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Short Communication

Iridium supported on MgF_2–MgO as catalyst for toluene hydrogenation

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ABSTRACT

The use of mixed magnesium oxo-fluoride support, obtained by one-step sol–gel method, for iridium active phase allowed obtaining new catalysts of high activities in the hydrogenation of toluene. The Ir/MgF_2–MgO catalyst was a hundred times more active than that of the iridium system supported on MgF_2. The effect of the MgO content and catalyst pre-treatment conditions appeared to have a clear influence on the activity of tested iridium catalysts. The highest activity, expressed as TOF, s^{-1}, was obtained for the catalyst activated at 500 °C supported on magnesium oxo-fluoride containing 60 mol.% MgO.

1. Introduction

Great significance of the processes of aromatic hydrocarbon hydrogenation is mainly related to their use for improvement of fuel quality [1] and has been a basic step of synthesis of many organic compounds [2,3]. Among the metallic phases highly active and often used in hydrogenation reaction is platinum [4]. A metal cheaper than platinum [5] but of limited application in catalysis is iridium. On industrial scale it is used for production of acetic acid (Cativa™ process) [6,7], and in the processes of hydrodesulphurization [8–10]. Lower cost of iridium and its greater resistance to deactivation caused by impurities present in the raw material processed makes it interesting for catalytic applications.

Recently, much interest has been devoted to the use of binary systems (SiO_2–TiO_2, Al_2O_3–SiO_2, Al_2O_3–TiO_2, MgO–Al_2O_3) [11–15] as catalytic supports because of their high performance, usually better than that of single-component systems. Surface properties of binary supports strongly depend on the method of their preparation. The most often used methods are based on mechanical stirring of components [11], co-precipitation [14] or sol–gel process [11–13,15]. In this paper the mixed MgF_2–MgO systems, pure MgF_2 and MgO obtained by sol–gel method have been tested as potential supports of iridium catalysts for toluene hydrogenation. The samples of MgF_2–MgO with different content of MgO and pure MgO have been prepared by one-step sol–gel method in the reaction of magnesium methoxide dissolved in methanol with hydrofluoric acid [16]. The sol–gel processes have become an important and useful method for the synthesis of catalyst supports or catalysts as such [17–19]. The advantages of this method are high purity of the materials obtained, possibility of control of particle size and porous structure of the products, relatively low temperature of the process (<100 °C) and relatively low cost.

In this work the catalytic properties of iridium supported on magnesium oxo-fluorides have been used to obtain new toluene hydrogenation catalysts. To the best of our knowledge, no data are available on investigation of Ir/MgF_2–MgO catalysts in toluene hydrogenation reaction. Activity of the new catalysts has been compared with iridium catalysts supported on pure MgF_2 or MgO.

2. Experimental

2.1. Synthesis of MgF_2–MgO, MgF_2 and MgO samples

Two MgF_2–MgO samples of different MgO content were synthesized by the sol–gel method from magnesium methoxide and an aqueous solution of hydrofluoric acid. 120 cm^3 of 0.5 M solution of freshly synthesized magnesium methoxide (from magnesium turnings for Grignard synthesis, MERCK) in methanol was added dropwise (20 $cm^3 \cdot h^{-1}$) at room temperature under intense stirring to an aqueous solution of hydrofluoride (40%, POCH – Polish Chemicals Reagents). The amount of hydrofluoride solution was chosen to ensure 30 and 60 mol% MgO in the samples. The resulting dense gels of MgF_2–$Mg(OH)_2$ were subjected to ageing for 40 h at RT, and then to drying at 80 °C for 3 h. The dried samples were calcined for 4 h at 400 °C. The MgF_2–MgO samples were labelled as **xMO**, where x is the mol% of MgO.

The MgF_2 support was obtained by the sol–gel method from $Mg(OCH_3)_2$ and anhydrous HF (48.8% HF in methanol, Aldrich) in a way analogous to the above described synthesis of MgF_2–MgO, but

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under strict anhydrous conditions. The dried sample was calcined for 4 h at 400 °C – denoted as **MF**.

MgO was obtained by the sol–gel method by hydrolysis of magnesium methoxide (120 cm^3 of 0.5 M solution) in water and treated similarly to MgF_2–MgO. The dried sample was calcined for 4 h at 400 °C – denoted as **MO**.

2.2. Synthesis of iridium catalysts

Iridium was deposited on MgF_2, MgO and MgF_2–MgO supports by conventional impregnation using methanolic solution of $Ir_4(CO)_{12}$. The content of Ir was 1 wt.%. The catalysts were dried at 80 °C for 24 h – fresh catalysts. Prior to the determination of metal dispersion by hydrogen chemisorption measurement, the samples were reduced with H_2 at 400 °C for 2 h — denoted as **Ir/support-4** and reduced with H_2 at 500 °C for 2 h — denoted as **Ir/support-5**.

2.3. Catalytic test — hydrogenation of toluene

Toluene hydrogenation was performed at atmospheric pressure using a fixed-bed flow reactor and H_2 as carrier gas. Fresh catalyst, after drying (0.025 g) was placed in the reactor and reduced for 2 h in a flow (100 $cm^3 \cdot min^{-1}$) of pure hydrogen (99.99% purchased from Messer) at the range of 300–550 °C. The H_2 (50 $cm^3 \cdot min^{-1}$) passed through a saturator filled with toluene. The concentration of toluene in feed was stable and was 0.75μmol·cm^{-3}. The catalysts were heated at the rate of 10 °C·min^{-1} and catalytic tests were carried out at 50–225 °C over the same catalyst. The reaction products were analyzed on a gas chromatograph equipped with a capillary column RESTEK - MXT - 1. The catalytic activity was presented as *apparent rate* calculated by following Equation:

$$r_t = \frac{FYC}{N}\left[\frac{mol_{Tl}}{mol_{Ir}\,\min}\right]$$

where F is the total flow rate of feed ($cm^3 \cdot min^{-1}$); Y the fractional conversion; C the concentration of toluene in the feed ($mol_{Tl} \cdot cm^3$) and N the iridium content (mol_{Ir}) in the sample.

Turnover frequency - TOF, s^{-1} was calculated by dividing the number of molecules converted per second by the number of active iridium atoms measured by H_2 adsorption.

2.4. Catalyst characterisation

2.4.1. Surface area

Surface area was determined by the low temperature (−196 °C) nitrogen adsorption carried out on ASAP 2010 analyzer (Micromeritics GmbH). Specific surface area was determined by using the Brunauer-Emmet-Teller (BET) method.

2.4.2. The determination of metal dispersion by hydrogen chemisorption

The reduced samples were placed in an ASAP 2010 C sorptometer and were evacuated for 15 min at room temperature and then at 400 °C for 60 min, followed by additional reduction in hydrogen flow (40 $cm^3 \cdot min^{-1}$) at 400 °C and evacuated again for 120 min at 400 °C. Chemisorption of hydrogen was carried out at 35 °C and the isotherms were determined using 5 different pressures in the range of 6–40 kPa. After the measurement carried out at the first set of pressures was completed, the catalyst was evacuated at 35 °C for 30 min to remove reversibly adsorbed hydrogen and the same procedure was repeated. The difference between adsorbed hydrogen extrapolated to zero pressure value for two isotherms equals to the amount of hydrogen irreversibly bound. Metallic dispersions were calculated by the ratio of irreversible uptake to the total metal content assuming an H:Ir = 1 surface stoichiometry [20,21].

3. Results and discussion

Iridium catalysts were obtained with the use of MgF_2, MgO and mixed magnesium fluoride–magnesium oxide supports. The magnesium oxo-fluoride supports were synthesized by the one-step sol–gel method [16] in contrast to the described in literature two-step method of preparation of MgO–MgF_2 support, based on hydrolysis of magnesium methanolate in the first stage and the treatment of the hydroxide obtained with hydrogen fluoride in the second stage [22]. In the one-step method, magnesium methanolate was treated by hydrofluoric acid of the concentration adjusted to obtain samples containing 0, 30, 60 and 100 mol% of MgO. The amount of magnesium oxide introduced to MgF_2 was estimated on the basis of the intensity of the XRD peaks (not included) assigned to relevant crystalline phases [16]. Parameters characterising the support and catalysts are given in Table 1.

Hydrogenation of toluene to methylcyclohexane was performed in a gas-phase in the temperature range 50–225 °C. The first parameters to be optimized were the content of MgO in the support and

Table 1
Characterisation of the support and catalysts.

Supports and catalysts[a]	Pre-treatment condition	MgO content in supports[b], mol.%	BET surface area[c], $m^2 \cdot g^{-1}$	H_2 chemis.[d], μmol·g_{Ir}^{-1}	Average Ir crystallite size[e], nm
MF	calcined at 400 °C, 4 h	0	32	–	–
30MO	calcined at 400 °C, 4 h	33.3	144	–	–
60MO	calcined at 400 °C, 4 h	59.9	208	–	–
MO	calcined at 400 °C, 4 h	100	152	–	–
Ir/MF-4	H_2 reduction at 400 °C, 2 h	0	31	1121	2.58
Ir/30MO-4	H_2 reduction at 400 °C, 2 h	33.3	158	1821	1.59
Ir/60MO-4	H_2 reduction at 400 °C, 2 h	59.9	252	2783	1.04
Ir/MO-4	H_2 reduction at 400 °C, 2 h	100	149	2299	1.26
Ir/MF-5	H_2 reduction at 500 °C, 2 h	0	23	667	4.33
Ir/30MO-5	H_2 reduction at 500 °C, 2 h	33.3	131	1429	2.02
Ir/60MO-5	H_2 reduction at 500 °C, 2 h	59.9	193	2085	1.39
Ir/MO-5	H_2 reduction at 500 °C, 2 h	100	122	1362	2.12

[a] See Experimental Section for nomenclature.
[b] MgO content was estimated from XRD signals intensity [16].
[c] The Brunauer-Emmet-Teller surface areas were determined by N_2 adsorption at −196 °C using a Micromeritics ASAP2010 sorptometer. The conditions of measurements are specified in Experimental Section.
[d] The amount of irreversibly chemisorbed hydrogen.
[e] Mean size of Ir particles calculated from the amount of irreversibly chemisorbed hydrogen. The conditions of measurements are specified in Experimental Section.