# MAGNESIUM OXIDE AS A CATALYST SUPPORT: THE INFLUENCE OF CHLORINE

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## ABSTRACT

The properties of MgO when used as a support material for Ru-Au catalysts have
been investigated by thermal analysis, chemical analysis, surface area measurements
and X-ray diffraction. During impregnation the support undergoes a bulk hydration
but heating to 673 K restores the oxide. In a sample impregnated by water only,
the dehydration occurs at 651 K and the surface area increases from 15 to > 300
$m^2 g^{-1}$, due to the formation of small pores. Great changes in the DTA peak
temperature and in the surface area after dehydration are found in the catalysts
and in MgO impregnated with HCl solutions. It is shown that these changes are
accurately correlated to the amount of chlorine which remains in the solid (deriving
from the metal precursor compounds or HCl). The formation of basic magnesium
chlorides, shown by X-ray diffraction, seems to favour an easier release of water
(i.e., lower DTA peak temperatures and lower apparent activation energies) and
to reduce the formation of small pores.

## INTRODUCTION

Previous studies on supported Ru, Au and bimetallic Ru-Au catalysts showed that
the MgO supported samples exhibit a different behaviour compared to the correspond-
ing $SiO_2$ supported samples. Strong metal-support interactions were observed when
ruthenium [1,2] or gold [3-6] were dispersed on MgO. In Au/MgO, also a 'reverse'
interaction was found, i.e., gold affected the oxygen-exchange capability of the
bulk MgO [7]. In supported bimetallic Ru-Au catalysts, an unexpected ruthenium
surface enrichment occurred on MgO [5,6,8] but not on silica [9]. Based on these
previous results, we focussed our attention on the characteristics of MgO under
typical catalyst preparation conditions. The characterization of the MgO samples

was performed by thermogravimetric analysis (TGA), differential thermal analysis (DTA), quantitative analysis of $H_2O$ and $CO_2$ developed at 793 K, quantitative analysis of chlorine, adsorption of nitrogen and wide-angle X-ray scattering (WAXS).

EXPERIMENTAL

Commercial MgO (Carlo Erba RPE-ACS, from a reagent grade magnesium carbonate, calcined at 1273 K) was used throughout the study. The samples were prepared by soaking MgO in distilled water, dilute HCl or aqueous solutions of $RuCl_3.H_2O$ and/or $HAuCl_4.3H_2O$. The resulting slurry was filtered and dried for 4 h at 383 K in air. The Ru-Au/MgO catalysts were the same as used previously [6,9].

Thermal analysis was performed in a Mettler TA2 instrument. Samples were first maintained for 1 h at 383 K and then heated at a rate of 4 K $min^{-1}$ to 773 K in flowing air, the reference sample for DTA being $\alpha-Al_2O_3$; 40 - 50 mg samples were used for each TGA - DTA test.

Immediately after a pretreatment in the thermobalance (2 h at 673 K), surface area measurements were performed by adsorption of nitrogen at 78 K, using a single-point BET method.

The pore distribution was measured by $N_2$ adsorption in a Carlo Erba Sorptomatic series 1800, after 2 h at 383 K under vacuum. The BJH method [10] was used.

WAXS was performed by a Philips X-ray powder diffractometer, equipped with a scintillation counter and a pulse height analyser. Ni filtered CuK$\alpha$ radiation was used.

Routine analytical methods were used for the analyses of $H_2O$, $CO_2$ and Cl. Water and carbon dioxide were released from the samples when the temperature was raised to 793 K in flowing air.

RESULTS AND DISCUSSION

The magnesium oxide used was a low surface area solid (15 $m^2$ $g^{-1}$ after 16 h at 383 K and 25 $m^2$ $g^{-1}$ after 2 h at 673 K), almost free of pores below 30 Å, (Table 1). After impregnation of this MgO with Ru or Au precursors, the BET surface measured after 2 h at 673 K was in most cases significantly higher than 25 $m^2$ $g^{-1}$ obtained on the untreated MgO (Table 2). A similar behaviour was observed with MgO soaked in water or in dilute HCl (Table 3).

TGA on the untreated MgO sample showed a small weight loss ($\Delta w \cong 4\%$) between 483 K and 603 K, accompanied by a small endothermic DTA signal. On the contrary, all the samples examined, previously soaked in aqueous solutions and then dried at 383 K, underwent considerable weight losses (mostly 25 - 35% of the initial weight) during the TGA experiments. These results were in good agreement with the amounts of $H_2O$ and $CO_2$ released during heating to 793 K. The percentage of $CO_2$ in the released gas ranged from 2 to 8 %v. This indicated that the weight losses were essentially due to the decomposition of magnesium hydrates and of small amounts of carbonates. The existence of such compounds in the examined samples, after

TABLE 1

Contribution of pores of different radius to the total pore volume, as measured by nitrogen sorption[a]

| Sample | Heated at[b] /K | Volume/cm$^3$ g$^{-1}$ due to pores in the range | | |
| --- | --- | --- | --- | --- |
| | | 15-30 Å | 30-60 Å | 60-150 Å |
| MgO not impregnated | } 383 | 0.00 | <0.01 | 0.09 |
| | 673 | 0.01 | 0.01 | 0.03 |
| 'MgO+H$_2$O' | 383 | 0.00 | 0.03 | 0.12 |
| | 673 | 0.27 | 0.08 | 0.10 |
| | 383$^c$ | 0.00 | 0.08 | 0.19 |
| | 673$^d$ | 0.20 | 0.09 | 0.15 |
| 'MgO+HCl' Cl = 0.42%w | } 383 | <0.01 | 0.10 | 0.24 |
| | 673 | 0.03 | 0.07 | 0.20 |
| 'MgO+HCl' Cl = 1.93%w | } 383 | 0.02 | 0.02 | 0.14 |
| | 673 | 0.01 | <0.01 | <0.01 |

[a]For the samples heated at 383 K, the volume per unit weight is referred to the weight reached after the 673 K treatment.

[b]383 = 4 h at 383 K; 673 = 4 h at 383 K + 2 h at 673 K.

[c]After the 673 K treatment, the sample was exposed to air overnight and then reheated to 383 K.

[d]This treatment followed that described in note c.

impregnation and drying, was confirmed by WAXS. $Mg(OH)_2$ was always found, while the diffraction lines of MgO were often weak or could not be detected at all. In some cases, the presence of $MgCl_2.2MgCO_3.Mg(OH)_2.6H_2O$ [11] and of $3MgCO_3.Mg(OH)_2.3H_2O$ [12] was also evident (Tables 2 and 3). After heating at 673 K in air, the diffraction lines found were mainly those corresponding to MgO.

For most of the samples, the greatest weight loss measured by TGA occurred above 498 K and corresponded to a further $\Delta w$ of 20-35% with respect to the weight reached by the samples after 1 h at 383 K. It is very likely that below 498 K only the weakly bound water molecules (e.g., water of crystallization) can be eliminated from the samples. The decomposition of magnesium hydrates and carbonates is known to start at higher temperatures, at least for the pure compounds, i.e., at 513 K for $3MgCO_3.Mg(OH)_2.3H_2O$ and at 623 K for $Mg(OH)_2$ and $MgCO_3$ [13]. In correspondence to the weight loss in the 498-773 K region, a strong endothermic peak appeared in the DTA profile. The peak temperature ($T_p$) varied between 588 and 651 K, the latter being the value found for MgO soaked in distilled water ($MgO + H_2O$). The $T_p$ of each sample was reproducible within ±2 K. No systematic dependence of $T_p$ on the $\Delta w$ values measured above 498 K was found. The variations of $T_p$ from 651 down to 588 K

TABLE 2
Characterization of the Ru/MgO, Au/MgO and Ru-Au/MgO catalysts

| Sample | Chemical analysis /%w | | | Surface area[a] /m² g⁻¹ | Differential thermal analysis | | Crystalline compounds by WAXS[b] |
|---|---|---|---|---|---|---|---|
| | Ru | Au | Cl | | Peak temperature $T_p$/K | Apparent activation energy, $E_a$/kcal mol⁻¹ | |
| Au/MgO | - | 3.46 | 0.02 | 248 | 649 | 35 | I,II |
| | - | 3.03 | 0.58 | 127 | 625 | 30 | I,II |
| Ru-Au/MgO | 0.26 | 4.45 | 1.39 | 32 | 621 | | II,III |
| | 1.25 | 2.70 | 0.53 | 106 | 622 | 33 | I,II,IV |
| | 2.36 | 2.97 | 1.88 | 63 | 603 | | II,III |
| | 2.12 | 2.34 | 0.75 | 98 | 617 | | II |
| | 3.48 | 0.81 | 2.20 | 41 | 608 | | (I),II,III |
| Ru/MgO | 4.50 | - | 1.95 | 43 | 606 | 26 | (I),II,III |
| | 2.10 | - | 1.30 | 46 | 608 | | II,(III) |
| | 0.75 | - | 1.00 | 51 | 612 | 28 | II |
| | 0.41 | - | 0.50 | 178 | 621 | 28 | II |
| | 0.16 | - | 0.15 | 212 | 653 | 39 | I,II |
| | 0.06 | - | ≦0.01 | 201 | 646 | | I,II |
| Ru/MgO from KRuO₄ | 1.60 | - | ≦0.01 | 203 | 634 | | I,II |

[a] After heating from room temperature to 673 K at 4 K min⁻¹ and then for 2 h at 673 K.
[b] I = MgO; II = Mg(OH)$_2$; III = MgCl$_2$·2MgCO$_3$·Mg(OH)$_2$·6H$_2$O; IV = 3MgCO$_3$·Mg(OH)$_2$·3H$_2$O.

TABLE 3

Characterization of MgO impregnated by water or diluted hydrochloric acid

| Cl /%w | Surface area[a] /$m^2$ $g^{-1}$ | DTA peak temperature $T_p$/K | Crystalline compounds by WAXS[b] |
|---|---|---|---|
| - | 317 | 651 | I,II |
| 0.01 | 253 | 638 | |
| 0.02 | 210 | 646 | I,II |
| 0.06 | 202 | 645 | |
| 0.24 | 206 | 639[c] | I,II |
| 0.24 | 163 | 633 | |
| 0.42 | 165 | 628 | I,II |
| 0.45 | 95 | 627 | |
| 1.20 | 24 | 610 | I,II,IV |
| 1.20 | 39 | 607 | |
| 1.30 | 32 | 595 | |
| 1.93 | 36 | 588 | I,(III) |

[a]After heating from room temperature to 673 K at 4 K $min^{-1}$ and then for 2 h at 673 K.

[b]I = MgO, II = $Mg(OH)_2$, III = $MgCl_2.2MgCO_3.Mg(OH)_2.6H_2O$, IV = $3MgCO_3.Mg(OH)_2.3H_2O$

[c]Apparent activation energy, from DTA, is 35 kcal $mol^{-1}$.

(Tables 2 and 3) indicate the existence of chemical modifications of the examined material. Considering the Ru/MgO catalysts (Table 2) it is evident that $T_p$ approaches 651 K when the Ru content is lower; the situation appears to be less clear in the bimetallic catalysts.

It was tempting to assume a specific effect on $T_p$ of the Ru compound supported on MgO, such an effect being eventually modified by the presence of gold compounds, but the behaviour of the samples prepared by impregnating MgO with dilute HCl (see Table 3 where large variations of $T_p$ are again found) excludes the presence of ruthenium as the main factor. Instead, for both supported metal catalysts and impregnated MgO samples, the value of the DTA peak temperature seems to correlate with the amount of chlorine that remains on the support after impregnation. Increasing the chlorine content leads to a systematic decrease in the $T_p$ values (Figure 1A). The role of chlorine is confirmed by a 1.6% Ru catalyst, prepared using $KRuO_4$: its $T_p$ value was significantly higher than that expected for a Ru/MgO sample of comparable metal content, but prepared starting from the usual chlorine containing compound (Table 2).

In the metal catalysts, chlorine generally derives from the ruthenium precursor compound, while chloroauric acid causes only a limited chlorine contamination of the solid. This is in agreement with the surface analysis performed by XPS on the
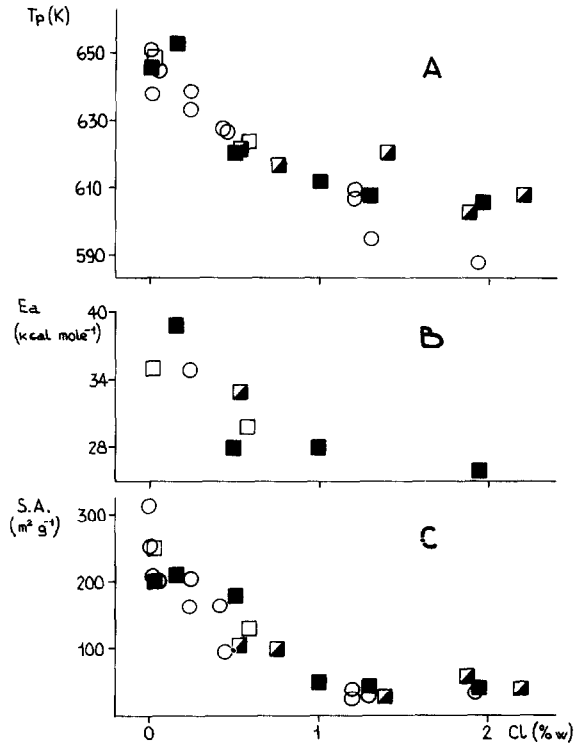
FIGURE 1   DTA peak temperature ($T_p$), apparent activation energy ($E_a$) estimated from DTA and surface area (S.A.) vs. the chlorine content in the samples: □, Au/MgO; ■, Ru/MgO; ◪, Ru-Au/MgO; O, 'MgO + $H_2O$' and 'MgO + HCl'

same samples [6], that showed the absence of chlorine in the Au/MgO catalysts and its presence in the Ru and Ru-Au/MgO samples, even after reduction by hydrogen at 673 K.

    WAXS has shown that chlorine is present in the form of a magnesium basic carbonate chloride (detectable when chlorine exceeds 1%). Possibly other basic chlorides can also form in the samples. Even if no data about the mechanism were collected, the presence of magnesium chlorides seems to favour a release of water (and $CO_2$) at lower temperatures. The apparent activation energy ($E_a$) of the decomposition corresponding to the DTA peak was roughly estimated, for a limited number of samp-samples, by the Kissinger method [14] applied to DTA experiments performed at different heating rates (2, 4 and 8 K $min^{-1}$) (Table 2). To a first approximation, $E_a$ seems to decrease with increasing chlorine content (Figure 1B). This again confirms that the presence of magnesium chlorides makes the release of $H_2O$ (and $CO_2$) easier.

    The amount of chlorine in the samples was never higher than 3% and therefore the decomposition of the basic chlorides alone cannot account for the observed Δw values. Probably the observed phenomena are essentially due to the decomposition

of $Mg(OH)_2$, the temperature of which is modified by the presence of chlorides. Also other species, present in the impregnating solution and able to react with MgO, could possibly exert similar effects. An example is given by the nitrate ion, where replacing HCl by $HNO_3$ solution of equal concentration gave almost the same $T_p$ values (627 and 628 K). However, much higher values (650 - 655 K) were found after impregnating MgO with $H_2SO_4$ of the same normality or molarity. This, together with the fact that no correlation exists between the pH and the observed $T_p$ shift, leads to the conclusion that the nature of the anion and not the proton plays a key role. From Figure 1A it can also be seen that, up to a chlorine content of 1%w, all the samples follow the same trend. At higher chlorine content, the experimental points are more dispersed. Indeed, some differences seem to exist among the samples which fall in this region of the plot. The ruthenium richest samples show a shoulder in the DTA spectrum (Figure 2), at about 643 - 653 K, which is absent in the 'MgO + HCl' samples and indicates the decomposition of another species, present in much smaller concentration. Furthermore, it is quite possible that in the ruthenium richest samples some chlorine is bound to the metal and not to the support.

After impregnation and drying at 383 K, 'MgO + $H_2O$' had approximately the same surface area as the untreated MgO (18 $m^2$ $g^{-1}$). The pore volume, measured by nitrogen adsorption, was mainly due to pores larger than 60 Å (Table 1). Heating this sample at 673 K produced a great number of pores below 60 Å, yielding a surface area of ca. 300 $m^2$ $g^{-1}$. Leaving this last sample in contact with moist air for some hours lowered the surface area to the initial value. Heating again restored small pores and high surface area (Table 1). The metal containing samples behaved in a similar way. It therefore seems likely that, when $Mg(OH)_2$ is decomposed to MgO, very small pores can open in the solid; exposure to the atmosphere causes a re-hydration of the oxide, which is sufficient to occlude smaller pores.

A pretreatment of the sample at 483 K, i.e., at a temperature lower than that of the DTA peak, did not significantly affect the surface area. This confirms that the formation of the small pores responsible for the increase of surface area is strictly connected to the decomposition of magnesium compounds which occurs in the 498 - 773 K region. It was therefore decided to investigate whether the surface area also depends on the composition of the samples, as it was found for the peak temperature in DTA. A pretreatment of 673 K was chosen, in order to be well above the $T_p$ value of each sample. Measured surface areas ranged between 30 and 250 $m^2$ $g^{-1}$ in the metal catalysts (Table 2). Similar results were found for the 'MgO + HCl' samples (Table 3). Results seem again to depend on the amount of chlorine that remains in the samples (Figure 1C). The higher the chlorine content, the lower was the BET surface area after heating at 673 K, due to a limited formation of small pores (Table 1). In most samples, the number of larger pores changes after heating at 673 K, but this has a minor effect on the surface area. The role of chlorine in explaining these results was again confirmed by the sample prepared
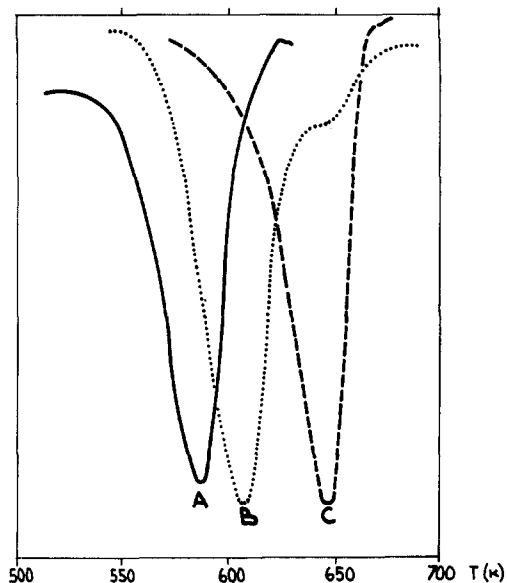
FIGURE 2   DTA endothermic peak for: A, 'MgO + HCl', 1.93% Cl; B,Ru/MgO, 4.50% Ru, 1.95% Cl; C, Au/MgO, 3.46% Au, 0.02% Cl.

using $KRuO_4$ instead of $RuCl_3.H_2O$: a high surface area was found after the usual pretreatment.

This investigation has given a better knowledge of the behaviour of MgO when used as a support for metal catalysts. During the impregnation, this material undergoes not only a bulk hydration, but also a reaction with other species (i.e., $Cl^-$, $NO_3^-$) present in the solution. This probably influences the dehydration behaviour of the solid and consequently the number of small pores that are formed. In the Ru, Au and Ru-Au/MgO catalysts, the main effects were due to chlorine and not to the supported metals. The formation of basic magnesium chlorides seems to favour the release of water at lower temperatures and to reduce the formation of small pores. Assuming that these pores derive from the breaking up of the solid, due to the development of water molecules, the results are consistent: an easier release of water could lead to a less severe breaking up. While the results have clearly shown that chlorine interferes with the properties of MgO, the role of chlorine is, however, not fully understood. On a purely speculative basis, it is possible to imagine that the presence of islands of chlorides (large enough to be detected by WAXS, at least in some of the catalysts) within the bulk of the solid or on its surface could influence the nucleation of MgO during the dehydration process or just modify some physical properties of the $Mg(OH)_2$ agglomerates. In fact, the $T_p$ value of $Mg(OH)_2$ is known to be shifted varying its physical properties and especially the particle size [15]. With respect to this, however, no significant correlation could be found between the % Cl or $T_p$ values and the particle size

of the hydroxide, as inferred from X-ray line broadening analysis.

The data reported in this paper have two important implications for the use of MgO as a catalyst support: a) In order to achieve high surface area, the concentration of anions such as $Cl^-$ + $NO_3^-$ should be kept as low as possible; b) Care must be taken in choosing the pretreatment conditions for BET area measurements, as these can lead to wide variations in the surface area.

## ACKNOWLEDGEMENTS

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