- 17. H. B. Kagan and T. P. Dang, J. Am. Chem. Soc., 94, 6429 (1972).
- 18. H. Brunner and W. Pieronczyk, Angew. Chem., 18, 620 (1979).
- 19. M. C. Hall, B. T. Kilbourn, and K. A. Taylor, J. Chem. Soc. A, 2539 (1970).
- 20. G. Gelbard, H. B. Kagan, and R. Stern, Tetrahedron, <u>32</u>, 233 (1976).
- 21. K. Achiwa, J. Am. Chem. Soc., <u>98</u>, 8265 (1976).
- 22. G. Descotes, D. Lafont, and D. Sinou, J. Organomet. Chem., <u>150</u>, C14 (1978).
- 23. M. Tanaka and I. Ogata, J. Chem. Soc., Chem. Commun., 735 (1975).
- 24. Y. Sugi and W. R. Cullen, Chem. Lett., 39 (1979).
- 25. K. Hanaki, K. Kashiwabara, and J. Fujita, Chem. Lett., 489 (1978).

ENANTIOSELECTIVE HYDROGENATION OF ETHYL ACETOACETATE ON COPPER - NICKEL CATALYSTS: INFLUENCE OF pH ON MODIFICATION AND THE NATURE OF THE MODIFIER

V. V. Chernysheva and E. I. Klabunovskii

UDC 541.128.1

It was shown in [1, 2] that Cu – Ni catalysts (CNC) of variable composition, modified with (+)-tartaric acid, manifest enantioselectivity in the hydrogenation of ethyl acetoacetate (EAA) and acetylacetone. However, the influence of the pH of the modifying solution and the nature of the modifier on the optical yield had not been investigated. Here we are reporting on an investigation of CNC of variable composition modified with tartaric acid and amino acids, in the hydrogenation of EAA, as influenced by variations of pH of modification and the catalyst composition.

EXPERIMENTAL

The starting materials were as follows: freshly distilled EAA, bp 63°C (12 mm); amino acids and tartaric acid with values of $[\alpha]_D$ corresponding to those reported in the literature. The CNC was obtained by reducing a mixture of oxides in a stream of N₂-H₂ (10:1) for 2 h at 180°C and 3 h at 280°C, following [3]. The CNC was modified with 0.5% solutions of the acids in a 1-h treatment at 50°C, using 200 ml of the modifier solution per gram of CNC (the modification with the amino acids was performed at 50°C and at the pH of the isoelectric point of the particular amino acid). The following conditions were used in autoclave hydrogenation: for the CNC-tartaric acid, 5 ml EAA without solvent, 0.5 g CNC, 100°C, 100 atm, hydrogenation time 3.5 h; for the CNC-amino acid, 5 ml EAA, 0.25 g CNC, 130°C, 100 atm, 3.5 h. The hydrogenated products were analyzed by GLC and polarimetry. The LKhM-8MD chromatograph had a katharometer detector and a glass column packed with 10% PEG M 15,000 on Chromatone N-AW. The polarimeter was a Hilger-Watts instrument (D line of Na). The optical yield was calculated, assuming for optically pure ethyl β -hydroxybutyrate (EHB) $[\alpha]_D^{20} = 24^\circ$. At conversions below 7%, a correction was applied for the change of $[\alpha]_D^{20}$ with the concentration of EHB in the catalysate.

DISCUSSION OF RESULTS

The reaction rate v, as determined from the conversion achieved in 3.5 h (Fig. 1, curve 1), and the optical yield p (Fig. 1, curve 2) vary antibatically with the pH of the solution of (+)-tartaric acid used to modify the catalyst with the 50:50 Cu:Ni composition, the reaction rate v reaching quite high levels at pH 3 and 12 (v = 0.26, conversion 70%), approaching the effectiveness of the unmodified catalyst (v = 0.36). This is explained by the low degree of adsorption of the tartaric acid on the catalyst surface, as indicated by the low values of p at these levels of pH. With pH > 4, the optical yield tends to increase, but the pH 6-8.5 region has not yet been investigated experimentally. As can be seen from Fig. 1 (curves 3-5), in the case of Ni catalysts, the optimal pH is in the 5-9 range. For the Cu catalysts, the pH range is somewhat lower, and a maximum in the

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2023-2026, September, 1983. Original article submitted December 6, 1982.



Fig. 1. Hydrogenation rate (1) and optical yield (2) in hydrogenation of ethyl acetoacetate on CNC with Cu:Ni = 50:50, as functions of pH of modifying solution of (+)tartaric acid. Curves 3-5 are plotted from data of [4-6] on the hydrogenation of methyl acetoacetate on skeletal Ni modified with (+)-tartaric acid. Curve 6 shows the results obtained in [7] in the hydrogenation of ethyl acetoacetate on Cu modified with (+)tartaric acid. Curve 7 shows the variation of w.

Fig. 2. Hydrogenation rate (2, 4), optical yield (1, 5), and magnitude of w (3) as functions of composition of CNC modified with S-phenylalanine (1-3) and (+)-tartaric acid, pH 5.1 (4, 5).

Cu:Ni Catalyst	Reaction rate, mmoles/min·g-cation(-10 ²) Amino acid used as modifier					
	50 : 50 10 : 90	52 63	56 67	63 66	93 62	23 68

TABLE 1

optical yield has been noted for pH 4.5 and 9.5 [4]. A comparison of our results with those reported in [5-8] shows that the relationship we found between p and the pH of modification in the case of the CNC is closer to the picture observed on the Ni catalysts. This statement is further supported by curve 7 in Fig. 1, which shows the variation of the rate of formation (w) of excess R(-) enantiomer (w = p·v), with a maximum at pH 5-6 the same as is characteristic for the Ni catalysts.

In [9], in the hydrogenation of EAA and methyl acetoacetate on Ni and Cu modified with a series of S-amino acids, it was found that on the Ni, S(+)- or R(-)-methyl β -hydroxybutyrate was formed, depending on the temperature of modification, whereas on the Cu catalyst, only S(+)-ethyl β -hydroxybutyrate (EHB) was formed within the interval of modification temperatures from 20° to 90°C. In this connection, if we assume an additive contribution to the asymmetric reaction from the chiral Cu and Ni centers of the mixed catalyst, we can expect that on mixed CNC modified with a S-amino acid, as the content of Cu in the CNC is increased, the configuration of the EHB that is formed will change from R to S at a certain composition of the catalyst. However, it is difficult to reproduce the experimental conditions accurately for the Cu and Ni catalysts, since skeletal catalysts were used in [9], and the conditions under which the experiments were conducted were different from those we used.

In preliminary studies with two samples of Cu-Ni catalysts with 50:50 and 10:90 metal ratios (wt.%), we investigated the influence of the nature of the S-amino acid used as a modifier on the rate of EAA hydrogenation. As can be seen from these data (Table 1), all of the catalysts modified with amino acids had rather high activities.

In [10], a detailed study was made of EAA hydrogenation on a Cu-Phe catalyst, and it was established that the values of p pass through a maximum at a modification temperature of 55°C. Therefore, we investigated CNCs of variable composition modified with S-phenylalanine at a similar temperature (45°C). However, at this temperature, the modification of the Ni catalyst with S-phenylalanine is quite ineffective (in the hydrogenation of MAA, p = 1.4% [11]. As a consequence, when the change is made from Cu to Ni catalyst, we should expect that on the copper and copper-rich mixed catalysts, S(+)-EHB would be formed, with a gradual drop of the optical yield as the content of Ni in the catalyst was increased. However, as shown by our results (Fig. 2), on all of the catalysts with variable composition, only R(-)-EHB was formed, the optical yield of which dropped almost to zero as the content of Ni in the catalysts was increased (Fig. 2, curve 1). Here we found that the reaction rate increased with increasing Ni content up to 50%, after which it remained almost unchanged (Fig. 2, curve 2). This is in agreement with the data of [3] for the hydrogenation of acetone on CNC. It should be noted that in our experiments, the Cu catalyst showed very little activity, and the introduction of 2% Ni favored the hydrogenolysis reaction (16% ethyl butyrate was formed); only with additional increases of the Ni content was any EHB formed. Hence we can assume that the catalyst component responsible for the asymmetric hydrogenation in these systems is the Ni component, its effect being manifested only when 10-15% Ni is introduced. Support for this view may be found by examining the coincidence of the maxima of the curves for the variation of w (Fig. 2, curve 3) and the content of surface hydrogen, which according to [3], occurs at 20-40% Ni in CNC. Also shown in Fig. 2 are the results from the hydrogenation of EAA on CNC modified with (+)tartaric acid. In this case, we note a monotonic increase of the reaction rate and optical yield as the Ni content is increased. The difference of these results from those we obtained previously [1] shows how strongly the enantioselectivity of the modified catalysts is influenced by their genesis and by the hydrogenation conditions.

Thus, the results show a substantial difference between the surface chiral complexes formed by modification of CNC with RR(+)-tartaric acid and S- α -amino acids, which is in agreement with [12]; the results also demonstrate the high sensitivity of the asymmetric reaction to the nature of the catalyst surface.

CONCLUSIONS

1. A substantial difference has been established between the surface chiral complexes formed by modification of copper-nickel catalysts with tartaric acid or amino acids.

2. It has been established that the nickel component of the catalysts plays an important role in the manifestation of enantioselective properties.

LITERATURE CITED

- 1. E. I. Klabunovskii, A. A. Vedenyapin, G. Kh. Areshidze, and A. K. Ivanov, Izv. Akad. Nauk SSSR, Ser. Khim., 2642 (1976).
- 2. Yu. V. Vlasenko, E. I. Klabunovskii, A. A. Vedenyapin, and I. A. Rubtsov, Izv. Akad. Nauk SSSR, Ser. Khim., 986 (1977).
- 3. E. Takai, Sci. Pap. Inst. Phys. Chem. Res. Jpn., 62, No. 1, 24 (1968).
- 4. V. I. Neupokoev, Yu. I. Petrov, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 113 (1976).
- 5. Y. Izumi, M. Imaida, H. Fukawa, and S. Akabori, Bull. Chem. Soc. Jpn., 36, 21, 150 (1963).
- 6. S. Tatsumi, Bull. Chem. Soc. Jpn., 41, 408 (1968).
- 7. T. Harada, M. Yamamoto, S. Onaka, M. Imaida, H. Ozaki, A. Tai, and Y. Izumi, Bull. Chem. Soc. Jpn., <u>54</u>, 2323 (1981).
- 8. E. I. Klabunovskii, V. I. Neupokoev, and Yu. I. Petrov, Izv. Akad. Nauk SSSR, Ser. Khim., 2839 (1970).
- 9. E. I. Klabunovskii and A. A. Vedenyapin, Asymmetric Catalysis. Hydrogenation on Metals [in Russian], Nauka, Moscow (1980), p. 105.
- 10. Yu. S. Airapetov, A. A. Vedenyapin, E. I. Klabunovskii, Ya. D. Fridman, and L. Ya. Mikhailyuk, Izv. Akad. Nauk SSSR, Ser. Khim., 2385 (1977).
- 11. S. Akabori and Y. Izumi, West Ger. Pat. 212,944 (1966), p. 10.
- 12. J. A. Groenewegen and W. M. H. Sachtler, J. Catal., 33, 176 (1974).