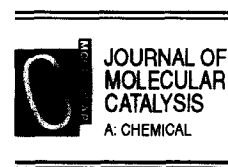




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Influence of the starting Ni–Al phases on the enantio-differentiating properties of tartaric acid-modified Raney nickel

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Abstract

Using well-defined pure phases: Al_3Ni_2 , Al_3Ni and the $\text{Al}/\text{Al}_3\text{Ni}$ eutectic we prepared tartaric acid-modified Raney nickel (RNi_{3-2} , RNi_{3-1} , RNiE). Their catalytic properties were investigated, in the hydrogenation of methyl acetoacetate at constant hydrogen pressure (1.1 MPa) and temperature (333 K) in ethyl acetate. The enantiomeric excess went from 16% on RNi_{3-2} to 25% on RNi_{3-1} and up to 45% on RNiE which has been prepared using an aluminium in a high state of purity. In the presence of sodium bromide in the modifying solution, RNiE remains the best catalyst: with an ee of 80%.

Keywords: Enantioselectivity; Nickel–aluminium; Tartaric acid modification; Raney nickel

1. Introduction

Raney nickel modified with tartaric acid (TA) is one of the earliest heterogeneous catalysts for the enantioselective hydrogenation of organic substrates. A second modifying reagent, sodium bromide, causes a strong enhancement of the enantio-differentiating ability. Carboxylic acids which are added to the reaction system exert a remarkable effect on the optical yield of the hydrogenation of prochiral ketones. Thus, with small amounts of acetic acid, a TA/NaBr modified Raney nickel gave about 90% enantiomeric excess (ee) in the hydrogenation of methyl ace-

toacetate to methyl 3-hydroxybutyrate [1], whereas large amounts of pivalic acid were used to obtain excellent optical yields in the hydrogenation of 2-alkanones [2,3]. A TA/NaBr-modified Raney nickel prepared from ultrasonicated Raney nickel showed excellent enantio-differentiating activity in the hydrogenation of diketones to 1,3-diols of C_2 symmetry [4].

It has been shown ([1–4] and references therein) that optical yields over modified Raney nickel depend on a large number of catalyst preparation and reaction variables, however the effect of the starting Ni–Al alloys on the enantio-differentiating properties of this catalyst has not been considered. Freel et al. [5] found the commercial 50–50 wt.% Ni–Al alloy to contain the phases Al_3Ni_2 , Al_3Ni and the $\text{Al}/\text{Al}_3\text{Ni}$

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eutectic. Catalysts obtained from alloy specimens of different phase compositions, i.e., with $\text{Al}_3\text{Ni}_2/\text{Al}_3\text{Ni}$ ratios equal to 9, 3 and 0.95, were investigated in the enantioselective hydrogenation of ethyl acetoacetate [6] but the alloys as well as the catalysts contained chromium and titanium, and the presence of these metals cast doubt on the conclusions.

Previously, Raney nickel catalysts, prepared from well-defined pure phases, have been characterized [7,8]. In this paper, the results of the enantioselective hydrogenation of methyl acetoacetate over RNi_{3-2} , RNi_{3-1} , RNi_E catalysts obtained from well-defined pure phases, Al_3Ni_2 , Al_3Ni and the $\text{Al}/\text{Al}_3\text{Ni}$ eutectic, respectively, are presented. In order to shed light on the effect of the starting Ni–Al phases on the enantioselective properties of the catalysts, the reaction was first examined with no other additive than tartaric acid. To make the study complete, reactions were also carried out, with catalysts obtained in the presence of sodium bromide using more drastic conditions for the modifying treatment.

2. Experimental

2.1. Precursor alloys

The precursor alloys were all prepared in an induction furnace by P. Colin-Urtado and S. Hamar-Thibaut (LTPCM CNRS, URA 29) or by fusing of their elements (Imphy. S.A).

2.2. Catalyst preparation

The alloys were crushed screened ($20 \leq d$ (μm) ≤ 40), with the exception of the eutectic alloy which was cut into thin chips, and treated twice with a sodium hydroxide solution (6 M) at its boiling point for 2 h, by a previously described procedure [8]. The catalysts were stored under a molar sodium hydroxide solution.

2.3. Characterizations

The overall composition of each catalyst was determined by chemical analysis of the samples dissolved in nitric acid.

The total surface areas were measured by nitrogen adsorption at the temperature of liquid nitrogen (BET method). Before measuring the total surface, the catalyst was first washed with water and methanol, which was slowly evaporated at room temperature and then desorbed at 373 K for 4 h under high vacuum.

The nickel surface area was determined from hydrodesulfurization of 3-methylthiophene (3-Meth) in the liquid phase. The stoichiometry of the reaction was taken as $\text{S}/\text{Ni} = 1/2$ [8]. The reaction was performed at 363 K under a hydrogen pressure of 1.1 MPa, using 0.3–0.6 g of the catalyst and 1.85 mmol of 3-Meth in 150 ml of cyclohexane. After 2 h, which is sufficient for complete reactive adsorption of 3-Meth on the catalyst surface, the amount of 3-Meth remaining in the reaction mixture was determined by gas chromatography with a (20%) Hallcomid on a Chromosorb W column, with n-octane as internal standard.

2.4. Modification of the catalyst

2.4.1. Procedure a (TA modified RNi)

The catalyst (0.8 g) previously washed with distilled water ($100 \text{ ml} \times 5$) was soaked in 100 ml of an aqueous solution containing (2*R*,3*R*)-tartaric acid (1.6 g) at 353 K for 1 h 30 min. The pH value of this solution was adjusted to 5.1 with NaOH 2 M.

2.4.2. Procedure b (TA–NaBr modified RNi) [9]

Modifying solution: (2*R*,3*R*)-tartaric acid (1 g/100 ml) and NaBr (10 g/100 ml) were dissolved in water and the pH of the solution was adjusted to 3.2 with NaOH 2 M. The resulting solution was heated at 373 K.

50 ml of the hot modifying solution was poured on the RNi (0.8 g) previously washed with water ($100 \text{ ml} \times 5$). The mixture was

maintained at 373 K for 30 min, then the supernatant solution was removed by decantation and the catalyst was washed with 20 ml of water. This catalyst was again immersed in 50 ml of the modifying solution and the procedure repeated.

After removal of the modifying solution (procedure a or b) by decantation, the catalyst was successively washed with a 10 ml portion of water, two 10 ml portions of 2-propanol and three 10 ml portions of ethyl acetate. The catalyst thus obtained was employed in the hydrogenation.

2.5. Methyl acetoacetate (MAA) hydrogenation

Hydrogenation was carried out in ethyl acetate solution in a 250 ml static reactor at constant hydrogen pressure (1.1 MPa) and temperature (333 K) with a stirring speed of 1600 rpm. Before the introduction of MAA, the reactor containing a suspension of the catalyst in ethyl acetate (70 ml) was purged with a flow of hydrogen. Temperature was then raised to 333 K and MAA was introduced.

The end of the reaction (conversion $\geq 98\%$) was controlled by gas chromatographic analysis of samples withdrawn from the reaction mixture.

After removal of the catalyst by decantation and that of ethyl acetate by evaporation, the solution was distilled under reduced pressure. This distillation gave methyl 3-hydroxybutyrate with a chemical purity higher than 98%.

2.6. Determination of enantiomeric excess (*ee*)

The enantiomeric excesses were determined from measurements of optical rotation (Perkin Elmer 241 Polarimeter)

$$ee (\%) = \frac{[\alpha]_D^{20} \text{ of hydrogenated product}}{[\alpha]_D^{20} \text{ of pure enantiomer}} \times 100$$

The specific optical rotation of the (*R*)-methyl 3-hydroxybutyrate used was: $[\alpha]_D^{20} = -22.95^\circ$ (neat).

3. Texture of tartaric acid modified Raney nickel prepared from commercial 50 wt.% Ni–Al

Since the catalyst is corroded during the modifying treatment with tartaric acid, the surface state of the resulting catalyst is no longer the same as initial Raney nickel. Therefore the total BET surface of the catalyst was measured by liquid nitrogen adsorption, (i) before soaking Raney nickel in the solution of tartaric acid, (ii) after soaking, and a (iii) after suspending the modified catalyst in a 1 M NaOH solution to remove the adsorbed tartaric acid [10]. The results are given (Table 1) with the nickel surface area measured by hydrodesulfurization of 3-methylthiophene [8] at the same stages of preparation.

The tartaric acid treatment increased the BET surface. Different possible explanations are envisaged for the increase in total surface with the modifying tartaric acid treatment:

(1) One could postulate a change in pore structure since the aluminium content of the catalyst was decreased by the TA treatment. It has been shown [11] that during the course of the alkali leaching of an alloy containing 50 wt.% of nickel, the surface area and the pore volume increased regularly with an increasing extent of aluminium extraction.

(2) It could be suggested that it resulted from a decrease in the crystallite size of nickel, this metal being partially oxidised by the TA treatment.

Table 1
Texture of the RNi catalyst prepared from commercial 50 wt.% Ni–Al alloy

Treatment	S_{BET}^a ($\text{m}^2 \cdot \text{g}^{-1}$)	S_{Ni}^b ($\text{m}^2 \cdot \text{g}^{-1}$)
none	74	65
TA treatment	95	35
TA treatment + NaOH treatment	91	32

^a Total surface area.

^b Metallic surface area.

(3) It could be attributed to aluminium hydroxide precipitate or alumina trihydrate since the pH of the TA solution fixed at 5.1 at the beginning of the treatment went up to 9 at the end.

The nickel surface area, measured in the liquid phase, by hydrodesulfurization of 3-methylthiophene is the area of the surface Ni atoms in the metallic state exposed to organic reagents since we showed previously that nickel oxide and aluminium did not react with thiophene. The TA treatment decreased the nickel area to half of the original value, but this area remained almost unchanged by the sodium hydroxide treatment, therefore the absorbed TA is efficiently removed from the surface by 3-methylthiophene.

The increase of the BET surface accompanied with the decrease of the nickel area, could be attributed to an increased extend of aluminium oxidation and to alumina deposition. Thus aluminium extraction could increase the total surface, whereas alumina could fill or block pores and make some of the nickel atoms inaccessible to 3-methylthiophene.

We think that the nickel metallic area is representative of the nickel atoms accessible to organic reactants, since the hydrodesulfurization of 3-methylthiophene is performed in the liquid phase with experimental conditions close to that used for the catalytic experiments. Thus the S_{Ni} will be used in order to compare the catalysts prepared from the pure phases.

4. Physical properties

4.1. Precursor alloys

According to the Ni–Al binary phase diagram, the 50 wt.% Ni–Al alloy contains three different binary phases formed during the solidification: Al_3Ni_2 (hexagonal lattice), Al_3Ni (orthorhombic lattice) and Al/ Al_3Ni eutectic. Thus, the commercial alloy is a mixture of

Table 2

Composition of the starting alloys expressed in atomic percentage

Alloy	Al (at.%)	Ni (at.%)
Al_3Ni_2	58.3	41.2
Al_3Ni	74.8	24.9
Al/ Al_3Ni eutectic	97.3	2.7

several intermetallic compounds. It has been shown by Anderson [5] that the average volume concentration of Al_3Ni_2 , Al_3Ni and eutectic are 58%, 40% and 2% respectively.

The metallurgical structure of the Al_3Ni_2 and Al_3Ni alloys show that they are monophasic (99 vol%). The elemental composition is given in Table 2.

The eutectic alloy presents two phases with a fibrous morphology. This eutectic is made of Al_3Ni fibres embedded in an Al matrix. The particular interest of this alloy as a Raney nickel precursor was pointed out for the first time in 1978 by Lemkey and Golden in their patent [12].

4.2. Catalysts

4.2.1. Structure

Raney nickel catalysts prepared from commercial alloy (RNi) Al_3Ni_2 alloy (RNi₃₋₂) and Al_3Ni alloy (RNi₃₋₁) are formed of small Ni crystallites of 6 to 8 nm connected in a porous agglomerate of several microns in diameter.

During the alkali leaching of the Al/ Al_3Ni eutectic alloy, the fibre morphology is kept. After the complete dissolution of the aluminium matrix, a porous fibrous nickel is produced by selective aluminium extraction out of the Al_3Ni fibres.

Thus the catalyst has the same fibrous structure as the starting alloy [13]. Furthermore, in the RNiE catalyst, the nickel crystallites which constitute these fibres have a definite orientation [14]. The RNiE catalyst can be regarded as single crystals having high specific area.

Table 3
Physical and catalytic properties of the catalysts modified with tartaric acid

Precursor alloy	Catalyst nomenclature	Atomic ratios				S_{Ni}^a ($m^2 \cdot g^{-1}$)		ee ^b (%)
		Unmodified		Modified		Unmodified	Modified	
		Al/Ni	Fe/Ni	Al/Ni	Fe/Ni			
50% wt Ni	RNi	0.0981	0.0051	0.0707	0.0053	61	35	27
Al ₃ Ni ₂	RNi ₃₋₂	0.2965	0.0024	0.2271	0.0027	65	35	16
Al ₃ Ni	RNi ₃₋₁	0.0587	0.0041	0.0558	0.0045	48	34	25
Al/Al ₃ Ni eutectic ^c	RNiE ₁	0.0400	0.0010	0.0406	0.0011	23	22	45
Al/Al ₃ Ni eutectic	RNiE ₂	0.0502	0.0393	0.0506	0.0386	35	25	17
Al ₇₅ Ni _{23.4} Fe _{1.6}	RNi ₃₋₁ (Fe promoted)	0.0908	0.0785	0.0801	0.0709	56	33	11

Procedure a: Catalyst (0.8 g) modified with 100 ml of an aqueous TA solution (1.6 g), pH = 5.1, 353 K, 1 h 30 min.

^a Metallic surface area.

^b ee = enantiomeric excess.

^c Prepared with highly pure (99.997%) aluminium.

4.2.2. Chemical compositions

4.2.2.1. Catalysts obtained by procedure a: i.e., using tartaric acid without additive at pH 5.1 (Table 3). The atomic ratios: Al/Ni and Fe/Ni were determined by chemical analysis of the catalysts before the TA treatment and after. One can notice that with all the catalysts, except those prepared from the eutectic, the TA treatment decreased the Al/Ni ratio, i.e., aluminium was more readily extracted by the acidic solution than nickel.

Furthermore, the higher the initial Al/Ni ratio was, the greater the aluminium extraction was. The RNiE₁ and RNiE₂ catalysts were corroded too, but the atomic ratio Al/Ni remained unchanged. Aluminium is usually contaminated with iron, during the preparation of the catalyst, aluminium is oxidized and dissolved as sodium aluminate, but iron remains on the catalyst. The higher the Al/Ni ratio in the alloy, the higher is the Fe/Ni ratio in the catalyst. For example RNi₃₋₁ prepared from the Al₃Ni phase contains twice as much iron as RNi₃₋₂ prepared from the Al₃Ni₂ phase. However the Fe/Ni ratio was small (< 0.005) but for RNiE₂ obtained from the Al/Al₃Ni eutectic (Al: 97.3 at.% Ni: 2.7 at.%) the Fe/Ni ratio was almost as high as the ratio Al/Ni: 0.039 as compared to 0.050. Therefore in order to obtain an iron free catalyst from the eutectic phase it is necessary to use in

the preparation of the alloy, an aluminium in a high state of purity.

Studies on chromium and molybdenum promoted Raney nickel [15,16] have shown that the residual aluminium content in the catalyst increases with the promoter atomic composition in the precursor alloy. Iron has the same effect, since the Al/Ni atomic ratio increases from 0.059 in RNi₃₋₁ to 0.091 in iron promoted RNi₃₋₁.

4.2.2.2. Catalysts obtained by procedure b: i.e., using a (TA + NaBr) solution at pH = 3.2 (Table 4). The drastic conditions of the procedure b have a large effect on the Al/Ni ratio, in particular, the aluminium content of RNi was only one half of that obtained with the procedure a. One can also notice that whereas the Al/Ni ratio in RNiE₁ remained unchanged with proce-

Table 4
Physical and catalytic properties of the catalysts modified with tartaric acid and NaBr

Catalyst	(Al/Ni) atomic ratio	S_{Ni}^a ($m^2 \cdot g^{-1}$)	ee ^b (%)
RNi	0.037	21	72
RNi ₃₋₂	0.195	27	65
RNiE ₁	0.033	17	80

Procedure b: Catalyst (0.8 g) modified twice with 50 ml of an aqueous solution (TA: 0.5 g NaBr: 5 g), pH = 3.2, 373 K, 30 mm.

^a Metallic surface area.

^b ee = enantiomeric excess.

cedure a, by procedure b, aluminium was more readily extracted than nickel, since the ratio dropped by 17%, from 0.040 to 0.033.

4.2.3. Metallic surface area

4.2.3.1. Catalysts obtained by procedure a (Table 3). The TA treatment decreased the metallic surface area and this phenomenon was more pronounced for catalysts with a high residual aluminium content. The behaviour of RNiE_1 was peculiar, no variation of the metallic surface area was observed, of course this unexpected result has been confirmed several times.

4.2.3.2. Catalysts obtained by procedure b (Table 4). Even with the drastic conditions of the procedure b, the metallic surface of RNiE_1 was almost unchanged. Whereas the nickel area of RNi was only one third of that measured without TA treatment. The unique morphology of the eutectic confers to the RNiE_1 catalyst this particular behaviour.

5. Hydrogenation of methyl acetoacetate (MAA) using Raney nickel modified with tartaric acid

The optical yield of the hydrogenation of MAA was known to be affected by the presence of sodium bromide in the modifying TA solution and by the presence of acetic acid in the reaction system as additive. However, in order to shed light on the effect of the starting Ni–Al phases on the enantioselective properties of the catalysts, the reaction was first examined with no other additive than tartaric acid. The enantiomeric excess (Table 3) went from 16% ($\text{RNi}_{3.2}$) to 25% ($\text{RNi}_{3.1}$) and up to 45% for the RNiE_1 issuing from the Al/Al₃Ni eutectic, which had been prepared using highly pure aluminium. In the same conditions, a catalyst obtained from a commercial 50 wt.% nickel alloy gave an ee of 27%.

Two possible explanations are envisaged for the remarkable properties of RNiE_1 .

(1) There is a correlation [9,10] between the aluminium content of Raney nickel catalysts and the ee of those catalysts modified with tartaric acid, thus RNiE_1 with the lowest Al/Ni atomic ratio is the most selective catalyst, the reverse is observed with $\text{RNi}_{3.2}$.

(2) It has been proposed [17] that the pure crystalline nickel domains are the enantioselective sites, thus the particular morphology of RNiE produced by selective aluminium extraction out of the Al₃Ni fibres, with preferential orientation of the nickel crystallites contributed to the good ee observed. The good performance of this catalyst could be attributed to its better fine scale order. Furthermore it has been reported by Nitta [18] that the enantioselectivities of nickel catalyst modified by TA are related to the mean crystallite size of nickel in the catalyst: a higher optical yield being observed with a larger crystallite size. It was also suggested that the size of ensembles of regularly arranged nickel atoms on the catalyst surface is an important factor for a catalyst to be enantioselective. Since the nickel crystallites are oriented in the fibres which constitute the RNiE catalyst, the nickel atoms are regularly arranged, and the high selectivity observed on RNiE is in accordance with the suggestions of Nitta et al. The detrimental effect of iron can be attributed to a decrease of the surface order, this metal being principally located at the catalyst surface.

In order to explain the dramatic drop in ee on going from RNiE_1 to RNiE_2 , an iron promoted $\text{RNi}_{1.3}$ has been tested. As expected the ee decreased from 25% to 11%, the residual aluminium content was also modified by the presence of the promoter but as compared to $\text{RNi}_{3.2}$ the negative effect of iron was unambiguously demonstrated.

As expected, in accord with the literature, the catalysts prepared by procedure b (Table 4) present higher ee than those obtained by procedure a. These results are explained, first by the presence of sodium bromide in the TA solution

and second by the lower values of the atomic ratio Al/Ni. However, the RNiE_1 catalyst remains significantly more selective than RNi and RNi_{3-2} .

The Japanese researchers used exclusively a 42 wt.% nickel alloy. It has been shown by Anderson [5] that such an alloy contains 25% of the eutectic phase, whereas this phase represents only 2% of the 50 wt.% nickel alloy. Therefore, we suggest that when it is available the 42 wt.% nickel alloy, has to be preferred to the 50 wt.% nickel alloy, since a higher proportion of the eutectic phase should afford a higher enantiomeric excess.

6. Conclusion

Soaking Raney nickels in an aqueous solution of tartaric acid decreases the Al/Ni atomic ratio and the metallic surface area, whatever the precursor alloy is, with the exception of the catalyst issuing from the eutectic phase, for which these two characteristics remain unchanged or are slightly modified by the conditions.

Raney nickel catalysts, prepared from well defined pure phases, modified by TA solution and by TA + NaBr solution gave different ee in the hydrogenation of methyl acetoacetate. The best results were obtained with the catalyst obtained from the Al/Al₃Ni eutectic phase. The catalytic properties of RNiE_1 are attributed to the low value of the Al/Ni ratio, but essentially to the eutectic fibre system which gives oriented nickel crystallites after aluminium leaching.

Furthermore, the iron content in the precursor alloy must be carefully controlled, since iron is not removed by the alkali leaching but segre-

gated at the catalyst surface, where it presents a negative effect on the enantiomeric excess.

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