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Properties of Magnesium Oxo-Fluoride Supports for Metal Catalysts

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Abstract A mixed MgF_2–MgO system has been tested as a potential support of iridium catalysts in the hydrodesulfurization of thiophene. Samples of MgF_2–MgO with different contents of MgO (0–100%) have been prepared by one-step sol–gel method in the reaction of magnesium methoxide dissolved in methanol with hydrofluoric acid. They have been used as supports for the synthesis of iridium (1 wt% Ir) catalysts. The supports have been characterized by XRD, low temperature nitrogen adsorption and thermogravimetric measurements. The one-step method of MgF_2–MgO synthesis has been shown to permit the control of MgO content in the mixed system. The MgF_2–MgO samples are classified as mesoporous, of large surface area (100–450 $m^2\ g^{-1}$) depending on the amount of MgO introduced, with the maximum for 71 mol% MgO. The presence of two phases in the mixture delays the process of both MgF_2 and MgO crystallization and increases the resistance of the MgF_2–MgO texture to treatment at temperatures up to 800 °C. The catalysts obtained by deposition of the iridium phase on MgF_2, MgO and MgF_2–MgO (62 mol% MgO) calcined at 400–700 °C, have been tested in the reaction of hydrodesulfurization of thiophene. The most active has been the iridium catalyst supported on MgF_2–MgO.

Keywords Sol–gel synthese · MgF_2–MgO · MgF_2 · MgO · Iridium catalyst hydrodesulfurization

1 Introduction

Magnesium fluoride has been studied for many years as a possible catalytic support. It has been tested successfully as a support of oxide and metallic phases [1], making active and selective catalysts of oxidation [2, 3], reduction [4, 5] and hydrogenolysis [6, 7]. However, its drawback in potential applications as a support is a low stability of texture above 400 °C—the surface area decreases from $\sim$45 at 400 to $\sim$23 $m^2\ g^{-1}$ at 500 °C and 4.3 at 700 °C [1]. It was expected that the synthesis of MgF_2 by sol–gel method [8–10] and addition of MgO might improve its textural stability.

The sol–gel method permits obtaining various materials of large surface area, narrow pore size distribution and well-developed mesoporous structure. Moreover the sol–gel method offers the possibility of obtaining materials of high purity by one-step synthesis of mixed systems at low temperature and at relatively low cost. These features are of great significance for synthesis of adsorbents, supports and catalysts of different applications. So far a wide range of materials used as catalytic supports have been obtained by the sol–gel method, e.g., metal oxides (Al_2O_3 [11], SiO_2 [12], TiO_2 [13] and MgO [14]), metal fluorides (AlF_3 and MgF_2 [9]) and dioxide systems (Al_2O_3–SiO_2 [15], Al_2O_3–TiO_2 [16], MgO–Al_2O_3 [17]).

High surface area of MgF_2 containing MgO described in literature [18], has prompted us to synthesize the mixed MgF_2–MgO supports by the sol–gel method. In contrast to the two-steps sol–gel method (precipitation of MgF_2 followed by its partial hydrolysis), in this paper we propose one-step synthesis of mixed MgF_2–MgO systems achieved

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by addition of an aqueous solution of hydrofluoric acid of controlled concentration to magnesium methoxide in methanol. By this method a series of samples characterized by different MgF_2/MgO ratio were obtained. The samples were calcined at different temperatures to establish the thermal stability of their texture. The properties of the mixed MgF_2–MgO systems were compared with those of pure MgF_2 obtained by the precipitation and sol–gel methods. The systems obtained were used as supports for the iridium phase. Iridium shows properties typical of the platinum group metals. It has been used as a catalyst in the industrial processes, e.g., acetic acid production in the Cativa™ process, BP Chemicals [19, 20] and hydrogen production by decomposition of hydrazine [21, 22]. A number of literature data [23, 24] have indicated high activity of iridium sulphide in hydrodesulphurisation.

2 Experimental

2.1 Synthesis of MgF_2–MgO and MgF_2 Samples

A series of MgF_2–MgO samples of different content of MgO were synthesized by the sol–gel method from magnesium methoxide and aqueous solution of hydrofluoric acid. The volume of 120 cm^3 of 0.5 M solution of freshly synthesized magnesium methoxide (from magnesium turnings to Gringard for synthesis, MERCK) in methanol was added dropwise (20 $cm^3\ h^{-1}$) at room temperature under intense stirring to an aqueous solution of hydrofluoride (40%, POCH). The amount of hydrofluoride solution was established to ensuring 10, 30, 60, 70, and 90 mol% MgO in the samples. The 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 dry samples were calcined for 4 h at desired temperatures (400–900 °C). The MgF_2–MgO samples of the series were labelled as *x*MgO, where *x* was the mol% of MgO in the sample.

The reference samples were MgF_2 obtained by the method of precipitation from magnesium carbonate and HF [1] (denoted as cMgF_2) and MgF_2 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 in strictly anhydrous conditions (denoted as mMgF_2). MgO was obtained by the sol–gel method as MgF_2–MgO samples by hydrolysis of magnesium methoxide (120 cm^3 of 0.5 M solution) in water.

2.2 Synthesis of Iridium Catalysts

MgF_2–MgO, mMgF_2 and MgO supports, calcined at 400, 500, 600 and 700 °C were impregnated with aqueous solution of H_2IrCl_6 in the amount ensuring 1 wt% of the iridium content in the catalysts. The samples were dried at 80 °C for 4 h. Prior to the catalytic activity measurements, the samples were sulphided with a mixture of 50 vol% H_2S/H_2 at 400 °C for 2 h.

2.3 X-ray Diffraction Analysis

The X-ray powder diffraction was performed on Bruker AXS D8 Advance diffractometer with Ni-filtered CuKα radiation over a 2θ range 20–60°. On the basis of (211) reflection for MgF_2 and (220) for MgO the average crystallite size was calculated using the Hall method.

The composition of MgF_2–MgO supports was determined from XRD data for the samples calcined at 900 °C for 4 h in order to develope well crystallized phases of MgF_2 and MgO using the DQuant program.

2.4 Determination of Surface Area and Porosity

The surface area and porous structure were determined by the low temperature (−196 °C) nitrogen adsorption using an ASAP 2010 analyzer (Micromeritics GmbH). The specific surface area was calculated by the BET method, while the pore size by the BJH method from the desorptive branch of the isotherm.

2.5 Thermal Analysis

Thermogravimetric analysis was carried out for samples dried at 80 °C in the temperature range of 30–1000 °C using a differential thermoanalyzer Setaram TGA, equipped with a TG measurement unit. The experiments were performed under nitrogen flow (99.995 % purity) and temperature increase rate of 8 °C min^{-1}.

2.6 Catalytic Test

The hydrodesulfurization (HDS) of thiophene was carried out by the continuous flow method at 400 °C under atmospheric pressure on 50 mg of catalyst with a grain size 0.15–0.25 mm. Hydrogen was saturated with thiophene at 0 °C (0.25 µmol mL^{-1}) and the mixture was supplied at the rate 20 mL min^{-1} to the reactor. The activities were measured after 2 h of the HDS reaction. The products were analysed by online gas chromatography. The rate of HDS of thiophene was calculated from the expression: HDS rate = FYC/N, where F is the total flow rate of feed; Y the fractional conversion; C the concentration of thiophene in the feed and N the number of metal moles in the sample [25].

3 Results and Discussion

The one-step synthesis of MgF_2–MgO systems by the sol–gel method in the reaction of magnesium methoxide with controlled amounts of hydrofluoric acid in an aqueous solution involves formation both MgF_2 and $Mg(OH)_2$. Upon thermal treatment $Mg(OH)_2$ decomposes to MgO. The content of MgO in the samples of MgF_2–MgO is determined by the amount of the hydrofluoric acid used.

Quantitative determination of MgO content in MgF_2–MgO was performed with the XRD method. The measurements were made for the samples calcined at 900 °C, to develope well crystallized MgF_2 and MgO phases. MgO contents determined by XRD were slightly higher than the desired values and equalled to 13.7, 33.3, 62.0, 71.4, 92.3 mol%, while the intended values were 10, 30, 60, 70, and 90 mol%, respectively. The proposed one-step method simplifies the synthesis of MgF_2–MgO and ensures reasonably good control of MgO content in the samples.

On the basis of low temperature N_2 adsorption the texture of magnesium fluoride, oxo-fluorides and magnesium oxide was characterized. All the samples were mesoporous materials of the mean pore diameters varying from 4 to 12 nm after calcination at 400 °C (Fig. 1) and the surface area changed from 32 to 450 $m^2\ g^{-1}$ (Fig. 2). The surface area of magnesium fluoride obtained by the reaction of the aqueous solution of HF with $MgCO_3$ ($cMgF_2$) was compared with that obtained by the sol–gel method ($mMgF_2$) to show that the latter method did not lead to obtaining MgF_2 of a greater surface area. A great effect of magnesium oxide on the surface area of the oxo-fluoride systems was observed; the surface area of MgF_2–MgO was much greater than that of pure MgF_2 (even one order of magnitude) and than that of pure MgO (even three times). The sample containing 71 mol% of MgO showed the largest surface area.

In order to determine changes in the texture of the samples as a result of thermal treatment, the low temperature N_2 adsorption measurements were also performed for 62MgO sample calcined at temperatures varied from 400 to 800 °C (Table 1). The choice of this sample was dictated by the fact that in the earlier study it had been shown to be the best support of iridium catalysts for thiophene HDS [26]. The texture of the 62MgO sample calcined in the range 400–800 °C was more stable than that of pure MgF_2 and MgO. After calcination at 800 °C, the surface area of pure magnesium fluoride decreased by almost two orders of magnitude to $\sim$0.5 $m^2\ g^{-1}$. Even after calcination at 800 °C the sample of 62MgO had the surface area sufficient for the application as a catalytic support. The surface of this support was stable enough to deposit on it active phases; e.g., for the Ir/62MgO catalyst calcined at 400 °C it was 194 $m^2\ g^{-1}$. According to literature suggestions [18] great surface areas of MgF_2–MgO obtained by the sol–gel method are related to the use of organic compounds in synthesis, as evidenced by the content of carbon in the samples. In our opinion, the large surface areas of the mixed MgF_2–MgO systems are not only related to the use of organic compounds in the synthesis but also to the delay in the crystallization processes. Our point is well illustrated by a comparison of the surface areas of pure MgF_2 samples obtained by the reaction of HF and $MgCO_3$ (without the organic phase) and obtained by the sol–gel method with magnesium methoxide. The sample obtained in the first reaction had the surface area of 42 $m^2\ g^{-1}$ and contained 0.022 wt% of carbon after calcination at 400 °C, while the surface area of the sample obtained by the sol–gel method was smaller, close to 32 $m^2\ g^{-1}$ at the much higher carbon content of 0.114 wt%. Therefore, in our opinion, the factor increasing the surface area of the MgF_2–MgO samples is

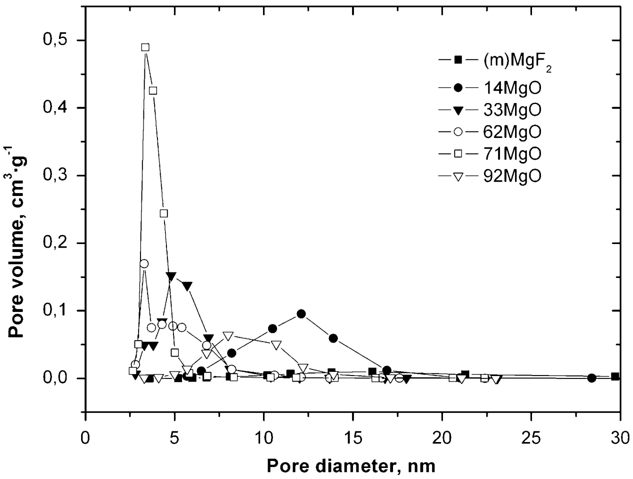

Fig. 1 Pore size distribution of MgF_2–MgO and MgF_2 calcined at 400 °C

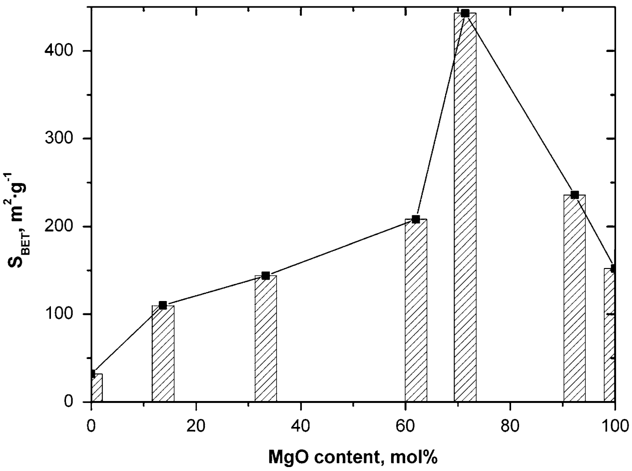

Fig. 2 Effect of MgO content in samples calcinated at 400 °C on their surface area

Table 1 Effect of calcination temperature on the texture of MgF_2, MgO and 62MgO sample

Calcination temperature, °C	Surface area, $m^2\ g^{-1}$			Average pore diameter, nm			Total pore volume ($p/p_0 = 0.99$), $cm^3\ g^{-1}$		
	62MgO	$cMgF_2$	MgO	62MgO	$cMgF_2$	MgO	62MgO	$cMgF_2$	MgO
400	208.0	42.0	152.0	5.3	11.0	7.7	0.463	0.245	0.411
500	194.1	22.7	–	7.4	14.6	–	0.484	0.182	–
600	147.7	18.8	101.7	8.5	–	11.7	0.420	–	0.430
700	99.8	4.3	65.9	10.5	9.5	14.5	0.353	0.014	0.327
800	32.0	0.5	–	24.6	–	–	0.238	–	–

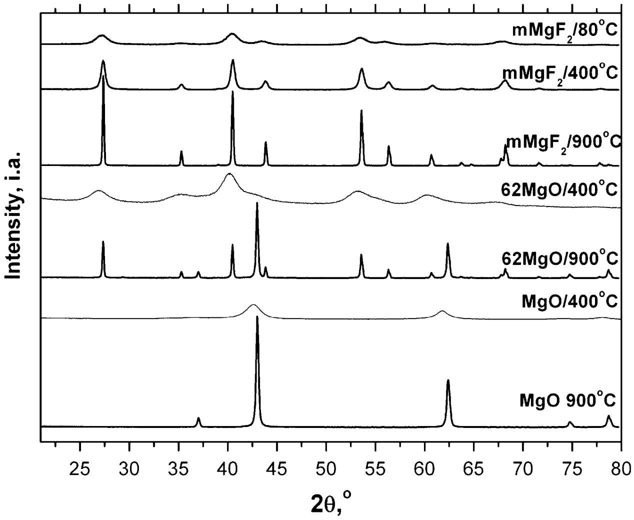

Fig. 3 X-ray diffraction patterns of selected samples treated at different temperatures

the presence of the second phase, affecting the rate of crystallisation of MgF_2 and MgO. In Fig. 3, the XRD patterns of MgF_2, MgO and 62MgO obtained by the sol–gel method are presented. MgF_2 begins to crystallize already on drying at 80 °C. After calcination at 400 °C it has a well-developed crystalline phase [27], and the calcination at 900 °C significantly enhances its crystalline character. MgO requires higher calcination temperatures in order to obtain well-developed crystalline phase, as—in contrast to MgF_2—after calcination at 400 °C it just begins to crystallise. The XRD patterns recorded for MgF_2–MgO calcined at 400 °C show reflexes typical of MgF_2 with traces of the MgO phase, while the calcination at 900 °C results in the crystallisation of MgF_2 and MgO. As follows from the diffractograms presented, in MgF_2–MgO system only pure MgF_2 and pure MgO phases exist, so no reaction leading to formation of the crystalline mixed phases takes place.

The large surface area of magnesium oxo-fluoride is a consequence of crystallisation of MgF_2 and MgO in the mixed system. Table 2 presents the sizes of the crystallites in MgF_2 and 62MgO calcined at different temperatures. As follows from these data, the presence of MgF_2 and MgO in the 62MgO sample causes a substantial delay in the growth of both MgF_2 and MgO. With increasing temperature of calcination the size of crystallites increases, which is accompanied by a decrease in the surface area (see Table 1).

Table 2 Effect of calcination temperature on crystallization of selected supports

Sample	Average crystallite size, nm	
	MgF_2 (211)	MgO (220)
$mMgF_2$/80 °C	6000	
$mMgF_2$/400 °C	2200	
$mMgF_2$/900 °C	43000	
62MgO/400 °C	290	amorphous
62MgO/900 °C	27000	11000

The delay in formation of the oxo-fluoride phase in sample 62MgO is also indicated by the results of thermogravimetric analysis—Fig. 4. For pure MgF_2 small mass loss was noted up to 400 °C, accompanied by endothermic effects. The effect at 91 °C is related to desorption of water, while the broad peak with the maximum at ~272 °C is assigned to dehydroxylation of the surface. For pure MgO and MgF_2–MgO containing 62 mol% MgO, the dehydration takes place at higher temperature (~104 °C). The second mass loss is related to decomposition of $Mg(OH)_2$ to MgO. For pure MgO it takes place at about 400 °C, while for the MgF_2–MgO sample is shifted to nearly 500 °C.

On the basis of the earlier results [26], sample 62MgO proved to be the best support for iridium phase in HDS of thiophene. In this study, the samples 62MgO, MgF_2 and MgO obtained by the sol–gel method were the supports of the active iridium phase in the amount of 1 wt%. The catalysts Ir/62MgO, Ir/MgF_2 and Ir/MgO were tested in HDS of thiophene. The effect of the calcination temperature of the support on the activity of the catalyst is illustrated in Fig. 5. The best catalytic performance was noted for the catalyst with the mixed support, the performance of the catalyst on MgF_2 was much poorer, and the

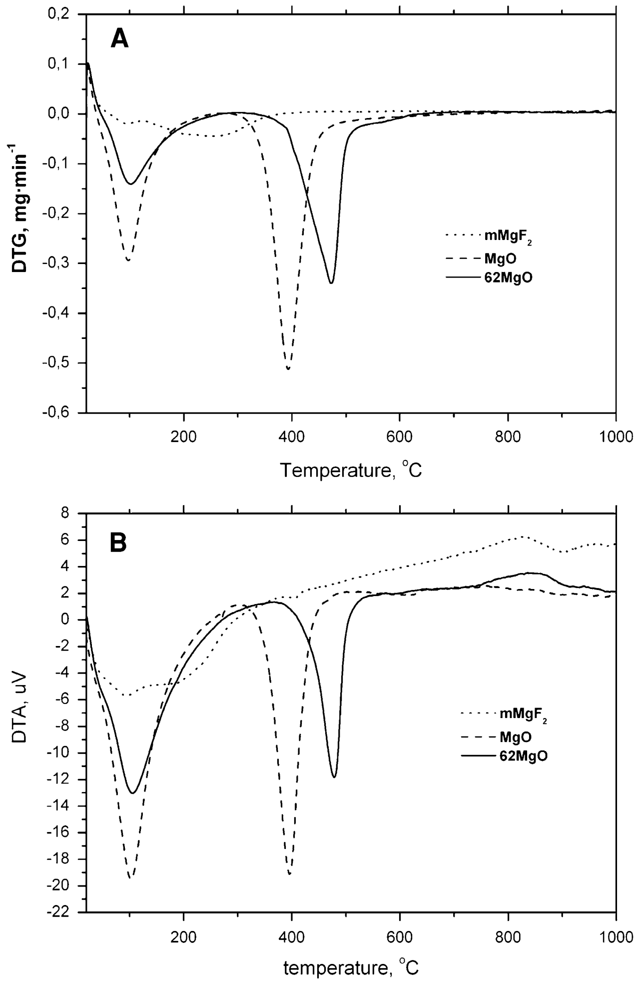

Fig. 4 DTG (**a**) and DTA (**b**) curves obtained for the samples of $mMgF_2$, 62MgO and MgO dried at 80 °C for 3 h

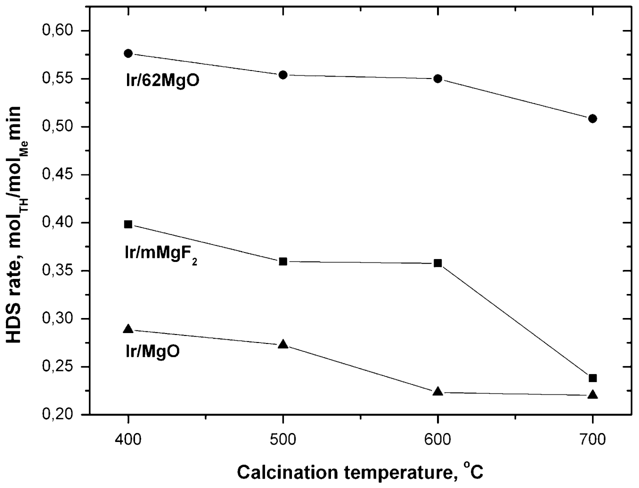

Fig. 5 Effect of support and support calcination temperature on thiophene HDS activity

poorest was that of the catalyst with the MgO. As mentioned above, the surface area of 62MgO sample decreases approximately twice on calcination in the range 400–700 °C, similarly as that of magnesium oxide. After calcination in the same range the surface area of MgF_2 decreases tenfold. Therefore, the catalytic performance test implies that the activity of the iridium phase does not depend on the surface area of the supports. With increasing temperature of the supports calcination, their surface areas significantly decrease, while the activities in HDS of thiophene show little changes. The activity also does not depend on the size of the metal crystallites. As has been shown in [26], for the supports calcined at 400 °C, the iridium dispersion was the highest for MgO (99.5%), then for Ir/62MgO (81.2%), and the lowest for Ir/MgF_2 (49.5%). Thus, it is reasonable to conclude that the factor determining the catalyst activity is the type of the support. As we have shown in [27], in HDS of thiophene the ruthenium catalysts supported on MgF_2 were more active than those supported on SiO_2 and Al_2O_3, and even more active than the industrial cobalt–molybdenum catalyst. The results presented in Fig. 5 implies that the mixed support MgF_2–MgO is a much better support for iridium sulphide than MgF_2 alone. The addition of MgO to MgF_2 not only stabilises the texture of the support but significantly improves the catalytic properties of the iridium phase deposited on it. This observation can be formulated in other words: the addition of MgF_2 to MgO improves the support properties of magnesium oxide.

As mentioned above, the activity of metal catalysts supported on the materials studied is determined by the type of support. It is known from earlier results [28] that the surface area of MgF_2 contains weak acidic Lewis centres (coordinatively unsaturated magnesium ions) and weak basic centres (OH groups). Weak acidic Lewis type centres also occur on the surface of MgO, although it contains predominantly strong basic centres. On the basis of CO_2 adsorption measurements [29] it has been shown that the basic centres on the surface of MgO are of two types (probably O^{2-} ions and OH^{-} groups). As reported by Prescott et al. [18], introduction of fluorine to MgO reduces basic strength of O^{2-} (OH^{-}) groups. In view of the above, it can be expected that the MgF_2–MgO samples have basic centres, weaker than those of MgO, besides the weak Lewis acidic centres. Moreover, it can be expected that the number of the former will increase with increasing content of MgO. This dependence has been confirmed by the results reported by Prescott et al. [18] obtained for the reaction of Michael addition of 2-methyl-cyclohexane-1,3-dione to methyl vinyl ketone catalysed by basic centres present in magnesium oxo-fluorides. The surface areas of the supports MgO (152 m^2 g^{-1}) and 62MgO (208 m^2 g^{-1}) do not differ much, but the differences in the catalytic activities of iridium sulphide supported on these two substances are significant. Therefore, these differences in activities should be related to the electron interactions between the support surface centres and the iridium phase rather then to the surface area of the support. The weakening of the basic centres of MgO by introduction of fluorine or strengthening of the basic centres of MgF_2 by addition of MgO seem to have beneficial effect on the activity of iridium sulphide in HDS.

4 Conclusions

1. A one-step sol–gel method has been proved to be suitable for synthesis of MgF_2–MgO supports with controlled content of MgO.
2. Texture of magnesium oxo-fluorides show mesoporous structure similarly as pure MgF_2 and MgO.
3. The MgO admixtures to MgF_2 strongly increase surface area of oxo-fluorides (even by one order of magnitude) relative to that of pure magnesium fluoride and substantially improves their thermal stability.
4. The presence of the second phase in the mixed 62MgO system delays crystallisation of MgF_2 and MgO.
5. The magnesium oxo-fluorides are prospective catalytic supports with improved thermal stability for sulphided nobel metal catalysts.

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