

Short communication

Synthesis and characterization of new Mg–O–F system and its application as catalytic support



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ABSTRACT

The Mg–O–F system (MgF₂–MgO) with different contents of MgF₂ (100–0%) and MgO is tested as support of iridium catalysts in the hydrogenation of toluene as a function of the MgF₂/MgO ratio. Mg–O–F samples have been prepared by the reaction of magnesium carbonate with hydrofluoric acid. The MgF₂–MgO supports, after calcination at 500 °C, are classified as mesoporous of surface area (34–135 m²·g⁻¹) depending on the amount of MgO introduced. The Ir/Mg–O–F catalysts have been tested in the hydrogenation of toluene. The highest activity, expressed as TOF, min⁻¹, was obtained for the catalyst supported on Mg–O–F containing 75 mol%MgF₂.

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1. Introduction

The activity of catalysts for aromatic hydrocarbons hydrogenation depends on many parameters characterizing the catalysts support. The support, the chemical character of its surface, porosity or crystal structure determine the dispersion of active phase and its reducibility in the presence of H₂. The texture of the support, its acidity or basicity are crucial for the formation of surface complexes with the metal. Commonly used iridium phase supports are Al₂O₃ or SiO₂ [1], MgO [2], and a binary system SiO₂–Al₂O₃ [3]. The supports differ in the surface character from acidic to basic, which affects not only the development of dispersed metal particles but also the type of metal–support interactions, determining the catalytic properties of the metallic phase.

This study concerns the catalysts consisting of iridium phase supported on MgF₂–MgO binary system and MgF₂, MgO. Magnesium fluoride itself is an excellent support for catalysts of reduction of nitrogen oxides [4], ammoxidation [5], acetone photodegradation [6], toluene hydrogenation [7] or selective hydrogenation of chloronitrobenzene to chloroaniline [8]. Its well-developed porous structure, considerable chemical inertness, as well as high hardness make MgF₂ a good

mesoporous support. Magnesium fluoride prepared from magnesium carbonate and aqueous solution of hydrofluoric acid, is characterized by specific surface area not greater than 40 m²/g after heating at 400 °C [9].

Literature perusal has revealed papers describing MgF₂ of surface areas a few times greater than those in the sample synthesized from magnesium carbonate and hydrofluoric acid. A method for the preparation of high surface area metal fluorides by fluorination of their organic precursors was developed by Kemnitz et al., initially for the synthesis of AlF₃ [10], and later adopted for the synthesis of MgF₂ [11]. However, detailed analyses have shown that the so-called high surface area MgF₂, reported in literature, is as a matter of fact, a mixed MgF₂–MgO system. The presence of MgO is responsible for high surface area of binary supports. Our studies [12] of chemically pure MgF₂, obtained by the sol–gel method from magnesium methoxide and hydrofluoric acid solution, later calcined at temperatures up to 400 °C, have shown that it does not differ in its surface area from magnesium fluoride prepared by the reaction between hydrofluoric acid and basic magnesium carbonate. The surface area increased only as a result of introduction of MgO to MgF₂. The sol–gel method gave good results in the preparation of binary Mg–O–F system. A detailed characterization of supports prepared by the above method was presented in papers [12–14].

In this work we have made an attempt at simplifying the procedure of preparation of mixed Mg–O–F systems. A more expensive

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magnesium methoxide, used in the sol–gel processes was substituted with basic magnesium carbonate. This enabled elimination of organic impurities from the support. The systems obtained in this way were used as supports for the iridium phase active in toluene hydrogenation. The hydrogenation activity of the Ir/MgF₂–MgO catalysts has been compared with that of iridium catalysts supported on MgF₂ and MgO.

2. Experimental section

2.1. Synthesis of supports and catalysts

Magnesium fluoride (MgF₂) was synthesized by adding small portions of basic magnesium carbonate powder (4 MgCO₃·Mg(OH)₂·5H₂O – Polish Chemicals Reagents) to 40 wt.% aqueous solution of hydrofluoric acid (Polish Chemicals Reagents) until neutralization, then the mixture was acidified by introduction of a few additional drops of the acid. The precipitate was then aged at room temperature for 40 h under stirring and dried at 80 °C for 24 h. After drying the support was calcined under air flow for 4 h at 500 °C.

The MgF₂–MgO supports with different MgF₂/MgO ratio were obtained in the reaction of 4 MgCO₃·Mg(OH)₂·5H₂O with controlled amounts of hydrofluoric acid (40 wt.% aqueous solution). The amount of HF was chosen to ensure 30, 50, 75 mol% of MgF₂ in the support. The resulting dense gels of MgF₂–unreacted magnesium carbonate were subjected to ageing for 40 h at room temperature then dried at 80 °C for 24 h and calcined under air flow at 500 °C for 4 h. The MgF₂–MgO samples were labelled as xMgF₂, where x is the mol% of MgF₂ in the support.

The MgO support was obtained by thermal decomposition of basic magnesium carbonate powder under air flow at 500 °C for 4 h.

The MgF₂–MgO supports with different MgF₂/MgO ratio were obtained by the sol–gel method. Details of the preparation method were presented in [12–14]. The MgF₂–MgO samples were labelled as xMgF₂ s-gel, where x is the mol% of MgF₂ in the support.

The Ir/support (support = MgF₂, MgO or xMgF₂) catalysts were obtained by conventional impregnation method using aqueous solution of H₂IrCl₆ in the amount ensuring 1 wt.% of the iridium content in the catalysts. The catalysts were dried at 80 °C for 24 h.

Prior to hydrogen chemisorption measurements, determination of surface area and porosity and catalytic activity measurements (toluene hydrogenation) the catalysts were reduced with H₂ (99.99%, Linde) at 500 °C for 2 h.

2.2. X-ray diffraction analysis and determination of the fluorine content

The X-ray powder diffraction studies were performed with Bruker AXS D8 Advance instrument equipped with a CuKα source and Ni filter in the range of 20–80° 2θ for the samples calcined at 500 °C for 4 h. Based on the XRD data, using DQuant program, quantitative determination of MgF₂ and MgO in the binary supports was measured. The contents of the two compounds (MgF₂ and MgO) will be evaluated on the basis of comparison of intensity of reflections assigned to the standards (mixture of MgF₂ and MgO) containing 85, 70 or 30 mol% of MgF₂. The calculations were made with the use of DQuant program. This method has been successfully applied for binary systems obtained by the sol–gel method [12].

2.3. Thermogravimetric analysis

The measurements were performed at temperatures 30–1000 °C using a differential Therm analyzer Setaram TGA, equipped with a TG measurement unit. Thermogravimetric analysis was carried out for supports dried at 80 °C. The experiments were performed under air flow (purity 99.99%, Linde) and a heating rate of 5 °C·min⁻¹.

2.4. Catalytic test – hydrogenation of toluene

Toluene hydrogenation was carried out by the continuous flow method under atmospheric pressure. The experiments were carried out with 25 mg of catalyst with a grain size 0.15–0.25 mm. Before the reaction was started, catalyst was reduced in situ for 2 h in a flow (100 cm³·min⁻¹) of pure hydrogen (99.99%, Linde) at 500 °C. Details of the hydrogenation reaction were presented in [7].

The catalytic activity was presented as *apparent rate* calculated by following the equation:

$$r_t = \frac{FYC}{N} \left[\frac{\text{mol}_{\text{H}_2}}{\text{mol}_{\text{total-Ir}} \text{min}} \right]$$

where *F* is the total flow rate of feed (cm³·min⁻¹); *Y* is the fractional conversion; *C* is the concentration of toluene in the feed (mol_{H₂}·cm³) and *N* is the iridium content (mol_{Ir}) in the sample. *Turnover frequency* – TOF, min⁻¹ was calculated by dividing the number of molecules converted per minute by the number of active iridium atoms measured by H₂ adsorption [7].

The activities were measured at 125 °C after 1 h of the toluene hydrogenation reaction.

3. Results and discussion

Synthesis of binary supports MgF₂–MgO with the use of 4 MgCO₃·Mg(OH)₂·5H₂O and controlled amounts of HF permits getting a mixture of MgF₂ and unreacted basic magnesium carbonate which upon thermal treatment undergoes decomposition to MgO. Thermogravimetric study revealed that all Mg–O–F supports give four mass loss maxima (Fig. 1). The thermal decomposition of 4 MgCO₃·Mg(OH)₂·5H₂O is expected to proceed via dehydration (removal of water of crystallisation) below 250 °C, dehydroxylation (decomposition of magnesium hydroxide to MgO) between approximately 250 and 350 °C (the maximum at 276 °C), and decarbonation (decomposition of magnesium carbonate to MgO) above 350 °C [15–17]. In view of the fact that in temperatures above 500 °C no mass loss signals were observed, this temperature was chosen for activation of the supports and catalysts.

The supports were subjected to XRD study to determine the content of MgF₂ in the mixed supports Mg–O–F (Fig. 2). After calcination at 500 °C, the supports studied revealed the presence of crystalline MgF₂ and MgO phases. As follows from the diffraction patterns of single MgF₂ and MgO supports and double Mg–O–F supports after calcination

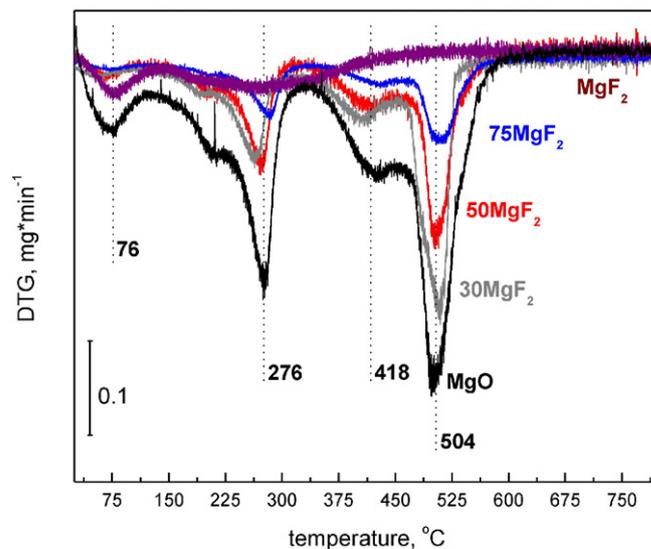


Fig. 1. DTG curves recorded for MgF₂, binary MgF₂–MgO supports and basic magnesium carbonate (precursor of MgO).

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