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Iridium supported on MgF_2–MgO as catalyst for CO oxidation

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ABSTRACT

A combination of iridium catalytic phase and a new MgF_2–MgO support, obtained by the sol–gel method, has been shown to be an active catalyst for CO oxidation reaction. A series of catalysts containing 1 wt.% Ir were obtained by impregnation of MgF_2–MgO and pure MgF_2 or MgO supports with different precursors, i.e. H_2IrCl_6, $Ir(acac)_3$ and $Ir_4(CO)_{12}$. The surface areas and pore size distributions of the catalysts obtained were determined by the BET and BJH methods, respectively. Dispersion of iridium and the mean size of the crystallites were evaluated on the basis of hydrogen chemisorption. The activity of the catalysts in the CO oxidation reaction was measured. The effect of MgO content in the support and the influence of iridium precursor on the structure and activity of the iridium catalysts in the CO oxidation reaction were studied. The results show that the use of MgF_2–MgO support with 60 mol % content of MgO and the use of $Ir(acac)_3$ precursor lead to the catalyst with high surface area, high iridium dispersion and the best catalytic performance in CO oxidation.

1. Introduction

The process of CO oxidation is very important from the point of view of the environment protection as it permits limitation of CO emission from car and industrial gas exhaust and clarification of cigarette smoke [1]. This process is also treated as a model reaction helpful in explaining the nature of many processes of heterogeneous catalysis.

One of the active phases most often used in CO oxidation is gold [2]. Compared with Au, iridium has received little attention as a catalyst in the CO oxidation reaction, but recent reports have pointed to a high activity of iridium supported on Al_2O_3 [3], SnO_2, TiO_2 [4], and CeO_2 in CO oxidation [5]. It is known that the metal–support interactions have important influence on the performance of metallic catalysts. Therefore, the use of new materials as supports may bring systems of certain specific catalytic properties. An interesting support is magnesium fluoride [6] or magnesium oxo-fluoride [7]. Our latest studies have revealed that a combination of iridium active phase with MgF_2 or magnesium oxo-fluoride (MgF_2–MgO) supports allow preparation of catalysts showing hydrodesulphurization (HDS) activity much higher than that of the industrial cobalt–molybdenum one [8]. In this study an attempt is made to use these supports and the iridium active phase for synthesis of new catalysts for CO oxidation.

2. Experimental

2.1. Supports preparation

A series of 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 $cm^3\,h^{-1}$) 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, 60 and 85 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 *x*MgO, 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 for MgF_2–MgO, but under strict anhydrous conditions. MgO was obtained by the sol–gel method by hydrolysis of magnesium methoxide (120 cm^3 of 0.5 M solution). Both MgF_2 and MgO were treated similarly as MgF_2–MgO.

2.2. Iridium catalysts preparation

Iridium catalysts were prepared by the conventional impregnation of the supports with the hexane solution of $Ir(acac)_3$, $Ir_4(CO)_{12}$

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Table 1
Surface area and porosity of supports calcined at 400 °C.

Support	Surface area ($m^2 g^{-1}$)	Average pore diameter (nm)	Total pore volume (p/p_0 = 0.99) ($cm^3 g^{-1}$)
MgF_2	32	15.5	0.12
30MgO	144	10.6	0.38
60MgO	208	8.2	0.43
85MgO	236	7.1	0.42
MgO	152	10.5	0.39

and aqueous solution of H_2IrCl_6. The solutions contained the appropriate amounts of iridium precursor to obtain samples containing 1 wt% Ir. The samples were dried at 80 °C for 4 h.

2.3. Physicochemical characterization of supports and catalysts

The surface area and porous structure of the supports were determined by the low temperature (−196 °C) nitrogen adsorption carried out on ASAP 2010 analyzer (Micromeritics GmbH). The samples were degassed at 350 °C at 0.5 Pa until the static vacuum. The surface area was established by the BET method, while the pore size distribution by the BJH method from the desorptive branch of the isotherm.

Prior to hydrogen chemisorption, the Ir/MgF_2–MgO catalysts were reduced with H_2 at 400 °C for 4 h and iridium crystallite size and dispersion were measured by hydrogen chemisorption at 100 °C. Measurements were performed on ASAP 2010. The isotherms were calculated for 5 different pressures in the range of 60–400 hPa.

2.4. Catalytic test

The catalyst activity in CO oxidation was tested by a continuous method. Before measurements, the samples were reduced *in situ* at 250 °C, for 1 h in hydrogen (flow rate 50 $cm^3 min^{-1}$). The conditions of the catalytic tests were as follows: catalyst weight 50 mg, gas mixture 3 vol.% CO in air (flow rate 50 $cm^3 min^{-1}$), reaction temperature range from 100 to 230 °C. Reaction products were analysed after 30 min on stream using a Carlo Erba 6000 gas chromatograph equipped with a RT-Msieve 13X PLOT column (30 m) and a TCD detector.

3. Results and discussion

As follows from Table 1, the system MgF_2–MgO is characterized by the same mesoporous structure as MgF_2 and MgO, but its surface area is much greater than the sum of surface areas each of these components. The surface area of MgF_2–MgO is about 8 times greater than that of MgF_2 and by 1/3 greater than that of MgO. This is a potential opportunity to introduce greater amount of the active phase on the combined system MgF_2–MgO.

The use of iridium as the active phase supported on MgF_2–MgO or pure MgF_2 or MgO permitted obtaining catalysts active in CO oxidation (Fig. 1a–c.). All the above-mentioned catalysts show a 100% conversion of CO in the range 150–220 °C. The tests have revealed a significant effect of the support composition and iridium precursor on the activity of the catalysts studied in CO oxidation. The highest activities were obtained for the catalysts on mixed supports with dominant contribution of MgO (60 and 85 mol.% MgO). Their use permitted achievement of 100% conversion already at 150 °C for the catalyst with iridium derived from $Ir(acac)_3$ (Fig. 1a). The results obtained for iridium supported on pure MgO or MgF_2 were worse as 100% conversion was obtained at 170 °C and 210 °C, respectively. The activity of the catalysts with the active phase obtained from different precursors decreases in the following sequence:

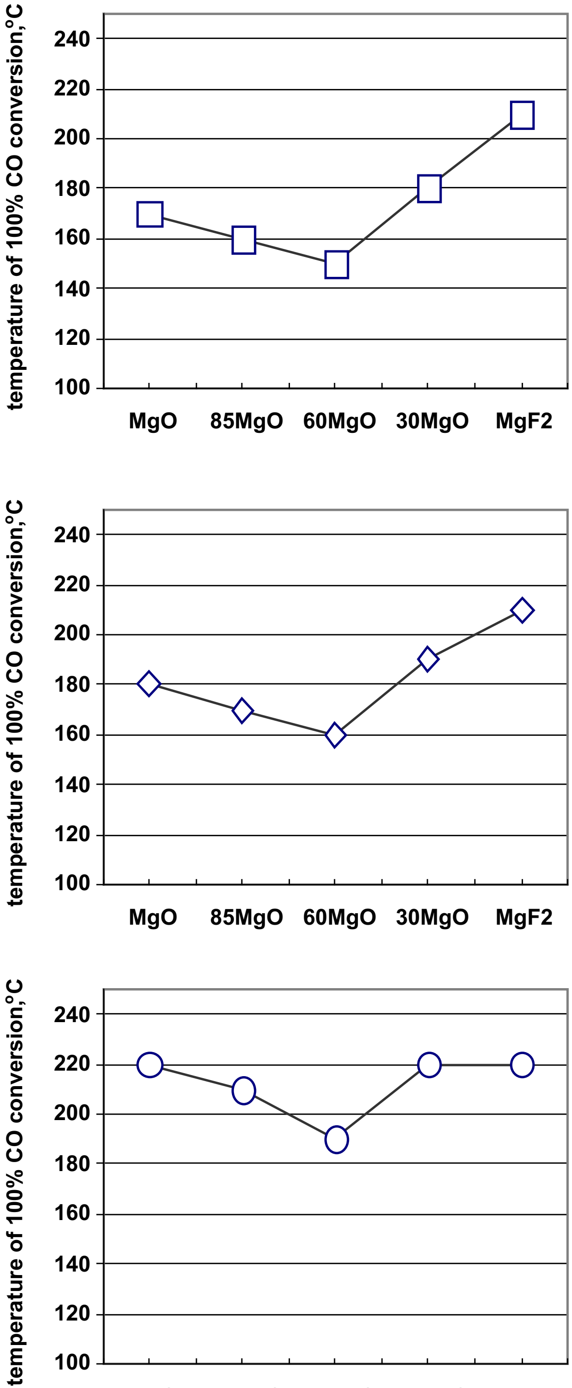

Fig. 1. The effect of support on temperature of 100% conversion in CO oxidation for iridium catalysts obtained from: $Ir(acac)_3$ (a), $Ir_4(CO)_{12}$ (b) and H_2IrCl_6 (c). Activation: H_2 = 50 $cm^3 min^{-1}$, 250 °C, 1 h.

$Ir(acac)_3 > Ir_4(CO)_{12} > H_2IrCl_6$

The use of the $Ir(acac)_3$ and $Ir_4(CO)_{12}$ precursors gives catalysts of similar activities, whereas the use of H_2IrCl_6 results in a significant decrease in the activity of the relevant catalysts. The possible explanation is the possible change in the surface area of the catalyst as a result of precursor deposition and

Table 2
Effect of iridium precursor on texture of Ir/60MgO catalyst reduced at 400 °C.

Sample symbol	Ir precursor	Surface area ($m^2 g^{-1}$)	Average pore diameter (nm)	Total pore volume (p/p_0 = 0.99) ($cm^3 g^{-1}$)
Ir(Cl)/60MgO	H_2IrCl_6	194	8.3	0.40
Ir(CO)/60MgO	$Ir_4(CO)_{12}$	244	9.0	0.55
Ir(Ac)/60MgO	Ir(acac)$_3$	235	8.5	0.50

Table 3
The effect of support and metal precursor on iridium dispersion and average crystallites size for iridium catalyst.

Catalyst	Ir precursor	Iridium dispersion (%)	Crystallite size (nm)
Ir(Cl)/60MgO	H_2IrCl_6	107.0	0.82
Ir(CO)/60MgO	$Ir_4(CO)_{12}$	115.1	0.75
Ir(Ac)/60MgO	Ir(acac)$_3$	81.2	1.15
Ir(Cl)/MgO	H_2IrCl_6	67.9	1.44
Ir(CO)/MgO	$Ir_4(CO)_{12}$	73.7	1.30
Ir(Ac)/MgO	Ir(acac)$_3$	70.3	1.38
Ir(Cl)/MgF$_2$	H_2IrCl_6	26.5	4.67
Ir(CO)/MgF$_2$	$Ir_4(CO)_{12}$	37.4	2.99
Ir(Ac)/MgF$_2$	Ir(acac)$_3$	6.7	24.11

incorporation of some part of chlorine ions in the support surface [9].

According to Table 2 data, the type of precursor used has clear influence on the specific surface area of the catalyst obtained. For the catalysts with iridium obtained from Ir(acac)$_3$ and $Ir_4(CO)_{12}$ the increase in the surface area (between 235 and 244 $m^2 g^{-1}$) relative to that of 60MgO support (208 $m^2 g^{-1}$) was observed. For the sample with iridium from H_2IrCl_6 the surface area decreased to 194 $m^2 g^{-1}$. This result may be a consequence of using an aqueous solution of H_2IrCl_6 instead of n-hexane solution used for the other precursors for the support impregnation. Water can cause hydration of magnesium oxide in the support, which can lead to changes in surface area of the sample. It has been observed that mixed supports ensure better dispersion of the iridium phase than pure MgO and pure MgF_2, which is manifested as a higher activity, i.e. a lowest temperature of 100% conversion of CO.

For all precursors the best catalytic performance was obtained for the catalysts with 60 mol.% MgO in the support. The above results indicate that the optimum catalytic performance is obtained for the concerted interactions of MgF_2 and MgO. According to our recent study, the presence of magnesium oxide has a great effect on the surface area of the fluoride-oxide systems [7], which affects the dispersion of the metal introduced (Table 3). MgF_2 has the lowest specific surface area and on this support the dispersion of iridium is the lowest and hence the lowest activity of Ir/MgF_2 catalysts. Magnesium oxide of much greater surface area allows to obtain catalysts of intermediate activity and on this support the active phase dispersion is much greater. The support ensuring the highest activity of the iridium phase is 60MgO and on it the metal dispersion is the highest. Unfortunately, for this support, the amount of chemisorbed H_2 exceeded the value implied by the amount of the metal introduced (dispersion was higher than 100%), which suggested the participation of other reactions in H_2 consumption. Such a high dispersion can be accounted for the spillover effect, which prevents reliable interpretation of iridium dispersion on the mixed systems by the method of H_2 chemisorption. To measure chemisorption of H_2 the reduction was performed at 400 °C, which ensured total reduction of iridium. TPR-H_2 measurement confirmed that after activation in hydrogen for 4 h at 400 °C no signals corresponding to reduction of the iridium phase were detected.

The catalysts activities also depend on the character of the active sites present on the surface of the supports. The surface of MgF_2 is inert, whereas that of MgO is strongly basic and both belong to insulators. The iridium crystallites will interact with the acidic or basic sites on the surface of the support. As proved by Prescott at al [10] an addition of MgO to MgF_2 increases the basic character of the mixed system. As follows from our studies of the number and strength of the basic centres by thermal desorption of chemisorbed CO_2, the concentration of strong centres on the surface of the supports is ordered as 62MgO > MgO > MgF_2 = 0. Similar series we observe in the catalysts activity with the exception of catalysts obtained from H_2IrCl_6. The interaction of the basic sites with iridium should induce negative charge on the metal crystallites. The presence of strong basic centres facilitates chemisorption and ionization of gaseous oxygen to O^{x-} anions by generation of surface species of $Ir^{\delta+}$. According to TPR-H_2 data, iridium introduced on the surface of the supports studied undergoes reduction at two stages: the low-temperature one (~200 °C) and the high-temperature one (>400 °C). In the conditions of the catalysts activation applied in our study, i.e. in hydrogen atmosphere at 250 °C (activation at 300 °C or 350 °C did not bring significant changes in activity), the iridium is reduced to Ir^0 in the process typical of the first stage of reduction. Therefore, iridium is not fully reduced and some amount of its ions remains in the oxidized form. Moreover, as the CO oxidation is carried out with involvement of oxygen, some iridium on the surface of the catalyst is oxidized and the catalytically active phase is a mixture of Ir^0 and $Ir^{\delta+}$.

According to literature data [11] the best support from among those of metallic catalysts obtained by the impregnation method, is TiO_2. With the use of Ir/TiO_2 catalyst of the same iridium content as in our study (1 wt.% Ir), a 100% conversion of CO was obtained above 200 °C. For MgF_2–MgO support the 100% conversion of CO was obtained at 150 °C, which emphasises that it is particularly beneficial for the iridium active phase in CO oxidation.

4. Conclusions

The use of iridium as the active phase supported on MgF_2–MgO and pure MgF_2 or MgO has been shown to give active catalysts in the CO oxidation reaction. For all the catalysts studied, a 100% CO conversion was achieved in the range 150-220 °C.

The support composition has been found to have a significant effect on the activity of iridium catalysts in the CO oxidation. The highest activity was obtained for the catalysts supported on the mixed supports containing 60 and 85 mol.% of MgO. These supports were also characterized by the largest surface area ensuring the best iridium dispersion.

The catalytic performance has been found to depend also on the type of precursor used. The activity of the catalysts obtained using different precursors in CO oxidation decreased in the order:

$$\mathrm{Ir(acac)_3} > \mathrm{Ir_4(CO)_{12}} > \mathrm{H_2IrCl_6}$$

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