



Influence of Cr addition to Raney Ni catalyst on hydrogenation of isophorone

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ABSTRACT

The influence of Cr (1–6 at.%) on the catalytic activity and selectivity of Ni–Al alloy in isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) hydrogenation was studied. The catalysts were obtained from the rapidly quenched precursors by leaching in NaOH aqueous solution. The catalytic tests were performed at various temperatures (20–80 °C) under the atmospheric or elevated pressure using gaseous hydrogen and 2-propanol as a solvent. Ni–Al–Cr alloy with 1 at.% Cr appeared to be the most active and selective catalyst, with the conversion level and selectivity to dihydroisophorone (3,3,5-trimethylcyclohexanone) exceeding 99%. On the other hand, further hydrogenation of dihydroisophorone to homomenthol (3,3,5-trimethylcyclohexanol) was strongly restrained by the Cr-containing catalysts.

Scanning electron microscopy, Auger electron spectroscopy, energy dispersive X-ray spectroscopy and X-ray diffraction allowed changes occurring during the catalyst preparation to be identified and their implications for catalytic function to be considered.

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1. Introduction

Metals from 7–11 group of periodic table and their alloys are important as hydrogenation catalysts [1,2]. An example are conventional Raney Ni catalysts [3–8], produced from binary Al–Ni alloys by Al leaching with NaOH aq. These systems have been widely used as hydrogenation catalysts because they offer high efficiency and selectivity in molecular hydrogen activation.

In particular, the materials in the form of nanocrystalline metals/alloys or amorphous alloys prepared by rapid quenching method are especially attractive for catalytic applications as precursors of active and selective catalysts [9–13]. Their single-phase character ensures that the active sites are in uniform dispersion in a chemically homogeneous environment. They also have a high concentration of coordinative highly unsaturated sites, which could make adsorption and surface reactions easier than on a corresponding crystalline catalyst. 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.

Selective hydrogenation of α,β -unsaturated carbonyl compounds is a process of high practical potential [1,14–18]. Hydrogenation of carbonyl group leads to the formation of unsaturated alcohols, hydrogenation of the C=C bond gives saturated carbonyl

compounds, whereas hydrogenation of both double bond and carbonyl group leads to saturated alcohols. Recent development in chemoselective hydrogenation of unsaturated aldehydes and ketones over heterogeneous catalysts have been thoroughly reviewed by Mäki-Arvela et al. [1]. They discussed the effect of reaction conditions, the electronic and geometric structures of reactants, and the choice of catalysts and method of their preparation on the catalytic activity and selectivity in various hydrogenation reactions. Additionally, catalyst characterization techniques, especially alloy formation and in situ characterizations were discussed in detail. The attempts of kinetic and molecular modeling in chemoselective hydrogenations were also presented.

Isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) is an α,β -unsaturated ketone. The product of the C=C bond hydrogenation (see Fig. 1) dihydroisophorone (3,3,5-trimethylcyclohexanone) plays an important role as a solvent for vinyl resins, lacquers, varnishes, paints and other coatings. However, the boiling point of dihydroisophorone and other products of isophorone hydrogenation, i.e. isophorol (resulting from the C=O bond hydrogenation) and homomenthol (resulting from both the C=C and C=O bonds hydrogenation) are close one to another, so that their separation by distillation is difficult and expensive [19]. Thus, the main goal is to obtain a high catalytic selectivity for a given, expected product.

Recently, common metal catalysts modified with an addition of transition metals [20,21] including Ni-based alloys with an addition of a few at.% of Fe, Cr or Co have been investigated [22–24].

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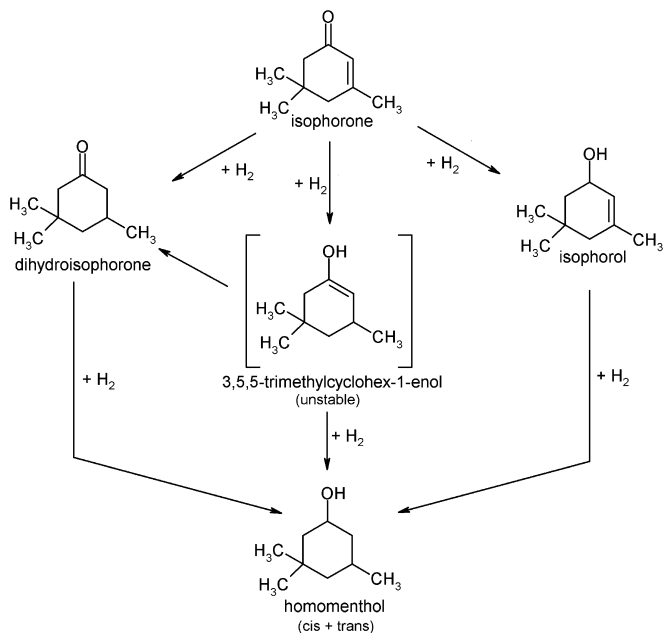


Fig. 1. Schematic representation of possible products of a catalytic hydrogenation of isophorone.

The results obtained so far suggest that these transition metals may successfully improve selectivity of the Ni-based catalysts, and in some cases – enhance their activity for hydrogenation of a number of organic compounds, e.g. adiponitrile [22], benzene [23], acetophenone and glucose [24]. Yet, isophorone hydrogenation has not been studied on those catalysts. In particular, it is known that small amounts of Cr distinctly alter electron density of Ni near the Fermi level, E_F [25–27] by introducing some “virtual impurity bound states” (VBS) into the electron density of states of Ni. This has a strong influence on the electronic properties (magnetization, thermoelectric power) of Cr doped Ni alloys. One can expect that such doping may modify also the catalytic properties of these systems by modifying local electron density on Ni and the ability to adsorb hydrogen. High resolution surface analysis may provide an insight into the mechanisms of selectivity of the modified catalysts.

In this paper we report on the influence of Cr addition (initially 1–6 at.%) to Ni–Al alloy on its catalytic activity and selectivity in isophorone hydrogenation. We show that Ni–Al alloys with small amounts of Cr are the promising precursors of efficient and highly selective catalysts of the C=C bond hydrogenation.

2. Experimental

2.1. Material preparation

Rapidly quenched $Al_{68}Ni_{32-x}Cr_x$ ($x = 1, 3, 6$) materials were used. 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 point ~ 1530 °C, copper wheel rotation speed 20 rpm, eject pressure 60 MPa. The method of continuous casting is described in detail elsewhere [28].

Rapidly quenched samples were subjected to leaching in order to remove Al and obtain skeletal Raney type catalysts possessing an increased catalytic activity for the hydrogenation of isophorone. Leaching in 1 M NaOH was applied up to the termination of hydrogen evolution from the alloy (indicating the end

of Al dissolution), which usually required 18 h or more. The resultant Raney type Ni–Al–Cr catalyst was washed with distilled water until pH = 7 was reached, to remove alkali and aluminates. It was then further rinsed with 2-propanol to remove water, and finally, kept in 2-propanol to avoid contact with air prior to the subsequent catalytic test. For comparison, a commercial Raney Ni catalyst was also prepared in the same way by alkali leaching of a commercial Ni–Al alloy (50 wt.% of each element, which corresponds to 31 at.% Ni).

2.2. Microscopic, surface analytical and structural investigations

The high resolution scanning Auger spectrometer, a Microlab 350 (Thermo Electron), was employed in order to monitor the topography of degradation products of the catalyst (SEM) and local chemical composition (AES). An Avantage-based (3.83) data system was used for data acquisition and processing. The pph signals for Al (KLL, 1396 eV), Ni (LMM, 849 eV) and Cr (LMM, 531 eV) were used for a semi-quantitative analysis of the materials. Sensitivity factors were taken from the Handbook of Auger Electron Spectroscopy [29].

For EDS analysis a Thermo Noran spectrometer coupled with STEM, Hitachi S-5500 scanning microscope was used. XRD patterns of the alloys were measured using a SIMENS D-5000 X-ray diffractometer equipped with a Cu tube (K_α line 1.5418 Å). The accelerating voltage was 40 kV and the current 40 mA.

2.3. Catalytic test

Isophorone hydrogenation was used as a catalytic test for the materials studied. The experiments were performed in 2-propanol in a glass reactor of 30 ml volume. The amount of catalyst was ~ 0.2 g. About 5 ml of 2-propanol was added and the mixture of the catalyst and 2-propanol was constantly agitated using a magnetic stirrer and, in addition, by a stream of pure hydrogen. The reactor content was then warmed up to the following reaction temperatures: 20 °C, 40 °C, 60 °C and 80 °C. Only after the temperature had reached the established value, was 1 ml of isophorone added and the reaction time was strictly controlled. After 2 h the reaction products were analyzed with the aid of gas chromatography in HP 6890N gas chromatograph equipped with a 30 m capillary column and flame ionization detector (FID). Temperature in both injection chamber and detector was 250 °C, while temperature in column changed according to the following program: 50 °C for 7 min, then increase to 250 °C at the rate of 20 °C/min, and 250 °C for 6 min. The analysis was performed with the method of standard addition. The amounts of the analyzed substances were determined from the area under respective chromatographic peaks after earlier calibration of the column with the use the mixtures of known composition. The chromatographic results were confirmed by the measurements of the refractive index.

Alternatively, several samples were used to carry out the reaction in an autoclave under pressure of 7 MPa at 40 °C or 80 °C up to 7 days. This was done to check whether the more severe reaction conditions may affect the kinetics of the hydrogenation process, thus limiting the selectivity of Ni–Al–Cr catalyst to mild conditions only. As a reference a commercial Raney Ni alloy (50 wt.% of each element, i.e. 31 at.% Ni) was used, and the reaction was carried out under above conditions for 2 h.

3. Results

Fig. 2 shows a SEM image of $Al_{68}Ni_{29}Cr_3$ catalyst after full leaching. A variety of particles are visible with dimensions

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