



The catalytic and physico-chemical properties of Ni/MgF₂–MgO catalysts

Michał Zieliński*

Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznań, Poland

ARTICLE INFO

Article history:

Received 17 May 2012

Received in revised form 3 August 2012

Accepted 18 September 2012

Available online 8 October 2012

Keywords:

Nickel catalysts

MgF₂

MgO

Magnesium oxo-fluoride

Al₂O₃

Toluene hydrogenation

ABSTRACT

The MgF₂–MgO system of different quantitative compositions was tested as a potential support for nickel catalysts to be used for hydrogenation of toluene. The catalytic performance of the system was studied as a function of the MgF₂/MgO ratio in the support and the reaction conditions. The hydrogenation was performed at temperatures ranging from 75 to 225 °C on the catalysts activated in hydrogen at different temperatures (400–550 °C). The activities of Ni/MgF₂–MgO catalysts were compared to those of Ni/MgF₂, Ni/MgO and Ni/Al₂O₃. The highest activities were observed in the case of the catalysts supported on MgF₂–MgO (containing 40 mol.% MgO), especially after the activation at 500 °C. The catalytic activity of nickel supported on magnesium oxo-fluoride tested in toluene hydrogenation was much higher than that of Ni supported on the commonly used supports such as Al₂O₃ or MgO.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The performance of nickel catalysts in hydrogenation of aromatic hydrocarbons significantly depends on the type of support, specific surface area of the metal, mechanical strength and thermal stability as well as the compatibility with the nickel phase. This is why the intensive work is conducted on the synthesis and modification of the commonly known supports such as Al₂O₃ [1,2], SiO₂ [3,4], MgO [5,6], active carbon [7,8] and mesoporous materials [9–12]. The supported nickel catalysts with high dispersion and loading can be prepared by sol–gel methods, but they usually require complicated procedures [2,5,13]. Another method for the synthesis of active catalysts of aromatic hydrocarbon hydrogenation is based on the introduction of nickel onto binary oxide systems such as SiO₂–TiO₂ [14,15] or SiO₂–Al₂O₃ [16].

This study concerns catalysts consisting of nickel phase supported on magnesium fluoride or on MgF₂–MgO binary system. Magnesium fluoride has been used for many years as a support for oxide and metal phases active and selective in processes important from the environmental viewpoint such as NO reduction in the presence of hydrocarbons as reducing agents [17,18], CO oxidation [18,19], HDS reaction [20,21], hydrogenation of benzene [22,23] and toluene [24–26], as well as selective reduction of chloronitrobenzene to chloroaniline [27,28]. Magnesium fluoride is a good

mesoporous support having well-developed porous structure, high chemical inertness, thermal stability and hardness [29,30]. Unfortunately, magnesium fluoride obtained by the reaction between magnesium carbonate and aqueous solution of hydrofluoric acid has a good thermal stability only up to 400 °C and its specific surface area after calcination at 400 °C is not greater than 40 m² g^{−1}. Calcination at higher temperatures results in a significant decrease in the specific surface area. However, when magnesium fluoride was modified by combining it with magnesium oxide to form the MgF₂–MgO binary system, surface area considerably greater than that of single components MgF₂ or MgO was created and thermal stability of the binary support appeared to be much better [31]. The so-obtained support has been used for iridium catalysts active for toluene hydrogenation to methylcyclohexane [32] and CO oxidation [33]. However, the sol–gel method proved to be complicated and expensive. One of the aims of this study was to simplify the method of preparation of MgF₂–MgO supports by applying the direct reaction between hydrofluoric acid and basic magnesium carbonate. The systems obtained in this way were used as supports for the nickel phase active in toluene hydrogenation.

To the best of our knowledge this is the first report on the potential application of MgF₂–MgO system (obtained by the direct reaction of hydrofluoric acid with basic magnesium carbonate) as the catalyst support. The binary systems obtained by employing the above direct reaction were tested as supports for the active nickel phase. Nickel catalysts containing 5 wt.% of the active phase were prepared by the impregnation method and supported on MgF₂, MgO and a mixed system of MgF₂–MgO and tested for toluene

* Fax: +48 61 829 1505.

E-mail address: mardok@amu.edu.pl