{C}$ ,  $t = 60 \text{ min}$ ; reaction conditions: methanol (4 mL), MAA (2 mL), catalyst (0.2 g),  $H_2$  (6 MPa),  $60^\circ\text{C}$ .

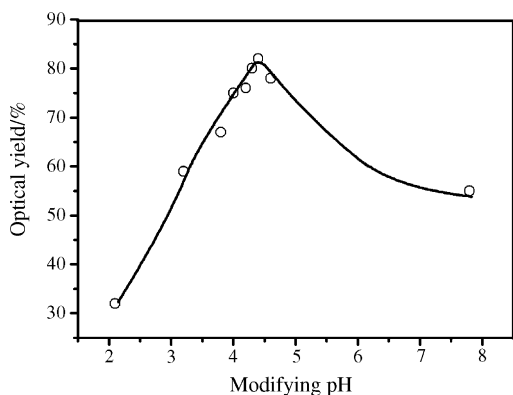


Fig. 3. Dependence of the optical yield on modifying pH. Modifying conditions:  $c_{TA} = 0.2 \text{ mol/L}$ ,  $T = 94^\circ\text{C}$ ,  $t = 60 \text{ min}$ ; reaction conditions: methanol (4 mL), MAA (2 mL), catalyst (0.2 g), NaBr (10 mg),  $\text{H}_2$  pressure (6 MPa),  $60^\circ\text{C}$ .

pH [41]. Since Raney Ni was modified only with the tartaric acid aqua solution in our experiments, the optimal pH of the modifying solution would be correspondingly different from that of the conventional modifying method (usually the optimal pH 3.2). Thus, the relation between the modifying pH and the optical yield of the improved TA-MRNi-NaBr catalytic system was examined in order to find out the optimal pH. As shown in Fig. 3, the optical yields first rose with increasing pH value, and then sharply declined for  $\text{pH} > 4.4$ . The highest optical yield could be achieved when the modifying pH was 4.4.

#### 3.2.4. The effect of the amount of NaBr

The effect of the amount of NaBr (which was directly added to the reaction medium) on the optical yield is shown in Fig. 4. Without addition of NaBr, the optical yield was lower than 13%, and the hydrogenation rate was much lower. The addition of 4 mg NaBr significantly increased the e.d.a. and hydrogenation activity. However, an excess of NaBr added into the reaction medium slightly decreased the e.d.a. of the TA-MRNi-NaBr catalyst. It could be seen that when the amount of NaBr was in the range of 15–20 mg, a high optical yield of 83% could be achieved. These results strongly indicated that  $\text{Br}^-$  could rapidly deactivate the n.e.d. sites before the hydrogenation reaction started.

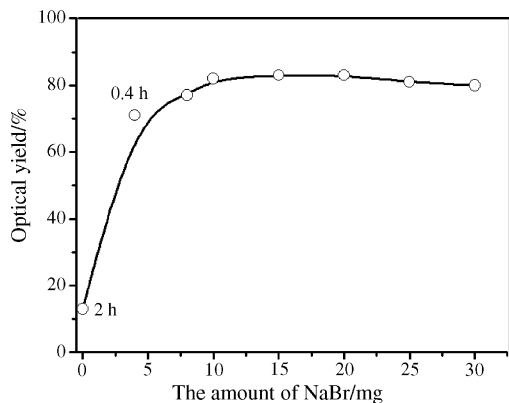


Fig. 4. Dependence of optical yield on the amount of NaBr. Modifying conditions:  $c_{TA} = 0.2 \text{ mol/L}$ ,  $\text{pH} = 4.4$ ,  $T = 94^\circ\text{C}$ ,  $t = 60 \text{ min}$ ; reaction conditions: methanol (4 mL), MAA (2 mL), catalyst (0.2 g),  $\text{H}_2$  pressure (6 MPa),  $60^\circ\text{C}$ .

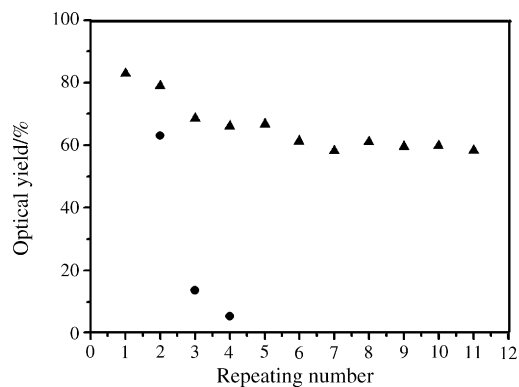


Fig. 5. Effect of the NaBr on the durability of the TA-MRNi catalyst. ( $\blacktriangle$ ) 15 mg NaBr was added to the reaction medium and ( $\bullet$ ) without NaBr. Modifying conditions:  $c_{TA} = 0.2 \text{ mol/L}$ ,  $\text{pH} = 4.4$ ,  $T = 94^\circ\text{C}$ ,  $t = 60 \text{ min}$ ; reaction conditions: methanol (4 mL), MAA (2 mL), catalyst (0.2 g),  $\text{H}_2$  pressure (6 MPa),  $60^\circ\text{C}$ .

#### 3.2.5. Recycling tests of the TA-MRNi-NaBr catalyst

The disadvantage of the conventional pre-modified Raney nickel catalyst is the lack of durability with repeated use. Tai et al. claimed that the e.d.a. of the conventional TA-NaBr-MRNi catalyst decreased to almost zero after three successive runs of hydrogenation of methyl acetoacetate [42]. Recently, Osawa et al. reported that the in situ modified Raney nickel catalyst showed low optical yields of ca. 30%, and these low optical yields were maintained during 10 runs [24]. We tried to improve the durability of the chirally modified Raney Ni catalysts. Fig. 5 shows the effect of NaBr on the durability of the TA-MRNi-NaBr catalyst. When 15 mg NaBr was added to the reaction media only during the first run, the optical yield was 83%; however, it sharply decreased to 5% in the next three runs, due to no further addition of NaBr. These results were in accordance with those obtained by Tai et al. [42]. However, the durability of the improved TA-MRNi-NaBr catalyst could be amended when 15 mg NaBr was added in every run. Although the optical yields decreased from the first to the sixth runs, it could remain about 60% till the eleventh run. These results strongly indicated that NaBr played an important role in attaining high durability. Since NaBr could be easily washed from its surface, no further addition of NaBr in the hydrogenation reaction would lead to lower e.d.a. In addition, the lapse of the e.d. sites may be one of the reasons for decreasing optical yields.

#### 3.2.6. Influence of the introduction of ultrasonic-irradiation, temperatures and hydrogen pressures

The application of ultrasonic-irradiation in the preparation process of Raney nickel removed most of the residual aluminum compounds, and the nickel particles were finely pulverized [33]. Table 6 shows that as far as the TA-MRNi-NaBr catalyst was concerned, with the application of ultrasonic-irradiation, no significant improvement on the e.d.a. and the hydrogenation activity was observed. By employing our improved modification method, nearly all the residual aluminum compounds were removed by acid-corrosion, which also led to the larger surface area of the TA-MRNi-NaBr catalyst.

Table 6  
Enantio-selective hydrogenation of MAA under different reaction conditions

Entry	Catalyst	T (°C)	H <sub>2</sub> (MPa)	Hydrogenation rate (mmol g <sup>-1</sup> h <sup>-1</sup> )	Optical yield (%)
1	TA-MRNi-U-NaBr <sup>a</sup>	60	6	230	81
2	TA-MRNi-NaBr	60	9	307	77
3	TA-MRNi-NaBr	60	6	230	83
4	TA-MRNi-NaBr	60	2	115	84
5	TA-MRNi-NaBr	60	0.6	230	85
6	TA-MRNi-NaBr	100	6	307	75
7	TA-MRNi-NaBr	100	2	153	75
8	TA-NaBr-MRNi <sup>b</sup>	100	9–10	9	80
9	TA-NaBr-MRNi-U <sup>c</sup>	100	9–10	18	86

Modifying conditions:  $c_{TA} = 0.2$  mol/L, pH 4.4,  $T = 94$  °C,  $t = 60$  min; reaction conditions: MAA (2 mL), methanol (4 mL), catalyst (0.2 g), NaBr (15 mg).

<sup>a</sup> The ultrasonic-irradiated Raney nickel was used.

<sup>b</sup> Ref. [14], modifying condition:  $c_{TA} = 1$  wt.%,  $c_{NaBr} = 10$  wt.%, pH 3.2; reaction solvent: methyl propionate.

<sup>c</sup> Ref. [2], the modifying conditions and reaction solvent were the same as Ref. [14], except that the ultrasonic-irradiated Raney nickel was used.

Table 6 also shows that at 60 °C, the optical yield was unaffected in the hydrogen pressure range of 0.6–6 MPa, but the hydrogenation rate decreased with decreasing hydrogen pressure. When the hydrogen pressure was increased from 6 to 9 MPa, the optical yield of the TA-MRNi-NaBr catalyst decreased. These results were in agreement with that obtained by Lipgart et al., who discovered that the optical yield of the ethyl acetoacetate hydrogenation over the TA-NaBr-MRNi catalyst was hardly changed by varying the hydrogen pressure [38]. Yet, the result was different from the findings of Kukula and Červený, who reported that the optical yield increased with an increasing of the pressure, and it remained almost constant at pressures higher than 10 MPa [37]. The optical yield and the hydrogenation rate were also affected by the reaction temperature. The higher optical yield was obtained at 60 °C than at 100 °C. Thus, high optical yields could be obtained under the conditions of low hydrogen pressure and low reaction temperature.

In our research, the high optical yield of 85% was achieved in the hydrogenation of MAA under much less demanding conditions (0.6 MPa, 60 °C, 1 h), which strongly suggested that the improved TA-MRNi-NaBr catalytic system had highly enantio-selective hydrogenation efficiency.

#### 4. Conclusion

The improved TA-MRNi-NaBr catalysts were prepared using a new modifying method (Raney nickel was modified only with (*R,R*)-tartaric acid). Characterization of the improved TA-MRNi catalyst by ICP, N<sub>2</sub> adsorption/desorption, SEM-EDAX and TEM revealed a lower weight ratio of Al–Ni, higher total surface area and more acid-corrosion on its surface, compared with the conventional TA-NaBr-MRNi catalysts. In the enantio-selective hydrogenation of MAA, the improved TA-MRNi-NaBr catalyst showed high efficiency when methanol was used as the hydrogenation reaction medium, in which an appropriate amount of NaBr was dissolved. The maximal optical yield of 85% was achieved under much less demanding conditions (0.6 MPa, 60 °C, 1 h), and the hydrogenation rate was greatly enhanced than ever before. In addition, the improved TA-MRNi-NaBr catalyst showed comparatively high durability. The optical

yield could remain about 60% till the eleventh run when 15 mg NaBr was added in every run.

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