

EFFECT OF THE CONDITIONS OF PREPARATION OF ASYMMETRIC  $\text{LaNi}_3\text{Co}_2\text{H}_n$   
CATALYSTS ON THEIR HYDROGENATING AND ENANTIOSELECTIVE PROPERTIES

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The hydrides of intermetallic compounds (HIMC)  $\text{LaNi}_{5-x}\text{Co}_x\text{H}_n$  ( $n = 2-4$ ;  $1 \leq x \leq 4$ ) modified with a 5% solution of R, R-(+)-tartaric acid (TA) are active catalysts in the reaction of enantioselective hydrogenation of ethyl acetoacetate (EAA) [1]. The optical yield of the product (p) (-)-ethyl- $\beta$ -hydroxybutyrate in these systems in the optimum conditions of modification and hydrogenation was 20-30% with conversion of  $y = 70-100\%$ . The optical yield of the reaction can be significantly increased in the presence of some inorganic salts [2-8] or organic acids [9] added to either the modifying solution or to the reaction mixture.

The effect of different organic and inorganic additives and the conditions of preparation and modification of  $\text{LaNi}_3\text{Co}_2$  and  $\text{LaNi}_3\text{Co}_2\text{H}_{3.5}$  on their hydrogenating and asymmetric properties in the reaction of hydrogenation of EAA was investigated in the present study.

#### EXPERIMENTAL

The  $\text{LaNi}_3\text{Co}_2$  intermetallic compounds (IMC) and HIMC were prepared by the method in [10]. The samples were modified for 2 h with variation of the temperature from 20 to 90°C in an aqueous solution of TA of varying concentration or 0.5% methanol solution of TA. This involved the use of 100 ml of solution, whose pH was brought to the required value with 20% NaOH solution, per 1.5 g of catalyst. The pH was 4.5 in all of the experiments. NaBr was added by several methods: NaBr was directly added to the modifying solution (method 1); remodification of the catalyst in 0.02 M methanol solution of NaBr was conducted at 60°C for 1 h (2); NaBr was added to the reaction mixture in the amount of 0.1 mole (3). After modification, the catalyst was separated from the solution by decantation and was washed 1-2 times in methanol and then three times with abs. methanol.

Hydrogenation of freshly distilled EAA (60°C, 5 torr) was conducted in a glass ampul in a rocking autoclave. The molar ratios of EAA to acetic (AA) and trimethylacetic (TMAA) acids were equal to 0.8 and 0.9. The experiments were conducted for 7 h at 80°C and 9.0 MPa. The products of the reaction were analyzed by the method in [11]. The mixture of TMAA and product were analyzed by GLC (flame-ionization detector, 1 m column length, column packed with 10% polyethylene glycol succinate on Celite-545,  $\text{N}_2$  carrier gas,  $V = 60$  ml/min). The specific rotation was determined on a Spektropol-1 spectropolarimeter at 589 nm ( $[\alpha]_{589}^{17} = 24^\circ$ ) or at 360 nm ( $[\alpha]_{360}^{17} 74^\circ$ ). In all of the experiments, p was not a function of y of EAA.

The saturation magnetization measurements  $\sigma_g$  were conducted by the Faraday method (vacuum, 20°C, H 500-3350 Oe). The values of  $\sigma_g$  were compared with H 3250 Oe.

#### DISCUSSION

The experimental data are reported in Tables 1-4. Table 1 shows that enantioselective hydrogenation of EAA takes place both on  $\text{LaNi}_3\text{Co}_2$  and on HIMC and p was 15.8 and 19.6% with  $y = 67.2$  and 100%. This finding indicates the higher activity of the catalyst studied in comparison to the  $\text{LaNi}_{5-x}\text{Cu}_x$  IMC [12]. The duration of work of the modified HIMC  $\text{LaNi}_3\text{Co}_2\text{H}_{3.5}$  without regeneration is brief. Large values of y are thus preserved. After 21 h of work, y decreases to 58.6% and p = 2%. On prolonged standing in air, significant attenuation of the hydrogenating and asymmetric properties of the catalyst takes place: p = 4.4 with y = 26.8%.

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TABLE 1. Catalytic, Asymmetric, and Magnetic Properties of  $\text{LaNi}_3\text{Co}_2$  and Their Hydrides Modified with R, R-(+)-Tartaric Acid (pH 4.5,  $T_{\text{mod}} 50^\circ\text{C}$ ,  $\tau$  2 h, Ar)

Catalyst	$\tau$ , hr	$y$ , %	$[\alpha]_{589}^{17}$ , deg	$p$ , %	$\sigma_g$ after the reaction
Modified IMC	7	67.2	11,66 **	15,8	3,3
Modified HIMC	7	100,0	4,70	19,6	-
The same	14	93,0	0,80	3,3	-
»	21	58,6	0,48	2,0	6,2
»	7*	26,8	3,28 **	4,4	22,6
Unmodified HIMC	7	17,8	0	0	

\*Left in air for 17 days before the experiment.

\*\*Optical rotation measured at 360 nm.

TABLE 2. Effect of the Solvent and Concentration of R, R-(+)-Tartaric Acid in the Modifying Solution on the Asymmetric Properties of Hydrides (pH 4.5,  $T_{\text{mod}} 50^\circ\text{C}$ ,  $\tau$  2 h)

Solvent	Concentration of TA, %	$y$ , %	$[\alpha]_{589}^{17}$ , deg	$p$ , %
$\text{H}_2\text{O}$	1,0	100,0	3,26	13,6
$\text{H}_2\text{O}$	5,0	72,3	7,47	31,1
$\text{CH}_3\text{OH}$	0,5	31,1	0,0	0,0

Unmodified HIMC is not a very active catalyst of hydrogenation of EAA ( $y = 17.8\%$ ). This finding is in agreement with the hypothesis in [9] that not only stereoselective sites but also additional sites of racemic hydrogenation of keto esters are formed in the reaction of the catalyst with the aqueous solution of TA, and this causes the higher activity of the modified catalyst.

As Table 2 suggests, a variation in the concentration of TA significantly affects the asymmetric properties of the catalyst: substitution of a 5% modifying solution by a 1% solution results in a decrease in  $p$  from 31.3 to 13.6% with preservation of elevated hydrogenating activity. Modification in methanol solution decreases the hydrogenating activity ( $y = 31.3\%$ ), and  $p = 0$ .

The data on the effect of  $T_{\text{mod}}$  on the properties of the catalyst are reported in Table 3. Note that  $T_{\text{mod}}$  of  $50^\circ\text{C}$  is optimum, where an enantioselective catalyst with elevated general and asymmetric activity is obtained ( $p = 16.5\%$ ).

The results of the experiments to study the effect of NaBr on the asymmetric properties of  $\text{LaNi}_3\text{Co}_2$  are reported in Table 4. On addition of NaBr in amounts of 0.2-0.8 mole to the modifying solution, there is a slight decrease in  $p$ . However, increasing the concentration of NaBr in the solution to 1 mole/liter results in an increase in  $p$  to 31.3%. The use of NaBr as a promoter did not intensify the asymmetric effect ( $p = 8.9\%$ ). Remodification of the hydride in a methanol solution of NaBr resulted in a sharp decrease in the activity of the catalyst:  $y = 25.8\%$  with  $p = 21.6\%$ . Based on the data obtained, it is thus possible to talk about the extreme dependence between the enantioselectivity of the catalyst and the amount of NaBr with minimum asymmetric activity in hydrides modified in a solution of TA with 0.8 mole/liter NaBr.

As Table 4 suggests, addition of AA results in a decrease in  $p$  to 6.9% with  $y = 100\%$ . On addition of TMAA, the value of  $p$  increases to 39.8%, and  $y$  decreases to 41.1%. Dual treatment of  $\text{LaNi}_3\text{Co}_2\text{H}_{3.5}$  with NaBr added to the modifying solution and TMAA added to the reaction mixture caused an increase in  $p$  to 52.2% with  $y = 34.8\%$ .

Measurement of  $\sigma_g$  of the starting and modified catalysts showed that they are all ferromagnetic both before and after the reaction, and the values of  $\sigma_g$  lie within the limits of 2.7-6.3. The data in Tables 1, 2, and 4 show that the catalysts studied are relatively stable in the conditions of modification and hydrogenation of EAA. A sharp increase in  $\sigma_g$  is only observed on contact of the catalysts with moist air ( $\sigma_g = 22.6$ ) and AA ( $\sigma_g =$

TABLE 3. Dependence of the Asymmetric Properties of the Catalysts on the Temperature of the Modifying Solution

T <sub>mod</sub> , °C	y, %	[α] <sub>589</sub> <sup>17</sup> , deg	p, %	σ <sub>g</sub> after the reaction
20	83,2	2,02	8,4	3,0
50	100,0	3,96	16,5	4,2
90	100,0	2,84	11,8	15,8

TABLE 4. Effect of NaBr and Acids on the Catalytic, Asymmetric, and Magnetic Properties of Modified LaNi<sub>3</sub>Co<sub>2</sub>H<sub>3.5</sub> (conditions of hydrogenation of EAA: P<sub>H<sub>2</sub></sub> = 8.0 MPa, 80°C, τ 7 h)

Experiment	Method of addition of NaBr	[NaBr], mole/liter	y, %	[α] <sub>589</sub> <sup>17 ***</sup>	p, %	σ <sub>g</sub> after the reaction
1	—	—	75,6	3,8	20,9	5,8
2*	—	—	100,0	1,7	7,1	20,6
3*	—	—	41,1	3,9	39,5	8,6
4	1	0,20	87,0	4,5	21,5	5,4
5	1	0,40	76,4	2,9	15,8	—
6	1	0,60	96,0	3,8	16,5	—
7	1	0,80	93,0	7,0**	10,2	—
8	1	1,00	72,3	5,4	31,3	6,3
9*	1	1,00	34,8	4,4	52,7	7,0
10	2	0,22	25,8	1,3	21,6	—
11	3	0,10	85,0	1,8	8,8	—

\*2 and 3: promotion with AA, 9: with TMAA.

\*\*Optical rotation at 360 nm.

\*\*\*Specific rotation for the indicated degrees of conversion.

20.6). Since it is a stronger acid than TMAA, AA causes deep destruction of the structure of the catalyst with separation of a ferromagnetic metallic phase of pure Ni, which causes preservation of 100% conversion of EAA but a sharp decrease in p.

It can thus be concluded from the data obtained that the changes in y and p observed in the presence of modified LaNi<sub>3</sub>Co<sub>2</sub>H<sub>n</sub> as a function of the conditions of modification (temperature, solvent, presence of NaBr) and hydrogenation of EAA (τ, added acids) distinguish these catalysts from the traditional (modified) Ni catalysts. First, the enantioselective properties of the catalysts studied worsen sharply on partial decomposition of the starting HMC, accompanied by the formation of a metallic Ni phase and an increase in the value of σ<sub>g</sub>; second, in contrast to the asymmetric Raney Ni and Ni/support catalysts for which the dependence of the values of p on the concentration of NaBr is in the form of a curve with a maximum, this dependence for asymmetric hydrides in the same conditions is given by a curve with a minimum; third, both catalyst groups differ sharply with respect to the effect in the presence of such promoters as AA and TMAA. Although addition of acids to asymmetric Ni tartrate complexes causes an increase in the yield of optically active product, asymmetric tartrate complexes of HMC undergo significant decomposition on addition of these acids to the reaction mixture (especially AA), accompanied by a decrease in the asymmetric activity. As in [1], we will hypothesize that the asymmetric effect is a function of the structure of the asymmetric tartrate complexes of the hydrides with TA formed and perhaps heterometallic tartrate complexes [13], which are sites of enantioselective hydrogenation of the prochiral EAA molecule.

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#### CONCLUSIONS

1. The conditions of modification (temperature, concentration of R, R-(+)-tartaric acid, solvent) affect the asymmetric properties of tartrate complexes of LaNi<sub>3</sub>Co<sub>2</sub>H<sub>n</sub> hydrides.
2. The combined effect of NaBr (as a comodifier) and trimethylacetic acid (as a promoter) on the optical yield of the reaction was established.

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### LIGAND EFFECT IN DISSYMMETRIC Cu-Ru AND Cu-Pd CATALYSTS

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The synergism of the asymmetric action of chiral Raney Cu-Pd catalysts (RCPC) in the hydrogenation of ethyl acetoacetate reported in [1, 2] was attributed to a ligand effect.

We presented new evidence of this phenomenon for Raney Cu-Ru catalysts (RCRC) as well as the Cu-Pd systems in [3, 4], where we provided preliminary information on their adsorption and catalytic properties.

### EXPERIMENTAL

The Raney Cu-Ru catalysts (RCRC) were prepared and studied as described in [3, 4]. The Cu-Pd and Cu-Ru catalysts were prepared by leaching Cu-Pd-Al or Cu-Ru-Al alloys containing 70% Al. The catalysts were modified with RR-(+)-tartaric acid. The products resulting from hydrogenation of the ethyl acetoacetate were analyzed as described in [3]. The apparent activation energy  $E_{app}$  of the reaction was determined over the temperature range 20-90°C. The adsorption of  $H_2$  on the catalysts was studied using charging curves and potentiometric current-voltage curves in solutions of  $H_2SO_4$  and NaOH obtained with a model P-5827 potentiostat [4].

### RESULTS AND DISCUSSION

Figures 1 and 2 present the data on the adsorption of  $H_2$  on Pd-Cu and Ru-Cu catalysts. Since Cu does not chemisorb  $H_2$  [5], the charging curves and the current-voltage curves apparently describe the adsorption of  $H_2$  on Ru or Pd atoms. From the charging curves, the potentials for the complete desorption of  $H_2$  ( $E_H$ , V) were determined for anodic polarization. Increasing the Cu content leads to a fall in  $E_H$  in both cases. A sharper decline is observed for the Pd-Cu system, with  $E_H$  falling from 280 to 40 mV; in the Ru-Cu system,  $E_H$  changes from 200 to 70 mV. This suggests a weakening in the Ru-H and Pd-H bonds as the Cu content rises. The current-voltage curves (Fig. 2) confirmed that  $H_2$  is bound more

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