ENANTIOSELECTIVE HYDROGENATION OF ETHYL ACETOACETATE

ON ASYMMETRIC RANEY Ni CATALYSTS

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The asymmetrizing ability of modified Raney nickel catalysts depends on the method of their preparation and, in particular, on the leaching conditions. However, the question of the effect of the composition of the starting Ni-Al alloys on the asymmetrizing properties of Raney Ni catalysts has not been considered.

In the present paper, we studied the asymmetrizing properties of Raney Ni catalysts from different Ni-Al alloys in the hydrogenation of ethyl acetoacetate (EAA) to (-)-ethyl- β -hydroxybutyrate.

EXPERIMENTAL

The catalyst specimens were prepared by leaching Al from industrial Ni-Al alloys according to [1]. The phase composition of the catalysts and alloys was determined by x-ray phase analysis on a DRON-2 instrument with K_{α} radiation of a Cu anode with a Ni filter. Modification of the catalysts by RR-(+)-tartaric acid solutions, hydrogenation of EAA, and treatment and analysis of the catalyzates were carried out according to [2].

DISCUSSION OF RESULTS

We investigated catalysts Ni-1, Ni-2, and Ni-3 obtained from alloy specimens 1, 2, and 3, respectively. Tables 1 and 2 give data on the chemical and phase analysis of the starting Ni-Al alloys and the catalysts obtained from them.

From the data of Table 1, it follows that the alloys differ not only in their chemical composition, but also in their intermetallic composition (different contents of the intermetallic compounds NiAl₃ and Ni₂Al₃). With decreasing Ni content in the alloy, the fraction of the NiAl₃ phase increased; according to [3], this phase is leached more easily than Ni₂Al₃. The unidentical abilities of the intermetallic compounds to undergo leaching and their different contents in the alloys lead to differences in the compositions of the catalysts obtained from them. The more of the NiAl₃ phase in the alloy, the more completely is the alloy leached, and the less Al remains in the catalyst. Indeed, in the specimen of Ni-3 obtained from the alloy enriched with the intermetallic compound NiAl₃, the content of residual Al was 7%, which is half that in Ni-2. The difficulty of leaching of alloy 2 also resulted in the fact that practically the starting amount of Cr and Ti contained in the alloy remained in the obtained catalyst. In the case of alloy 3, Cr and Ti were completely removed during leaching.

An investigation of the hydrogenation of EAA on the obtained catalysts after their modification by (+)-tartaric acid showed that the composition of the starting alloys affected the catalyst characteristics and the reaction parameters. Figure 1a and b shows the relations of the reaction rate v to time and of the optical yield p to the degree of conversion y. From Fig. 1, it is evident that the obtained catalysts differed not only in the enantioselectivity of their action, but also in their operating stability. Each catalyst specimen was characterized by its curve of the relation of p to y. Higher optical yields also corresponded to the more active catalysts 1 and 3, with the optical yield on catalyst Ni-3 changing little with increasing conversion of EAA within the entire range of values of y. Apparently, to carry out enantioselective hydrogenation of EAA, it is appropriate to use precisely the catalyst Ni-3.

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Alloy specimen	Chemica	l compositi	Phase composition, wt. 7		
	Ni	Al	Cr+Ti	NiAl ₃	Ni ₂ Al ₃
1 2 3	$50.0 \\ 45.2 \\ 38,3$	50.0 51,2 59,7	$3.6 \\ 2.0$	10.0 25.1 51.2	90.0 74.9 48.8

TABLE 1. Chemical and Phase Compositions of the Starting Alloys

TABLE 2. Chemical and Phase Compositions of the Raney Ni Catalysts

Catalyst specimen	Chemical composition, wt. %					Phase composition, wt. %		
	Ni	Al	Cr	Ti	balance (Na, H, O)	Ni	Al	bayerite
Ni-2 Ni-3	70.6 73.0	$\begin{array}{c} 15.8\\ 6.8\end{array}$	0.9 0.1	1,9 0,02	$10.8 \\ 20.1$	91.6 97.9	5,4 0,0	3.0 2.1



Fig. 1. Relation of the optical yield of the reaction (a) to the degree of conversion of EAA (Y, %) and change of the specific reaction rate with respect to time (b) in the hydrogenation of EAA on the catalysts: 1) Ni-1; 2) Ni-2; 3) Ni-3. The numbering is from the lower axis.

The relation of the enantioselective properties of the investigated Raney Ni catalysts to the composition of the starting alloys is probably due to the difference of the physicochemical properties of the alloys and the catalysts obtained from them. It was determined by calorimetry [4], thermal desorption [5], and electrochemistry [6] that on the surface of the catalysts there were several forms of adsorbed hydrogen with different strengths of bonding with the surface. The catalysts obtained from NiAl₃ contained more weakly bonded hydrogen than the catalysts obtained from Ni₂Al₃. The catalyst obtained from NiAl₃ had a higher initial activity in the liquid-phase hydrogenation reaction than the catalyst from Ni₂Al₃, but it decreased more rapidly [7]. This was also confirmed by our experiments: as is evident from Fig. 1b (curve 1), the rate of hydrogenation of EAA on the Ni-1 specimen obtained from the Ni-Al (1:1) alloy and consisting of the Ni₂Al₃ phase was lower and more constant with respect to time than on Ni-2 and Ni-3. The nonequivalence of the hydrogen adsorbed on the surface also affected the enantioselectivity of hydrogenation. When we used the Ni-1 specimen containing mostly more strongly bonded hydrogen, the value of p, even at

the maximum point (see Fig. 1a, curve 3), was much less than in the case of Ni-2 and Ni-3. The low value of p could also be related to an increased content of residual A1 (~17% according to [3]) in catalyst Ni-1, with the residual Al worsening the asymmetrizing properties of the modified nickel catalyst [8]. There is also apparently a relation between the nonequivalence of the adsorbed hydrogen and the fact of the increase of p with the degree of conversion in the beginning of the reaction for the Ni-1 and Ni-2 specimens (see Fig. 1a, curves 1 and 2). When the catalyst contained much weakly bonded hydrogen (Ni-3), the optical yield was rather high, even at low degrees of conversion, and changed little during the reaction (see Fig. 1a, curve 3). In the case of catalysts Ni-2 and Ni-3, in the beginning of the reaction, while the hydrogenation process occurred because of the small amount of strongly bonded hydrogen contained on the surface, the optical yield was low. As the hydrogen weakly bonded to the surface and coming form the bulk began to participate in the reaction, the value of p increased. The decrease of the optical yield with a further increase of the degree of conversion can be explained by inhibition by the reaction product, as shown in [2]. As concerns the Cr and Ti impurities present in Ni-2, apparently their effect on the enantioselectivity of hydrogenation was insignificant because their concentration was low in comparison with the concentration of the residual Al. Their role amounted to some increase of the total hydrogenation rate.

Thus, under identical preparation conditions, both the catalytic and asymmetrizing properties of the Raney Ni catalysts modified by (+)-tartaric acid depended on the composition of the starting Ni-Al alloys. A decrease of the Ni content in the alloy and, therefore, an increase of the fraction of the NiAl₃ phase contributed to an increase of both the total catalytic activity and the enantioselectivity in EAA hydrogenation.

CONCLUSIONS

1. The properties of Raney nickel catalysts modified by (+)-tartaric acid and active in enantioselective hydrogenation of ethyl acetoacetate depend on the chemcial and phase compositions of the starting Ni-Al alloys.

2. A decrease of the Ni content in the Ni-Al alloy specimens which corresponds to an increase of the fraction of the NiAl₃ intermetallic compound in them contributes to an increase of the catalytic activity and enantioselectivity of the action of the obtained catalysts.

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