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Catalytic activity of Cr- or Co-modified Ni-based rapidly quenched alloys in the hydrogenation of isophorone

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ABSTRACT

Raney-type Ni-based catalysts containing a small amount of Cr or Co were prepared from $Ni_{32-x}Al_{68}Cr_x$ and $Ni_{32-x}Al_{68}Co_x$ (x = 1, 3 or 6) rapidly quenched alloys by leaching in 1 M NaOH. These degradation processes occurring at the surface and in the bulk of the alloys were used for promoting the catalytic activity of these materials. The modifications of the internal structure, chemical composition and morphology of the alloys proved to be a useful method for transforming inactive Ni–Al–Cr and Ni–Al–Co alloy precursors into active and selective catalysts.

The hydrogenation of isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) was used as a catalytic test for the modified materials. The catalytic tests showed that the conversion of isophorone hydrogenation increases with temperature but decreases with the addition of Cr or Co to the Ni–Al alloy. Conversely, selectivity to dihydroisophorone (3,3,5-trimethylcyclohexanone) formation drops with temperature but for Cr- or Co-containing catalysts it is distinctly higher than for that of a conventional Raney Ni catalyst. The most promising catalyst seems to be that obtained from $Ni–Al–Cr_1$ alloy; it is characterized by both high conversion and high selectivity.

Further hydrogenation of dihydroisophorone to homomenthol (3,3,5-trimethylcyclohexanol) appeared to be strongly restrained on the above catalysts and the reaction did not proceed even after 7 days under $p = 70$ atm.

Scanning electron microscopy (SEM), Auger electron spectroscopy (AES), scanning Auger microscopy (SAM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) allowed the changes occurring during the activation process to be identified, and their implications for catalytic function to be considered.

1. Introduction

The catalytic hydrogenation of α,β-unsaturated carbonyl compounds is a process of great practical potential [1–3]. Hydrogenation of the carbonyl group leads to the formation of unsaturated alcohols. Hydrogenation of the C=C bond gives saturated carbonyl compounds, whereas hydrogenation of both the double bond and the carbonyl group leads to saturated alcohols.

Isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) is an α,β-unsaturated ketone. The possible products of the hydrogenation of isophorone are shown schematically in Fig. 1. All of these products are of practical importance [4]. Notably, dihydroisophorone (3,3,5-trimethylcyclohexanone) is used as a solvent for vinyl resins, lacquers, varnishes, paints and other coatings. However, the boiling points of these important products are close to one another, so that their separation by distillation is difficult and expensive [5]. Thus, the main goal is to obtain high catalytic selectivity for a given, expected product.

Nanocrystalline metals/alloys or amorphous alloys (especially those from groups 7 to 11 of the periodic table of the elements) are catalyst precursors for a number of chemical reactions, including the hydrogenation of organic compounds [6,7]. Such materials can be prepared by the rapid quenching method. Their single-phase character ensures that active sites are uniformly dispersed in a chemically homogeneous environment. They also have a high concentration of coordinative highly unsaturated sites, which can make adsorption and surface reactions occur more readily than on their corresponding crystalline catalysts. All these features make amorphous and nanocrystalline alloys attractive for catalytic applications as precursors of active and selective catalysts [8–13].

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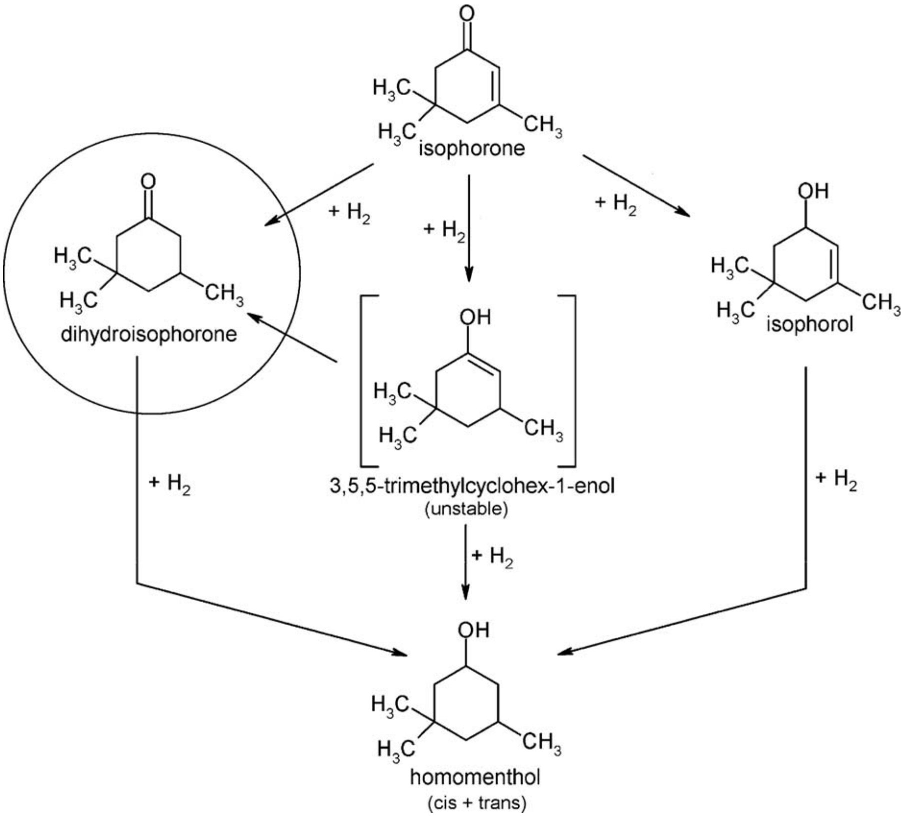

Fig. 1. Schematic representation of possible hydrogenation products of isophorone.

One may anticipate that even if rapid quenching does not always lead to full amorphisation, a grain refinement is often obtained, which also provides some of the above features facilitating adsorption and promoting surface reactions.

It has been found that further enhancement of catalytic activity can be achieved by appropriate modifications of catalyst precursors. In particular, various processes of material degradation may be utilized for transforming such precursors into active and selective catalysts [13–15], for example, the conventional Raney Ni catalysts produced by removing Al from binary Ni–Al alloys by leaching with NaOH aq, widely applied as hydrogenation catalysts [9,16,17].

Recently, Raney-type Ni alloys with the addition of a few at.% of Fe, Cr or Co have been investigated as hydrogenation catalysts [9,16–18]. The results obtained so far suggest that these transition metals may successfully improve the selectivity of the catalysts, and in some cases enhance their activity in the hydrogenation of a number of organic compounds.

The aim of this work was to determine the effect of Cr and Co on the catalytic properties of Ni–Al alloys. These two elements were chosen because they affect the electronic structure of Ni near the Fermi level in different ways, as will be discussed in Section 3.2. An attempt was made to determine the interrelation between the chemical and phase composition of the catalysts and their morphology, as well as their activity and selectivity in isophorone hydrogenation.

2. Experimental

2.1. Material preparation

Rapidly quenched $Ni_{32-x}Al_{68}Cr_x$ and $Ni_{32-x}Al_{68}Co_x$ ($x = 1$, 3 or 6) materials were used. All stoichiometric formulas given in the text and in the figures correspond to those initial compositions, expressed in at.% and denoted as $NiAlCr_x$ or $NiAlCo_x$. The alloys were produced in the form of ribbons by continuous casting from melt on a rotating copper wheel in an inert atmosphere of pure argon. The parameters of the quenching process were: melting temperature 1400–1500 °C (depending on Cr content), copper wheel rotation speed 20 rps, pressure 600 mbar. The method of continuous casting is described in detail elsewhere [19].

Rapidly quenched samples were subjected to leaching in order to remove Al and to obtain *Raney-type materials* expected to possess increased catalytic activity for the hydrogenation of isophorone. In order to follow the progress of the degradation process, leaching in 1 M NaOH was applied from 10 min up to 4 h, or alternatively, until the termination of hydrogen evolution from the alloy, which usually required 18 h or more. Leaching was performed at room temperature, with constant agitation, by using a magnetic stirrer. The final products (denoted as “after full leaching”) were used for the catalytic tests.

The resultant Raney-type Ni–Al–Cr or Ni–Al–Co catalysts were washed with distilled water until pH 7 was reached, to remove alkali and aluminates. They were then further rinsed with 2-propanol to remove water, and finally, stored in 2-propanol to avoid contact with air prior to the subsequent catalytic tests. For comparison, a Raney Ni catalyst was also prepared in the same way by alkali leaching of a commercial Ni–Al alloy (50 wt% of each element, i.e., 31 at.% Ni).

2.2. Microscopic and surface analytical investigations

The following degradation products of the catalysts were analyzed: (a) the surface on both sides of the ribbon after 30 min of leaching in alkali solution, and (b) the degradation products formed after full leaching.

For the purpose of microscopic examination, the full leaching degradation products of Ni–Al–Cr and Ni–Al–Co alloys were first centrifuged in 2-propanol at a rate of 50 rps to separate the small metal particles. After removal of the upper 2-propanol layer the