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Short communication

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



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ABSTRACT

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Keywords: Magnesium fluoride Magnesium oxide Iridium Toluene hydrogenation X-ray techniques Thermal analysis 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. © 2015 Elsevier B.V. All rights reserved.

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

*Corresponding author E-mail address: mardok@amu.edu.pl (M. Zieliński). mesoporous support. Magnesium fluoride prepared from magnesium carbonate and aqueous solution of hydrofluoric acid, is characterized by specific surface area not greater than 40 m^2/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 AlF_3 [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



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 (MgF_2) was synthesized by adding small portions of basic magnesium carbonate powder $(4 MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O - Polish Chemicals Reagents)$ 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 $xMgF_{2 s-g}$, 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 H_2 (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 CuK α source and Ni filter in the range of 20–80° 2 Θ 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 solgel method [12].

2.3. Thermogravimetric analysis

The measurements were performed at temperatures 30-1000 °C using a differential Thermoanalyzer 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 $(100 \text{ cm}^3 \cdot \text{min}^{-1})$ 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:

$$r_{t} = \frac{FYC}{N} \left[\frac{mol_{Tl}}{mol_{total \cdot Ir} \min} \right]$$

where *F* is the total flow rate of feed $(\text{cm}^3 \cdot \text{min}^{-1})$; Y is the fractional conversion; C is the concentration of toluene in the feed $(\text{mol}_{\text{II}} \cdot \text{cm}^3)$ and N is the iridium content (mol_{II}) 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 $^\circ\mathrm{C}$ after 1 h of the toluene hydrogenation reaction.

3. Results and discussion

Synthesis of binary supports MgF_2-MgO with the use of $4 MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ and controlled amounts of HF permits getting a mixture of MgF_2 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 $4 MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ 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).



Fig. 2. X-ray diffraction patterns of supports treated at 500 °C.

at 500 °C, MgF₂ and MgO form separate crystalline phases. MgF₂ contents determined by XRD were slightly lower than the desired values (75, 50 and 30 mol%) and equalled to 72, 44 and 28 mol% (Table 1).

Table I

Dhucical	charactorictics	of cumporte	and inidium	a atalysta	after calcination	and roduction	at E00 °C
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According to our earlier study, decomposition and reduction of H₂IrCl₆ occur up to 450 °C [7], therefore the catalysts tested in toluene hydrogenation were performed (H₂ reduction) at 500 °C. A comparison of the parameters of the analogous catalysts on the supports obtained by the sol-gel method [12–14] and by the method proposed in this study (Table 1), the former ones have larger surface areas and smaller pores. The use of the catalysts on the supports obtained by the sol-gel method also ensures a better dispersion of iridium, for instance for Ir/70MgF_{2 s-g} $D_t = 54.5\%$, while for Ir/70MgF₂ $D_t = 48.0\%$. However, it has no decisive influence on the activity in the hydrogenation of toluene reaction (Fig. 3b). The apparent rate (Fig. 3a) and TOF (Fig. 3b) are much higher for the catalysts on the supports obtained by the direct reaction of basic magnesium carbonate with HF. Fig. 3a and b shows the hydrogenation activity of the catalysts as a function of MgF₂ content in the supports and method of support preparation. The supports itself did not show any activity in toluene hydrogenation. The highest activity, expressed in terms of TOF, min⁻¹, showed that the activity of the most active catalysts (Ir/50MgF₂ and Ir/75MgF₂) was by over 25% higher than that of Ir/MgF₂ and twice as high as that of Ir/MgO. Irrespective of the type of support used, despite an increase in dispersion of the active phase and surface area (Table 1), further addition of MgO causes a decrease in activity. The highest dispersions of iridium, calculated from the amount of total adsorbed hydrogen, $D_t = 86.3$ and 94.7%, and the smallest iridium particle sizes were found for Ir/30MgF2 and Ir/MgO catalysts, respectively. A similarly high dispersion ($D_t = 94.1\%$) was observed for the system Ir/40MgF_{2 s-g}, Table 1. Another parameter that depends on the content of MgO in the support is the surface area. In general, the surface area of mixed supports increased with increasing amount of MgO introduced, irrespective of the support synthesis method. The surface area of MgO was almost five times greater than that of MgF₂. All the samples (supports and catalysts) obtained were mesoporous with the mean pore diameters ranging from 8 to 29 nm. The surface of MgF₂ is inert, whereas that of MgO is basic and both supports belong to insulators. A decrease in the catalytic activity with increasing amount of MgO introduced can be explained by a growing number of basic sites on the support with increasing content of MgO. As proved

Sample symbol ^a	Physical characterization of supports and iridium catalysts					Hydrogen chemisorption data for Ir/support catalysts ^e					
	MgF ₂ content ^c mol%	Method of activation	Surface area ^d , m ² ·g ⁻¹	Total pore volume, cm ³ ·g ⁻¹	Average pore diameter, nm	Volume adsorbed, $\text{cm}^3 \cdot \text{g}^{-1}$		Dispersion,%			
						H _t	H _{irr}	H _r	D _t	$\mathbf{D}_{\mathrm{irr}}$	Mean size of Ir ^f , nm
MgF ₂	100	Calcination	31.7	0.17	21.3	-	-	-	-	-	-
75MgF ₂	72	(air, 4 h, 500 °C)	33.8	0.25	29.4	-	-	-	-	-	-
50MgF ₂	44		106.4	0.35	13.8	-	-	-	-	-	-
30MgF ₂	28		135.0	0.33	9.9	-	-	-	-	-	-
MgO	0		142.7	0.29	8.2	-	-	-	-	-	-
Ir/MgF ₂	-	Reduction	27.5	0.16	23.5	0.158	0.025	0.133	27.1	4.4	25.5
Ir/75MgF ₂	-	(H ₂ , 2 h, 500 °C)	30.6	0.19	25.4	0.280	0.045	0.235	48.0	7.7	14.4
Ir/50MgF ₂	-		98.5	0.30	12.8	0.431	0.187	0.244	70.9	32.0	3.5
Ir/30MgF ₂	-		139.2	0.39	11.3	0.503	0.283	0.220	86.3	48.5	2.3
Ir/MgO	-		191.0	0.62	13.0	0.552	0.255	0.297	94.7	43.7	2.5
Ir/MgF _{2 s-g} ^b	100	Reduction	39.1	0.19	19.4	0.155	0.042	0.113	26.5	7.2	15.4
Ir/70MgF2 s-g ^b	67	(H ₂ , 2 h, 500 °C)	102.9	0.29	11.3	0.318	0.163	0.231	54.5	27.9	3.9
Ir/40MgF _{2 s-g} b	39		175.1	0.37	8.45	0.549	0.315	0.234	94.1	54.0	2.1
Ir/MgO s-g	0		169.9	0.40	9.42	0.569	0.244	0.325	97.6	41.9	2.7

^a See Experimental Section for nomenclature.

^b The supports were synthesized by sol-gel method. Details of the supports preparation were presented in [12–14]. The Ir/sol-gel support catalysts were obtained by conventional impregnation method as in paragraph 2.1.

^c MgF₂ content was estimated from XRD signals intensity – see Experimental Section.

^d The Brunauer–Emmett–Teller surface areas were determined by N₂ adsorption at -196 °C using a Micromeritics ASAP2010 sorptometer. Total pore volume and average pore radius were determined by the Barrett–Joyner–Halenda (BJH) method.

^e Dispersion and mean size of Ir particles were determined by H_2 chemisorption using a Micromeritics ASAP2010C sorptometer. Prior to hydrogen chemisorption, the catalysts were reduced with H_2 at 500 °C for 2 h. Chemisorption of hydrogen was carried out at 35 °C and the isotherms were determined using 5 different pressures in the range of 12–40 kPa. After first set of pressures (isotherm H_t – total adsorbed hydrogen) the catalyst was evacuated at 35 °C for 30 min to remove reversibly adsorbed hydrogen (H_r) 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 (H_{irr}).

^f Mean size of Ir particles calculated from the amount of irreversibly chemisorbed hydrogen. The conditions of measurements are specified in [7].



Fig. 3. The effect of support composition and method of preparation on *the apparent rate* (calculated on total Ir – **Figure 3a**) and *TOF* (calculated by dividing the number of molecules converted per minute by the number of active (surface) iridium atoms measured by H₂ adsorption – **Figure 3b**) of iridium catalysts for hydrogenation of toluene. Methylcyclohexane was the only product in all catalytic tests. Activation of catalyst: 500 °C, H₂ = 100 cm³·min⁻¹, 2 h; reaction: $c_{II} = 0.75 \mu mol·cm⁻³, H_2 = 50 cm³·min⁻¹, 125 °C, activity after 1 h.$

by Prescott et al. [18] an addition of MgO to MgF₂ increases the basic character of the mixed system. The decrease in hydrogenation activity for different processes with increasing number of basic sites has already been reported in several papers [13,19].

A comparison of the apparent rate and TOF values obtained by us for the Ir/75MgF₂ catalyst ($r_t = 0.95 \text{ min}^{-1}$; TOF = 1.98 min⁻¹ at 60 °C) with those reported in literature for iridium deposited on other supports, shows that the values we obtained are higher. The author of [1] who studied hydrogenation of toluene at 60 °C on Ir/Al₂O₃ and Ir/SiO₂ catalysts, after direct reduction at 400 °C, has reported the activities TOF = 0.612 min⁻¹ and TOF = 1.158 min⁻¹, respectively. The authors of [7] for Ir/Al₂O₃ catalyst after reduction at 400 °C obtained $r_{t.}$ = 0.348 min⁻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, and Mg–O–F supports are better than the commonly used Al₂O₃ and SiO₂.

4. Conclusions

The use of iridium active phase and magnesium oxo-fluoride support allows obtaining new catalysts of high activities in the hydrogenation of toluene, higher than that of the iridium system supported on MgF₂ or MgO. The binary systems containing about 75 mol% MgF₂, obtained by the proposed method were proved to be attractive supports of the iridium active phase, ensuring high dispersion of this active phase and thus a high catalytic activity in the toluene hydrogenation reaction. In our opinion, this new class of Mg–O–F mixed supports irrespective of the method of their synthesis, either a direct reaction basic magnesium carbonate with HF or sol–gel method, offers an attractive alternative to other supports for metals.

References

- D.S. Cuhna, G.M. Cruz, Hydrogenation of benzene and toluene over Ir particles supported on γ-Al₂O₃, Appl. Catal., A 236 (2002) 55–66.
- [2] A.M. Argo, J.F. Odzak, J.F. Goellner, F.S. Lai, F.S. Xiao, B.C. Gates, Catalysis by oxidesupported clusters of iridium and rhodium: hydrogenation of ethene, propene, and toluene, J. Phys. Chem. B 110 (2006) 1775–1786.

- [3] J. Silvennoinen, O.J.T. Jylhä, M. Lindblad, H. Österholm, A.O.I. Krause, Supported iridium catalysts prepared by atomic layer deposition: effect of reduction and calcination on activity in toluene hydrogenation, Catal. Lett. 114 (2007) 135–144.
- [4] M. Wojciechowska, M. Zieliński, W. Przystajko, M. Pietrowski, NO decomposition and reduction by C₃H₆ over transition metal oxides supported on MgF₂, Catal. Today 119 (2007) 44–47.
- [5] V.N. Kalevaru, B.D. Raju, V. Venkat Rao, A. Martin, Preparation, characterisation and catalytic evaluation of MgF₂ supported V₂O₅ catalysts for ammoxidation of 3-picoline, Appl. Catal. A 352 (2009) 223–233.
- [6] F. Chen, T.H. Wu, X.P. Zhou, The photodegradation of acetone over VO_x/MgF₂ catalysts, Catal. Commun. 9 (2008) 1698–1703.
- [7] M. Zieliński, M. Pietrowski, M. Wojciechowska, New promising iridium catalyst for toluene hydrogenation, ChemCatChem 3 (2011) 1653–1658.
- [8] M. Pietrowski, M. Zieliński, M. Wojciechowska, High-selectivity hydrogenation of chloronitrobenzene to chloroaniline over magnesium fluoride-supported bimetallic ruthenium-copper catalysts, ChemCatChem 3 (2011) 835–838.
- [9] M. Wojciechowska, M. Zielinski, M. Pietrowski, MgF₂ as a non-conventional catalyst support, J. Fluor. Chem. 120 (2003) 1–11.
- [10] E. Kemnitz, U. Groß, S. Rüdiger, C.S. Shekar, Amorphous metal fluorides with extraordinary high surface areas, Angew. Chem. Int. Ed. 42 (2003) 4251–4254.
- [11] J.K. Murthy, U. Groß, S. R\u00eddiger, E. Kemnitz, J.M. Winfield, Sol-gel-fluorination synthesis of amorphous magnesium fluoride. I. Solid State Chem. 179 (2006) 739-746.
- [12] M. Wojciechowska, A. Wajnert, I. Tomska-Foralewska, M. Zieliński, B. Czajka, Properties of magnesium oxo-fluoride supports for metal catalysts, Catal. Lett. 128 (2009) 77–82.
- [13] M. Zieliński, M. Wojciechowska, Preparation of MgF₂–MgO supports with specified acid–base properties, and their influence on nickel catalyst activity in toluene hydrogenation, Stud. Surf. Sci. Catal. 175 (2010) 429–432.
- [14] M. Zieliński, M. Wojciechowska, Iridium supported on MgF₂-MgO as catalyst for toluene hydrogenation, Catal. Commun. 18 (2012) 1–4.
- [15] V.R. Choudhary, S.G. Pataskar, V.G. Gunjikar, G.B. Zope, Influence of preparation conditions of basic magnesium carbonate on its thermal analysis, Thermochim. Acta 232 (1994) 95–110.
- [16] B.V. King, F. Freund, Surface charges and subsurface space-charge distribution in magnesium oxides containing dissolved traces of water, Phys. Rev. B 29 (1984) 5814–5824.
- [17] M. Serra, P. Salagre, Y. Cesteros, F. Medina, J.E. Sueiras, Design of NiO–MgO materials with different properties, Phys. Chem. Chem. Phys. 6 (2004) 858–864.
- [18] H.A. Prescott, Z.-J. Li, E. Kemnitz, J. Deutsch, H. Lieske, New magnesium oxide fluorides with hydroxy groups as catalysts for Michael additions, J. Mater. Chem. 15 (2005) 4616–4628.
- [19] J. Zhao, M. Xue, Y. Huang, J. Shen, Hydrogenation of dioctyl phthalate over supported Ni catalysts, Catal. Commun. 16 (2011) 30–34.