Contents lists available at SciVerse ScienceDirect



Catalysis Communications



journal homepage: www.elsevier.com/locate/catcom

Short Communication

Iridium supported on MgF₂-MgO as catalyst for toluene hydrogenation

Michał Zieliński*, Maria Wojciechowska

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

ARTICLE INFO

Article history: Received 29 September 2011 Received in revised form 31 October 2011 Accepted 3 November 2011 Available online 15 November 2011

Keywords: Iridium catalyst Sol-gel synthesis Magnesium fluoride Magnesium oxide Toluene hydrogenation

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 (SiO₂-TiO₂, Al₂O₃-SiO₂, Al₂O₃-TiO₂, MgO-Al₂O₃) [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 MgF₂-MgO systems, pure MgF₂ and MgO obtained by sol-gel method have been tested as potential supports of iridium catalysts for toluene hydrogenation. The samples of MgF₂-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

E-mail address: mardok@amu.edu.pl (M. Zieliński).

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/MgF₂-MgO catalyst was a hundred times more active than that of the iridium system supported on MgF₂. 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.

© 2011 Elsevier B.V. All rights reserved.

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 $^{\circ}$ 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 MgF₂ or MgO.

2. Experimental

2.1. Synthesis of MgF₂-MgO, MgF₂ and MgO samples

Two MgF₂–MgO samples of different MgO content were synthesized by the sol–gel method from magnesium methoxide and an aqueous solution of hydrofluoric acid. 120 cm³ of 0.5 M solution of freshly synthesized magnesium methoxide (from magnesium turnings for Grignard synthesis, MERCK) in methanol was added dropwise ($20 \text{ cm}^3 \cdot \text{h}^{-1}$) 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 MgF₂–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 MgF₂–MgO samples were labelled as **xMO**, where x is the mol% of MgO.

The MgF₂ 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 MgF₂-MgO, but

^{*} Corresponding author at: Faculty of Chemistry, Adam Mickiewicz University in Poznań, Grunwaldzka 6, 60–780 Poznań (Poland). Fax: +48 61 829 1505.

^{1566-7367/\$ –} see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.catcom.2011.11.006

under strict anhydrous conditions. The dried sample was calcined for 4 h at 400 $^{\circ}$ C – denoted as **MF**.

MgO was obtained by the sol-gel method by hydrolysis of magnesium methoxide (120 cm³ of 0.5 M solution) in water and treated similarly to MgF₂-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 MgF₂, MgO and MgF₂–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 H₂ at 400 °C for 2 h – denoted as **Ir/support-4** and reduced with H₂ 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 H₂ 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.} min⁻¹) of pure hydrogen (99.99% purchased from Messer) at the range of 300–550 °C. The H₂ (50 cm^{3.} 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 (cm³·min⁻¹); Y the fractional conversion; C the concentration of toluene in the feed (mol_{II}·cm³) 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 H₂ adsorption.

Table 1

Characterisation of the support and catalysts.

2.4. Catalyst characterisation

2.4.1. Surface area

Surface area was determined by the low temperature $(-196 \,^{\circ}C)$ 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 cm³·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 MgF₂, MgO and mixed magnesium fluoride–magnesium oxide supports. The magnesium oxo-fluoride supports were synthesized by the one-step solgel method [16] in contrast to the described in literature two-step method of preparation of MgO–MgF₂ 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 MgF₂ 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

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] , μ mol \cdot 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.

temperature of toluene hydrogenation. Results of the catalytic studies are given in Fig. 1. The MgF₂, MgO and magnesium oxo-fluoride supports did not show any activity in the gas phase toluene hydrogenation, while the reduced Ir-catalysts were active in this process. In all catalytic tests the only product was methylcyclohexane.

Fig. 1 illustrates the effects of reaction temperature and MgO content in support on the activity of iridium catalyst. Prior to the reaction, the catalysts were activated at 500 °C. This temperature was chosen to avoid decomposition of the active phase precursor, i.e. tetrairidium dodecacarbonyl– $Ir_4(CO)_{12}$. Our earlier studies of iridium catalysts supported on magnesium fluoride (obtained in a reaction of basic magnesium carbonate with an aqueous solution of hydrofluoric acid) have shown that the process of decarbonylation of $Ir_4(CO)_{12}$ is complete at ~475 °C [23], while according to Alexeev and Gates the process of decarbonylation of $Ir_4(CO)_{12}$ supported on Al₂O₃ [24] or MgO [25] is complete at 300 °C. That is why the plot in Fig. 1 presents the activities of the catalysts activated in hydrogen flow at 500 °C.

All catalysts exhibit a maximum of activity as a function of the reaction temperature. For the catalysts supported on pure MgF₂ and MgF₂–MgO the temperature of the maximum activity was 125 °C. For the catalyst supported on MgO (Ir/MO-5) the temperature of the maximum activity was shifted towards higher temperatures, i.e. to 150 °C. The hydrogenation activities of Ir/MgF₂–MgO systems were much higher than that of Ir/MO-5 and the lowest activity exhibited the Ir/MF-5 catalyst. The introduction of MgO to MgF₂ has a great effect on the Ir/MgF₂–MgO catalysts activity in toluene hydrogenation reaction. The activity optimum was observed for the MgO content of about 60 mol% for Ir/60MO-5. The hydrogenation activity of the catalyst with 33.3 mol.% (Ir/30MO-5) was comparable with that of Ir/MO-5 and was about 25% lower than that of Ir/60MO-5. The activity of Ir/MF-5 catalyst was almost two orders of magnitude lower.

Besides the optimum temperature for the reaction of hydrogenation, another important parameter is the temperature of catalyst activation. A decrease in the activation temperature at high degree of conversion allows first of all to save the energy needed for the catalyst activation. Fig. 2 presents the Ir/60MO catalyst activity versus the temperature of its activation; with increasing activation temperature the activity of this catalysts increases. After the activation at



Fig. 1. The effect of reaction temperature and MgO content in the magnesium oxofluoride support on apparent rate of toluene hydrogenation reaction by iridium catalyst activated at 500 $^{\circ}$ C.



Fig. 2. The effect of activation temperature on apparent rate of toluene hydrogenation reaction on Ir/60MO catalysts at 125 °C.

400 °C the catalyst activity rapidly increases, which can be explained by full decomposition of the iridium precursor $Ir_4(CO)_{12}$. Further increase in temperature, to 500 °C, did not cause significant changes in the catalyst activity, while the activation at 550 °C was observed to cause a decrease in the catalyst activity. This decrease was interpreted as related to changes in the specific surface area of the catalysts and dispersion of the active phase (Table 1).

As follows from the data presented, the activity of iridium catalysts is first of all dependent on the content of MgO in the MgF₂-MgO support and the temperature of reduction of the catalysts studied. On the basis of the low-temperature nitrogen adsorption data, see Table 1, the introduction of MgO to magnesium fluoride was found to significantly affect the surface area of the support. The surface area of the systems MgF₂-MgO changed from 144 to even $208m^2 g^{-1}$ for 30MO-4 and 60MO-4, respectively, and was almost five to seven times greater than that of pure magnesium fluoride $(32m^2 \cdot g^{-1})$. All the supports obtained were mesoporous materials of the mean pore diameter of 4-12 nm. After the introduction of the active phase, the specific surface area of the catalysts supported on MgF₂ or MgO slightly decreased, while that of the catalysts supported on MgF₂–MgO increased. As the above changes in the specific surface area were small, it can be concluded that the impregnation of the support with the iridium precursor and its later thermal treatment in hydrogen at 400 °C did not have great influence on the porous structure of the catalysts. Greater changes in the surface area and in particular for the catalysts supported on MgF₂, were recorded after the catalysts activation at 500 °C. MgF₂ has almost chemically inert surface, high hardness and good thermal stability up to ~500 °C, and already at 500 °C crystallisation of MgF₂ proceeds and surface area decreases [26]. Introduction of MgO to MgF₂ delays the process of crystallisation, which allows to obtain supports of greater surface area and greater thermal resistance.

Another parameter influencing the activity of iridium catalysts in hydrogenation of toluene is the dispersion of the metal. The dispersion and size of crystallites of iridium in the Ir/MgF₂–MgO catalysts were characterised on the basis of the hydrogen chemisorption isotherms at 35 °C (Table 1.). The use of magnesium oxo-fluoride as a support provided catalysts of very good dispersion of iridium, reaching even 100% in the sample Ir/60MO-4. The dispersion of iridium was found to depend on the content of MgO in the support. With increasing surface area of the MgF₂–MgO supports the dispersion of iridium increases, which is in agreement with literature data [27]. With increasing temperature of the catalysts reduction, the active phase dispersion decreased, which was the most pronounced for Ir/MF-5 and Ir/MO-5 catalyst and the least pronounced for the catalysts supported on MgF₂–MgO. A similar influence of the temperature of catalysts reduction on the size of iridium crystallites was reported in [28] concerning the Ir/Al₂O₃ systems.

In our study we have employed hydrogen chemisorption, because the amount of chemisorbed hydrogen enables determination of not only the average size of metallic particles, but also the number of iridium surface atoms required for the calculation of turnover frequency (TOF, s^{-1}) of hydrogenation reaction at 60 °C. As to a comparison of the TOF, s⁻¹ values obtained by us for the best catalysts Ir/60MO-4 (TOF = 0.0267 s⁻¹) and Ir/60MO-5 (TOF = 0.0588 s^{-1}) with those reported in literature, we can say that they are very close to or higher than the values obtained by other authors. For example Cuhna et al. [29] who studied hydrogenation of toluene at 60 °C on alumina-supported iridium catalyst have reported the activities $TOF = 0.0019 \text{ s}^{-1}$ (after calcination/ reduction at 400 °C) or TOF=0.0102 s⁻¹ (after direct reduction at 400 °C), while for the Ir/SiO₂ catalyst they obtained TOF = 0.0193 s⁻¹ (after direct reduction at 400 °C). The authors of [25] for Ir/MgO catalyst after direct reduction at 400 °C obtained TOF = 0.0131 s^{-1} . Thus, the results have shown that the catalytic activity in toluene hydrogenation depends not only on the method of the catalyst activation but also on the type of iridium support.

Therefore, we can conclude that in the iridium catalysts on mixed MgF₂–MgO supports both the surface area and the dispersion of the metal depend strongly on the content of MgO in the support. On the other hand, the content of a certain amount of MgF₂ in the support is necessary to ensure the greatest specific surface area and the best dispersion of iridium, which determine the catalyst activity in the toluene hydrogenation reaction.

4. Conclusions

In conclusion, we can say that the introduction of magnesium oxide into magnesium fluoride by the sol-gel method permits obtaining the catalyst supports showing much greater surface area than that of each separate component. The binary systems were proved to be attractive supports of the iridium active phase, ensuring high dispersion of this active phase and thus a high catalytically activity in the toluene hydrogenation reaction. The present study is the first ever on the application of Ir/MgF₂-MgO catalyst in the reaction of toluene hydrogenation to methylcyclohexane.

Acknowledgments

The financial support of the Polish Committee for Scientific Research (grants N N204 141339 and N N204 214140) is gratefully acknowledged.

References

- [1] Worldwide Fuel Charter, Fourth Edition, September 2006, http://oica.net/ wp-content/uploads/2007/06/wwfc-fourth-edition-sep-2006.pdf.
- K. Weissermel, H.-J. Arpe, Industrial Organic Chemistry, Third Edition, Wiley-VCH, Weinheim, 1997.
- S. Nishimura, in: L.A. Pasquette (Ed.), Encyclopedia of Reagents for Organic Synthesis, [3] Vol. 4, Wiley, Chichester, U.K., 1995, p. 2868.
- [4] S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, A Wiley-Interscience Publication, 2001, p. 30.
- http://www.platinum.matthey.com.
- J.H. Jones, Platinum Metals Review 44 (3) (2000) 94–105. [6] Ì7Ì
- G.J. Sunley, D.J. Watson, Catalysis Today 58 (2000) 293-307. T.A. Pecoraro, R.R. Chianelli, Journal of Catalysis 67 (1981) 430-445. [8]
- Z. Vit, Applied Catalysis A 322 (2007) 142-151. [9]
- [10] A. Wajnert, M. Wojciechowska, M. Pietrowski, W. Przystajko, Catalysis Communications 9 (2008) 1493-1496.
- [11] J.R. Grzechowiak, I. Szyszka, J. Rynkowski, D. Rajski, Applied Catalysis A 247 (2003) 193-206
- [12] B. Pawelec, R.M. Navarro, J.M. Campos-Martin, A. López Agudo, P.T. Vasudevan, J.L.G. Fierro, Catalysis Today 86 (2003) 73-85.
- [13] G. Murali Dhar, B.N. Srinivas, M.S. Rana, M. Kumar, S.K. Maity, Catalysis Today 86 (2003) 45-60.
- [14] K. Foger, J.R. Anderson, Applied Catalysis A 23 (1986) 139–155.
- P. Kirszensztejn, R. Przekop, A. Szymkowiak, E. Maćkowska, J. Gaca, Microporous and Mesoporous Materials 89 (2006) 150-157.
- [16] M. Wojciechowska, A. Wajnert, I. Tomska-Foralewska, M. Zieliński, B. Czajka, Catalysis Letters 128 (2009) 77-82.
- LA Schwarz C Contescu A Contescu Chemical Reviews 95 (1995) 477–510 [17]
- [18] Z. Lu, E. Lindner, H.A. Mayer, Chemical Reviews 102 (2002) 3543–3578.
 [19] V. Meille, Applied Catalysis A 315 (2006) 1–17.
- [20] G.B. McVicker, R.T.K. Baker, R.L. Garten, E.L. Kugler, Journal of Catalysis 65 (1980) 207-220.
- [21] R. Frety, B. Benaichoura, P. Bussieu, D. Santos Cunha, Y.L. Lam, Journal of Molecular Catalysis 25 (1984) 173-182
- [22] H.A. Prescott, Z.-J. Li, E. Kemnitz, J. Deutsch, H. Lieske, Journal of Materials Chemistry 15 (2005) 4616-4628
- [23] M. Zieliński, M. Pietrowski, M. Wojciechowska, ChemCatChem 3 (2011) 1653-1658.
- [24] O. Alexeev, G. Panjabi, B.C. Gates, Journal of Catalysis 173 (1998) 196–209.
- [25] O.S. Alexeev, D.-W. Kim, B.C. Gates, Journal of Molecular Catalysis A: Chemical 162 (2000) 67-82.
- [26] M. Wojciechowska, M. Zieliński, M. Pietrowski, Journal of Fluorine Chemistry 120 (2003) 1 - 11
- [27] R. Vieira, C. Pham-Huu, N. Keller, M.J. Ledoux, Chemical Communications (2002) 954-955.
- [28] O. Alexeev, B.C. Gates, Journal of Catalysis 176 (1998) 310-320.
- [29] D.S. Cuhna, G.M. Cruz, Applied Catalysis A 236 (2002) 55–66.