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Review

# $MgF_2$ as a non-conventional catalyst support

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## Abstract

This review reports progress in the study of the surface structure of $MgF_2$ and its use as a support of catalytically active phases. Magnesium fluoride was applied first as a support in catalysis for systems containing individual oxides of transition metals (Mo, V, W, Cu, Cr) and then two different oxide phases (Cu-Cr, Cu-Mn), a metal phase (Ru, Pd) or heteropolyacids. Its use as a support enabled determination of the structure and surface properties of these catalysts. The $MgF_2$-supported catalysts are characterized by high activity and selectivity in such processes as: hydrodechlorination of chlorofluorocarbons (CFCs), hydrodesulfurization of organic compounds and purification of fuel combustion products from nitrogen oxides. Magnesium fluoride has been also used in $MgF_2$-doped chromium or aluminum fluoride catalysts for Cl/F exchange on hydrochlorocarbons.

*Keywords:* Magnesium fluoride; Surface complexes; Supported metal oxides; Ruthenium catalysts; Heteropolyacids; Hydrodesulfurization; $DeNO_x$; CFCs hydrodechlorination; Fluoride active phases

## 1. Introduction

A subject of major interest in heterogeneous catalysis has been systems containing an active phase supported on the surface of oxides such as $Al_2O_3$, $SiO_2$, $TiO_2$, $ZrO_2$ and MgO. Among compounds other than oxides used as supports, fluorides have received much attention. From this group of compounds fluorinated alumina [1], metal fluorides [2–10] and mixed fluoride catalysts, for example, $MgF_2$/LiF [11], $CrF_3/MgF_2$ or $CrF_3/MgF_2$-$AlF_3$ [12–14], $AlF_{3-x}(OH)_x$ with aluminum replaced by chromium and magnesium [15], $CrF_{3-x}(OH)_x$ with substitution of chromium by magnesium and iron [16] have been described as heterogeneous catalysts.

This paper reviews the literature concerning characterization of magnesium fluoride and the use of $MgF_2$ as a catalyst support. The first work on magnesium fluoride relevant from the point of view of heterogeneous catalysis was reported by Wojciechowska et al. [17]. The results of the study led to a model of the magnesium fluoride surface and structure of the acid–base and redox centers formed on this surface [18]. The use of $MgF_2$ as a support resulted in a significant modification of the active phase. The mechanism of the formation of oxide, double oxide or metallic layers on the surface of $MgF_2$ has been recognized and the physico-chemical properties of such systems have been determined. The data have been used for syntheses of catalysts for possible use in reactions important for environmentally friendly processes. The catalysts obtained were characterized by high activity and selectivity in the reduction of $NO_x$ by carbon oxide [19] and hydrocarbons [20]. Magnesium fluoride proved to be a suitable support for a ruthenium catalyst effective in hydrodesulfurization [21]. Ruthenium or palladium catalysts supported on $MgF_2$ were also found effective in hydrodechlorination of CFCs [22,23]. The subject of interest are also $MgF_2$-doped aluminum fluorides or chromium fluorides for halogen exchange on hydrochlorocarbons and chromium fluorides supported on mixed $MgF_2$-$AlF_3$ active in the fluorination of chloroalkanes [14,24].

## 2. Characterization of $MgF_2$

Magnesium fluoride crystallizes in the rutile-type structure [25], space group $P4_2/mnm$ [26], in which each $Mg^{2+}$ ion is surrounded by six $F^-$ ions and each $F^-$ ion by three $Mg^{2+}$ ions. The cation is surrounded by a distorted octahedron made up of two fluoride ions located at a slightly longer distance than the four remaining ones: $4(Mg-F) = 1.94$ Å; $2(Mg-F) = 1.99$ Å.

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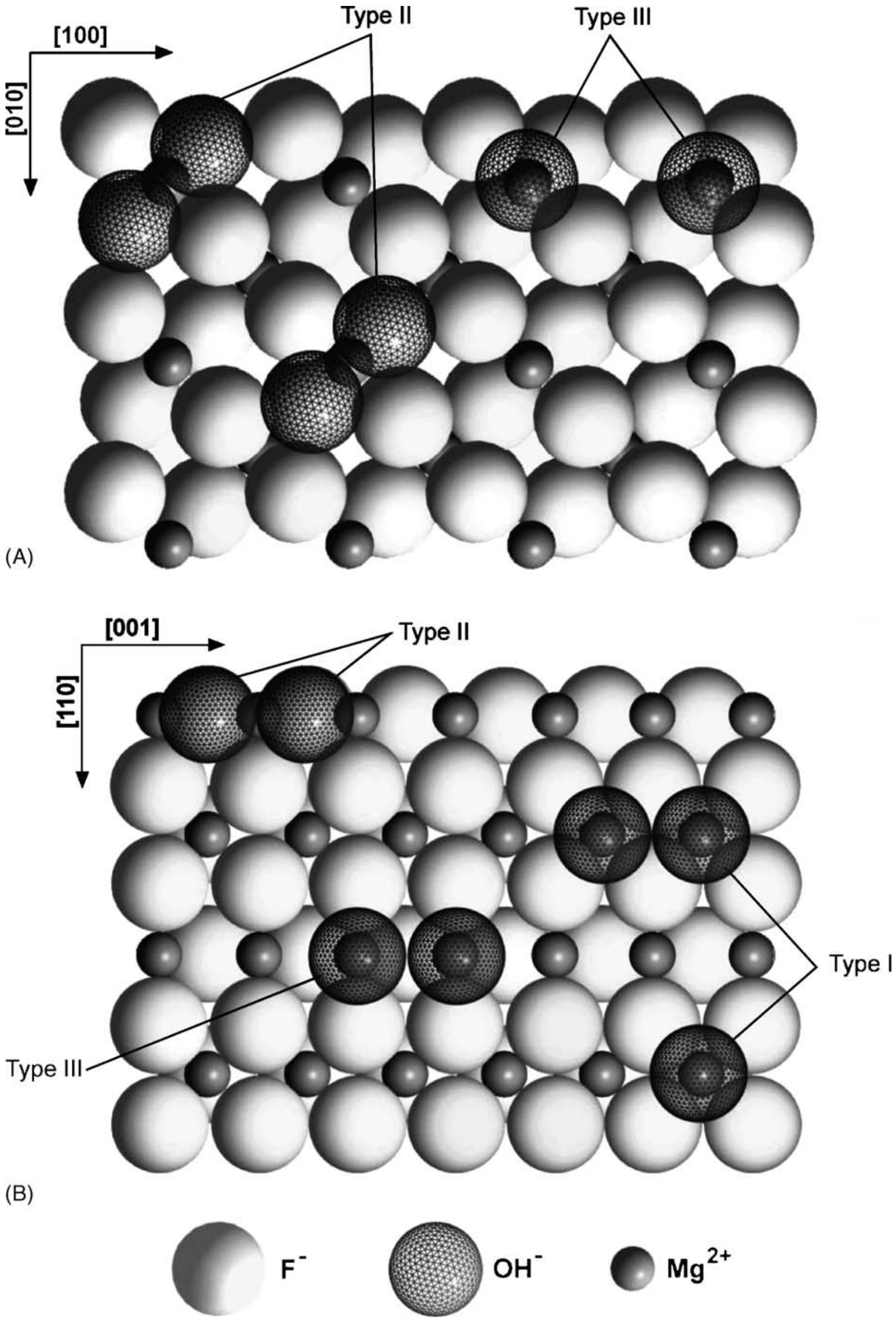
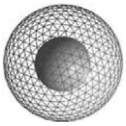
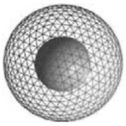
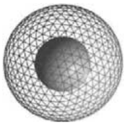


Fig. 1. The arrangement of OH groups on the surface of magnesium fluoride: (A) the (0 0 1) crystal plane; (B) the (1 1 0) crystal plane.

The model of the magnesium fluoride surface was proposed by Wojciechowska [18]. Fig. 1 shows the location of particular ions in the crystal planes (0 0 1) and (1 1 0) of $MgF_2$. The coordination shell of each $Mg^{2+}$ ion located in the (1 1 0) plane, has one or two fluorine atoms missing ($Mg^{2+}$ ions with coordination number (CN) $= 5$ or 4, respectively), whereas in the (0 0 1) plane, besides the coordinatively unsaturated ions $(Mg_{cus})^{2+}$ ($CN = 4$), coordinatively saturated ions are also present. Electric charge of $(Mg_{cus})^{2+}$ ions is not balanced by the surrounding negative ions and amounts to $+2/3$ for $Mg^{2+}$ ions with $CN = 4$, and $+1/3$ for magnesium ions with $CN = 5$. In the preparation of magnesium fluoride, or when it is contacted with water vapor, water dipoles interact with $(Mg_{cus})^{2+}$ ions and fill their coordination sphere leading to the formation of surface hydroxyl groups (Fig. 1). The presence of OH surface groups has been confirmed by infrared spectroscopy (IR) studies showing bands at three frequencies 3770, 3620 and $\sim 3400\,cm^{-1}$ [18] corresponding to the three types (I–III) of OH groups. Descriptions of these groups are given in Table 1.

Table 1
Characterization of hydroxyl groups occurring on the surface of magnesium fluoride [18]

| Lattice plane | Type of OH group | Net electric charge at OH group | CN of the surface cation over which OH group is located |
|---|---|---|---|
| (1 1 0) |  (I) | −2/3 | 6 |
| |  (II) | −1/5 | 5 |
| |  (III) | −3/5 | 5 |
| (0 0 1) |  (II) | −1/5 | 5 |
| |  (III) | −3/5 | 5 |

$OH^-$ is denoted by ● and $Mg^{2+}$ by ●.

The three types of hydroxyl groups differ in the electric charge and in geometric configuration, consequently they reveal different properties. The charges of OH groups, as calculated from a simple ionic model, are −2/3 for type I, −1/5 for type II and −3/5 for type III. The Brønsted acidity of the OH groups diminishes and their basicity increases when their electrical charges become more negative [27]. All three types of OH groups are basic. On the basis of the TPE-$H_2O$ (temperature-programmed water elimination) and thermogravimetric studies, the OH group surface density was of the order of 3–4 $nm^{-2}$ [28], two times lower than on a typical oxide support such as $Al_2O_3$ (five to six OH groups/$nm^2$) [29].

Structural investigation of $MgF_2$ has allowed a precise determination of diffraction parameters of polycrystalline $MgF_2$ [28]. Fig. 2 presents the X-ray results of magnesium fluoride calcined at 673 K (MF-4). It consists of over 40 diffraction patterns in the range $2\theta = 2$–$152^\circ$ and has been used to determine the interplanar distances, relative intensities of particular reflections and $(h\,k\,l)$ indices for the recorded diffraction lines [28]. The data presented are more detailed than those published in American Standards for Testing Materials (ASTM) Card No. 6-0290 (1955) [30] and are the best diffraction characteristics of polycrystalline $MgF_2$ available so far. The presence of the three orders of reflections in the XRD spectra of $MgF_2$ presents an opportunity to study the effect of the preparation parameters (such as calcination temperature, calcination atmosphere, and cooling procedure) on the structure of magnesium fluoride. $MgF_2$ calcined in the temperature range 673–1173 K shows only slight internal tension of the second type, but then the size of the crystallites considerably increases. Internal tensions of the second type determined by the history of the polycrystal, refer to the dislocations and defects in the area comparable with that of monocrystals. The lack of considerable internal tensions on thermal treatment of $MgF_2$ is consistent with the presence of a low number of defects [28]. Magnesium fluoride calcined at 673 K has a specific surface area of 45 $m^2/g$ and is characterized by the narrow pore size distribution in the mesoporous range with a maximum diameter of 160 Å [28] (Table 2 and Fig. 3). With increasing calcination temperature, the surface area decreases. Above 873 K, the sintering of fine pores becomes significant and the specific surface area decreases drastically (0.6 $m^2/g$ for calcination at 1073 K). Similarly, the mechanical resistance of magnesium fluoride samples improves with increasing calcination temperature [28]. Fujihara et al. [31] who studied magnesium fluoride thin films on silica glass substrates have also found the effect of the calcination temperature on the texture of $MgF_2$. They recorded an increase in the particle size of $MgF_2$ with temperature increasing from 573 to 773 K. It has been established that heat-treatment below 673 K is necessary to ensure good optical quality of $MgF_2$. Infrared properties of polycrystalline $MgF_2$ are described in [32].

Table 2
Characterization of $MgF_2$ samples calcined at different temperatures [28]

| Sample | Calcination temperature (K) | Surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Pore diameter (Å) |
|---|---|---|---|---|
| MF-6 | 673 | 44.6 | 0.228 | 164 |
| MF-7 | 773 | 22.7 | 0.182 | 291 |
| MF-9 | 973 | 4.3 | 0.014 | 190 |

The surface of magnesium fluoride hosts very weak acid–base centers. The indicator tests showed the strength of the acidic sites to be $H_o \geq 3.3$ and basic sites $H_- = 9.3$ [33] (Table 3). The acid centers are coordinatively unsaturated

Table 3
Acidic, basic and redox properties of magnesium fluoride [33]

| | |
|---|---|
| Amount of pyridine adsorbed[a] ($\mu mol/m^2$) | 0.31 |
| Amount of acetic acid adsorbed[a] ($\mu mol/m^2$) | 5.82 |
| Acidic strength ($H_o$) | 3.3 |
| Basic strength ($H_-$) | 9.3 |
| Concentration of $Pe^+$ ($spin/m^2$) | $1.0 \times 10^{14}$ |
| Concentration of $TCNE^-$ ($spin/m^2$) | $1.8 \times 10^{14}$ |

$Pe^+$, perylenium cation radicals; $TCNE^-$, tetracyanoethylene anion radicals.

[a] The amount of pyridine and acetic acid adsorbed determined by elemental analysis using a Perkin-Elmer elemental analyzer.

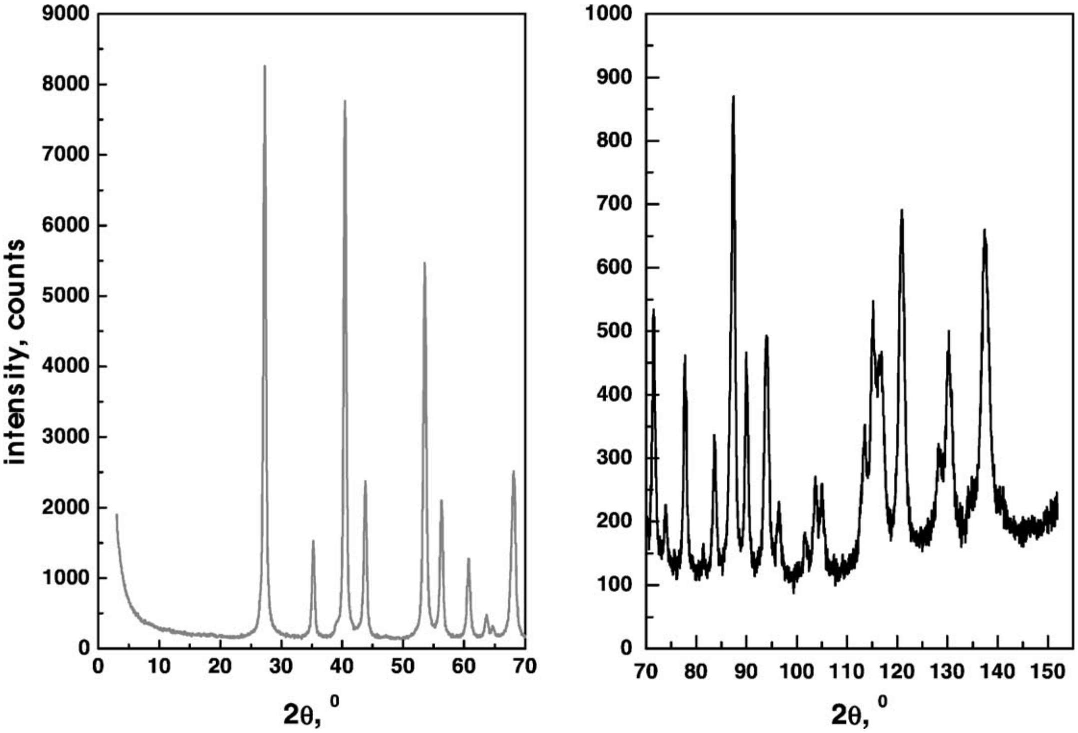


Fig. 2. XRD spectra of $MgF_2$ calcined at 673 K.

magnesium ions or pairs of such ions making Lewis-type sites. The basic centers are certain surface hydroxyl groups or oxide and fluoride anions. The adsorption of perylene revealed that these acid centers could also play the role of oxidizing centers for hydrocarbons with condensed rings. Similarly, the basic centers can act as reductants for compounds of high electron affinity (adsorption of tetracyanoethylene (TCNE)) [33]. It should be emphasized that the concentration of the centers on the $MgF_2$ surface is by one to two orders of magnitude lower than on amorphous silica-alumina or $Al_2O_3$. Therefore, the $MgF_2$ surface can be described as relatively chemically inert compared with pure silica. More detailed information on the surface structure of magnesium fluoride was provided by the infrared spectroscopy study [18]. The IR spectrum recorded after pyridine adsorption revealed a band at 1450 $cm^{-1}$, characteristic of Lewis acidic centers. The IR spectrum did not show the band characteristic of the pyridinium ion ~1535 $cm^{-1}$, which indicated the absence of Brønsted acid centers.

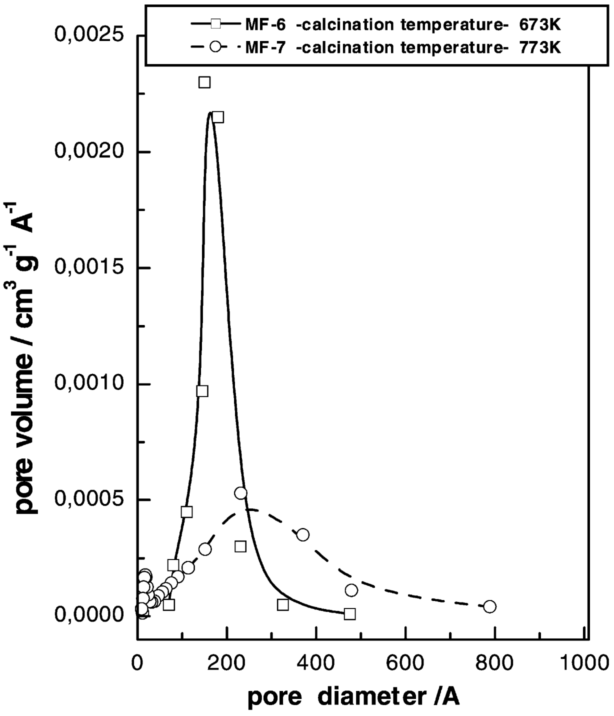


Fig. 3. The effect of calcination temperature of $MgF_2$ on pore distribution.

The results discussed above show that magnesium fluoride is characterized by an almost chemically inert surface, which suggested its use as a support rather than a catalyst. It shows good thermal stability, relatively high hardness and high resistance to calcination in oxygen. $MgF_2$ has a relatively large surface area of 45 $m^2/g$ after calcination at 673 K, and a narrow range of pore size in the scale of mesopores thus being an almost model support of mesoporous structure.

## 3. Magnesium fluoride as a support

Research work on the catalysts supported on $MgF_2$ has developed in three main directions.

1. Study of the structure and surface properties of the catalysts with:
   - (a) metal oxides (Mo, V, W, Cu, Cr);
   - (b) binary metal oxide phases (Cu-Cr, Cu-Mn);
   - (c) metallic catalysts (Ru).
2. Studies of the heteropolyacids supported on $MgF_2$.
3. Catalysts for environmentally friendly processes.

### 3.1. Metal oxides

Transition metal oxides—Cr, V, Mo, W, Nb, Cu, Co and Re dispersed on the surface of supports such as $Al_2O_3$, $SiO_2$, $TiO_2$, $ZrO_2$ and MgO [34–42] have become a subject of interest in recent years. One of the main difficulties in identification of surface complexes occurring in these systems was that oxide ions of the transition metal–oxygen polyhedra formed under thermal treatment of catalysts were indistinguishable from those of the oxidic support. Wojciechowska and co-workers attempted to resolve this problem using systems with transition metal oxide deposited on magnesium fluoride [43–51]. This attempt revealed that deposition of transition metal ions on the surface of $MgF_2$ proceeded via simple adsorption [46]. Apparently, the OH groups on the surface of $MgF_2$ crystallites did not have enough basic or acidic character to react with a precursor of the active phase and thus they remain unchanged after deposition of the active phase. As a result of $MgF_2$ impregnation with the precursors of active phases, the transition metals are adsorbed as oxo-ions $MO_x$ ($M = Mo, V, W, Cu, Cr$). Deposition of $MO_x$ is structure-sensitive and takes place as a result of adsorption only on the crystal planes (1 1 0) of the rutile structure of $MgF_2$ where only $(Mg_{uns})^{2+}$ are present. On the other crystal faces, e.g. (0 0 1), (1 0 0) and (0 1 0) where both coordinatively unsaturated magnesium and fluorine ions are present, heterolytic dissociation of water takes place [46]. The cleavage plane on which only $(Mg_{uns})^{2+}$ ions are present and along which the smallest number of bonds must be disrupted is the (1 1 0) plane [45]. Two $F^-$ ions are missing in the coordination spheres of unsaturated $Mg^{2+}$ ions in every second row, whereas $F^-$ ions are fully saturated. On the plane (1 1 0), the adsorption of an oxo-anion can take place, with two oxygen atoms of these ions completing the coordination spheres of unsaturated $Mg^{2+}$ ions (Fig. 4). On outgassing at higher temperatures, the polyanions decompose and the $MO_6$ octahedra or $MO_4$ tetrahedra spread over the (1 1 0) plane due to wetting, their oxygen atoms occupying the vacant sites of further surface of $(Mg_{cus})^{2+}$ ions. These ions generate the Lewis acidic sites when anion vacancies are formed. Whereas the Lewis acidic sites exposed to water vapor become hydroxylated giving Brønsted acidic sites.

Apart from $MO_x$ ions, surface complex formation may involve fluorine anions from the support lattice. The formation of such complexes in the systems $V_2O_5/MgF_2$ and $CuO/MgF_2$ was described in [44,46], while for the other catalysts (Cr, Mo, W) no formation of fluoride compounds was observed. Fluorine compounds are formed as a result adsorption of $VO^{3+}$ species of the surface of $MgF_2$. On preparation, at $pH = 4$, the ions are at equilibrium with $H_2VO_4^-$ and $H_3VO_4$ (according to the pH diagram [52]). The $VO_2^+$ becomes hydrated to form $VO(OH)_2$, which in the presence of protons at the surface of $MgF_2$ may be stripped of the hydroxyl groups to give $VO^{3+}$ species. These cations adsorb at the sites with excess negative charge. Such sites exist at the (2 1 0) crystal planes, where five fluoride ions surround a square pyramidal vacancy. This vacancy shows the total charge of $-3$ units and can easily adsorb the $(V{=}O)^{3+}$ cation forming the $VOF_5$ octahedron (the total

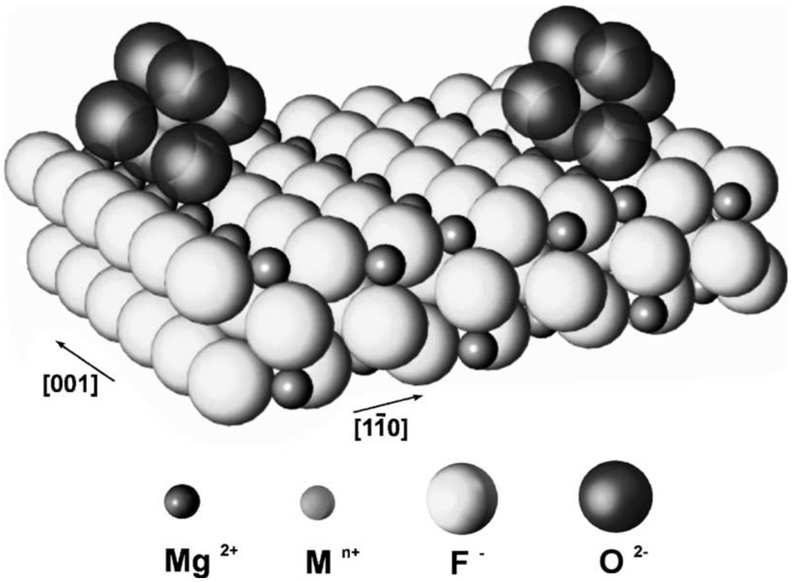


Fig. 4. The $MO_x$ groups located on $MgF_2$ (1 1 0) crystal plane.

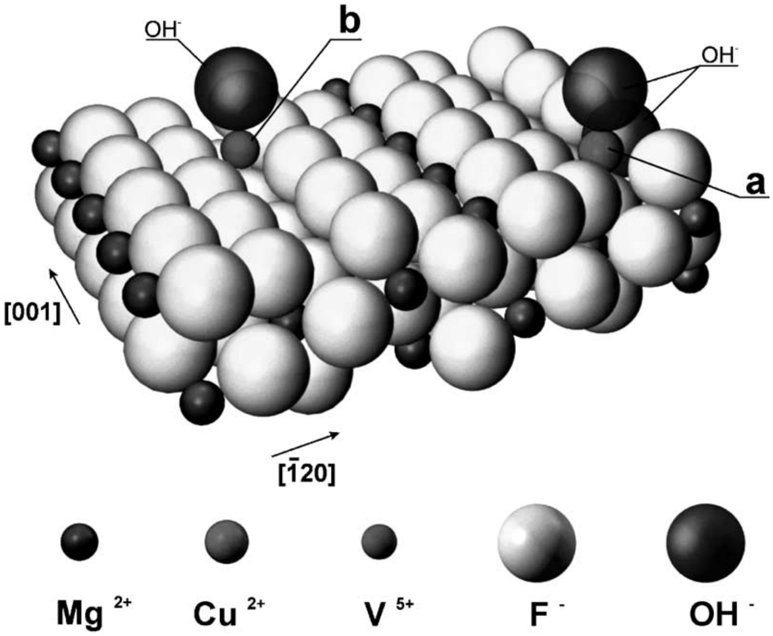


Fig. 5. Surface complexes of $CuF_4(OH)_2$ (a) and $VF_5OH$ (b) at the (2 1 0) crystal plane of $MgF_2$.

charge of fluoride ions is −3 as the other two negative charge units are used to neutralize the charge of $Mg^{2+}$ from the fluorine lattice) (Fig. 5). The presence of such species at the surface of $MgF_2$ at low coverage was detected by electron paramagnetic resonance (EPR) and IR methods [46]. Similarly, the presence of fluoride complexes on the surface of $CuO/MgF_2$ samples can be explained by the interaction of a copper precursor with the surface of the support. As a result, copper fluoride species of a structure similar to that of $CuF_2{\cdot}2H_2O$ are formed, where four fluoride ions and two water molecules (or OH groups) surround the $Cu^{2+}$ ion. Such sites exist in the (2 1 0) crystal plane (Fig. 5).

Deposition of $MO_x$ and $MOF_x$ species in contact with water vapor leads to formation of the complexes $MO_{x-1}OH$ and $MOF_{x-1}OH$. Their formation is evident from the appearance of many new bands in the IR spectrum assigned to OH groups bonded to these complexes [45]. The OH groups of $WO_3/MgF_2$ catalysts have the highest, while $V_2O_5/MgF_2$ the lowest acid strength, which is reflected in the catalytic properties. For example, 100% selectivity to propene was observed in the reaction of 2-propanol decomposition for $WO_3/MgF_2$ catalysts, whereas $V_2O_5/MgF_2$ and $Cr_2O_3/MgF_2$ showed very small selectivity towards dehydration [45]. A similar situation was observed in cumene cracking involving strong acidic centers in which $WO_3/MgF_2$ catalysts showed the highest activity. In the same reaction $MoO_3/MgF_2$ catalysts were less active and $V_2O_5/MgF_2$, $Cr_2O_3/MgF_2$, $CuO/MgF_2$ were completely inactive. In the dehydrogenation of cyclohexane the order of activity was [45]:

$$Cr_2O_3/MgF_2 > V_2O_5/MgF_2 > MoO_3/MgF_2 > WO_3/MgF_2 > CuO/MgF_2.$$

Catalytic activity is proportional to the $MgF_2$ surface coverage with $MO_x$ or $MOF_x$, which can indicate that molecularly dispersed surface species are the active sites.

### 3.2. Two different oxide phases

The solution of the mechanism of the monolayer oxide species bonding with the surface of $MgF_2$ has prompted a study of the structure and physico-chemical properties of more complex systems containing two different oxide phases. The results of X-ray photoelectron spectroscopy (XPS), IR, EPR, X-ray diffraction (XRD) and chemical analysis have indicated the interaction between the oxo-copper, oxo-chromium ions and surface ions of $MgF_2$ taking place on the surface of the catalysts containing both copper and chromium oxides deposited on $MgF_2$ [53,54]. As a result, the oxo-ions adsorbed on the coordinatively unsaturated $Mg^{2+}$ ions and $Cu^{2+}$ ions interact with the surface $F^-$ ions forming oxide and oxofluoro-oxide $Cu^{2+}$ complexes. The interaction between copper and chromium ions led to an electron transfer from chromium to copper. As a consequence $Cr^{6+}$ and $Cu^+$ centers were formed, which played the role of active sites in catalytic dehydrogenation reactions [53,54]. The surface was covered by highly dispersed copper chromate and $Cr_2O_3$ crystallites. It contains a considerable number of $Cr^{6+}$ ions, stabilized by the presence of copper ions in the copper chromate matrix. Because of the presence of $Cr_2O_3$, the surface contains also $Cr^{3+}$ ions, which are resistant to oxidation in the course of pretreatment. In the processes of decomposition of 2-propanol and dehydrogenation of cumene, the systems containing both copper and chromium oxides deposited on the surface of the $MgF_2$ support showed the catalytic activity one order of magnitude higher than that of the preparations containing single oxides only.

The structure and catalytic activity of the catalysts containing copper and manganese oxides supported on $MgF_2$ [55] have been also studied. Using XRD and temperature-programmed reduction (TPR) techniques it has been established that copper and manganese oxides as well as spinel structure $CuMn_2O_4$ are present on their surface. The introduction of the oxides onto the support resulted in an increase of its redox centers and Lewis acid centers. The double oxide system Cu-Mn-O/$MgF_2$ was found more effective in CO oxidation and NO reduction by propene than catalysts based on individual oxides.

### 3.3. Metallic phase

The interaction between metal and support may lead to changes in the surface structure and catalytic properties of the metallic catalysts. The interaction is possible because of a modification of the metal electronic structure by shift in electron density towards the support. We have chosen ruthenium for our study because of its high activity in many reactions, which distinguishes it among metals of group 8. Literature provides the information on ruthenium deposited on various supports, i.e. $SiO_2$ [56], $Al_2O_3$ [57], $TiO_2$ [58] and active carbon [59]. Wojciechowska et al. were the first to obtain ruthenium catalysts supported on $MgF_2$. The catalysts were synthesized from two different precursors of ruthenium $RuCl_3$ or $Ru_3(CO)_{12}$. The effect of the precursor on the structure and catalytic properties of the Ru/$MgF_2$ system was reported in [60]. The EPR study of ruthenium catalysts after adsorption of probe molecules (CO and $O_2$) indicated the presence of ruthenium centers able to transfer an electron. The samples obtained from $Ru_3(CO)_{12}$ were characterized by a considerably greater ability to undergo electron transfer than the samples obtained from $RuCl_3$. On the surface of the former, there were $Ru^0$ as well as the $Ru^{\sigma+}$ species endowed with charge between 0 and 1. Both series of preparations were active in redox or acid–base reactions. The activities of the carbonyl samples were higher than those of the chloride catalysts, particularly in the reactions requiring the presence of acid centers.

The effect of the chlorine precursor of ruthenium on the metal dispersion on the surface of Ru/$MgF_2$-type catalysts has been studied. Results of the dispersion measurements performed by the static method of hydrogen chemisorption have shown that the dispersion decreases with ruthenium loading, similarly as for the majority of the known metallic catalysts. The mean size of the crystallites obtained from the transmission electron microscopy (TEM) study proved much smaller than that implied by the chemisorption measurements. This difference was explained by a strong metal–support interaction (SMSI) or the decrease of the chemisorption by the chlorine or fluorine ions of the support left in the catalyst [61].

### 3.4. Heteropolyacids

Polyoxometalates of the formula $H_mXY_{12}O_{40}$, where $X = P$, Ni, As, Te, Mn, Si; and $Y = Mo$, W, V are known as heteropolyacids (HPA). Their structure is well recognized and thus they can be modified in a controlled way, which permits a regulation of their acid–base and redox properties. Therefore, they have found application in many interesting catalytic reactions. Heteropolyacids can be used as catalysts for homogeneous as well as heterogeneous chemical processes. In the latter, they are supported an porous materials, usually $SiO_2$ [62], polymeric matrices [63,64], on mesoporous materials [65] or on $MgF_2$ [66]. Mastikhin et al. [66] studied heteropolyacid $H_3PW_{12}O_{40}$ supported on $MgF_2$, and reported changes in the structure of HPA due to the interaction with the support, using $^1H$, $^{31}P$ nuclear magnetic resonance spectroscopy–magic angle spinning (NMR–MAS) and IR spectroscopic methods. The results revealed formation of several different surface species upon supporting of HPA on $MgF_2$ surface. At small $H_3PW_{12}O_{40}$ content ($\sim$1–3 wt.%), HPA interacts strongly with the specific surface centers including surface F atoms, which results in destruction of HPA anions. At intermediate HPA contents (5–20 wt.%) the isolated monomeric HPA molecules loosely bonded with the support surface are also presented in the catalyst. At still greater HPA contents, the crystals of HPA are formed. Different types of surface species exhibit different catalytic properties.

The evidence reported in [66] permits drawing a conclusion that $MgF_2$ is a suitable support to study the interactions of heteropolyacids with the support surface. It should be emphasized that $MgF_2$ is transparent for infrared radiation in the range 4000–600 $cm^{-1}$ and in contrast to other supports ($SiO_2$, $Al_2O_3$, $TiO_2$), it does not show bands in the range of frequencies characteristic of HPA, i.e. in the range $\sim$1400–600 $cm^{-1}$ (Fig. 6).

### 3.5. Catalysts for environmentally friendly processes

The information on the way of formation of oxide layers, dioxide layers or metallic layers on the surface of $MgF_2$ and determination of the physico-chemical properties of the systems prompted the search for catalysts of prospective interest in the environment protection.

The process in which the catalysts with a metallic phase supported on $MgF_2$ were used was hydrodechlorination of CFCs. It is known that chlorofluorocarbons used as coolants and aerosol propellants are responsible for depletion of the stratospheric ozone layer. Replacement of chlorine atoms in such compounds with hydrogen atoms is one of the methods aiming at restricting this effect and hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) have attracted much attention as the alternatives of CFCs. The production of HFCs and HCFCs involves catalytic processes, namely fluorination of chloroalkanes over $AlF_3$ or $Cr_2O_3$ as catalysts, and hydrodechlorination of CFCs over

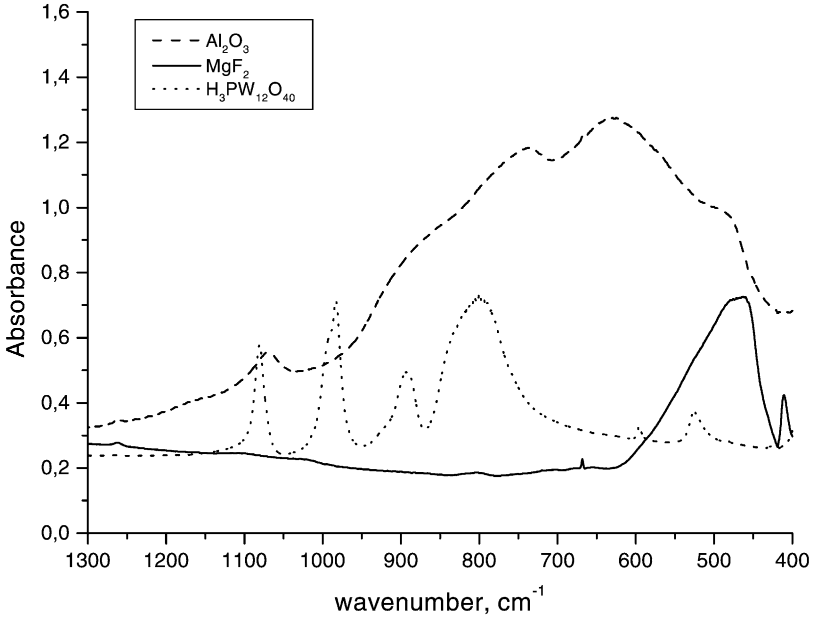


Fig. 6. IR spectra of $Al_2O_3$, $MgF_2$ and $H_3PW_{12}O_{40}$.

metal catalysts. In the last process, the most often used are heterogeneous catalysts containing such transition metals as iridium, ruthenium [23] and especially palladium [7,22] supported on active carbon, $Al_2O_3$, $TiO_2$, $ZrO_2$, MgO [23] and on several metal fluorides $AlF_3$, $ZrF_4$, $TiF_3$ [6,7]. The selectivity of the reaction is highly dependent on the nature of the support. For example, using the Pd catalysts supported on $ZrF_4$ in $CF_2Cl_2$ hydrogenation allows reaching a selectivity to $CH_2F_2$ of up to 90% [6], whereas on graphite the $CH_2F_2$ selectivity was 56% [7]. The oxide supports are not resistant to the highly corrosive conditions of this reaction which results from considerable evolution of HCl, which can transform the support, for example, MgO into $MgCl_2$. Similarly due to the inevitable formation of HF during CFCs hydrodehalogenation, MgO is transformed into $MgF_2$, which, when located at the metal–support interface, might favorably modify the electronic state of the metal particles. The use of fluorides as supports prevents this process and yields systems resistant to the reaction environment. For instance, Pd and Ru catalysts supported on $MgF_2$ appeared to be useful catalysts in the reaction of $CCl_2F_2$ hydrodechlorination [22,23]. Their selectivity towards $CH_2F_2$ production was reasonably high (>70%), resembling the catalytic behavior of $AlF_3$-supported palladium catalysts. After doping Pd/$MgF_2$ with gold, the selectivity for $CH_2F_2$ increased from ~70 to almost 90%. Generally, the use of metal fluorides as supports favors both the selectivity to $CH_2F_2$ and the specific activities per surface metal atoms.

The systems tested for the heterogeneous dismutation of $CCl_2F_2$ were $AlF_{3-x}(OH)_x$ [15] and α-$CrF_{3-x}(OH)_x$ [16] doped by magnesium fluoride. The introduction of $MgF_2$ to $AlF_3$ in the amount of up to 10 mol% of Mg resulted in a considerable increase in the $CCl_2F_2$ conversion, up to 90% [15] (Fig. 7). Consequently, the catalytic activity was diminished with increasing Mg content. The situation was different for the system $CrF_3$-$MgF_2$ whose activity increased with increasing $MgF_2$ and above 56% Mg it remained on the level of ~60% [16] (Fig. 8). The authors of these works have

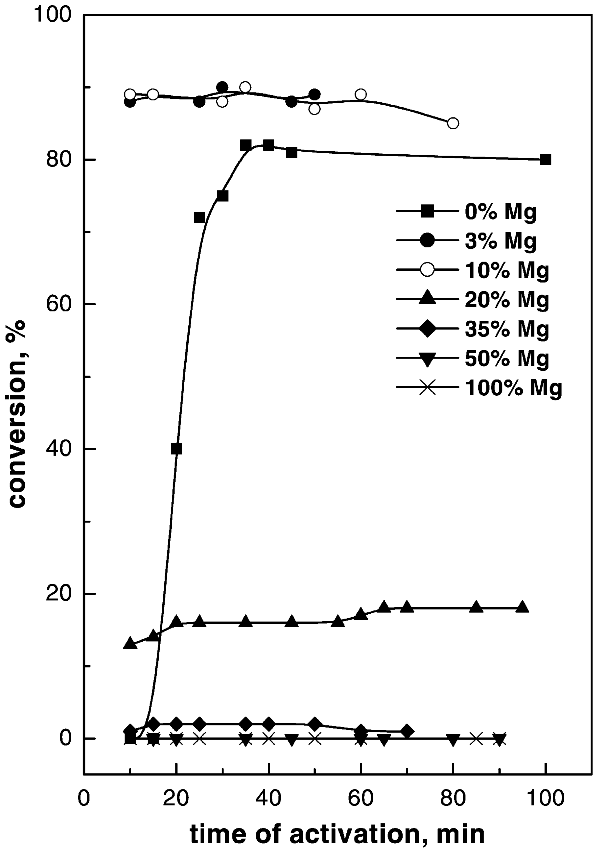


Fig. 7. Conversion of $CCl_2F_2$ vs. activation time for various Mg-replaced α-$AlF_3 \cdot 3H_2O$ calcination products [15].

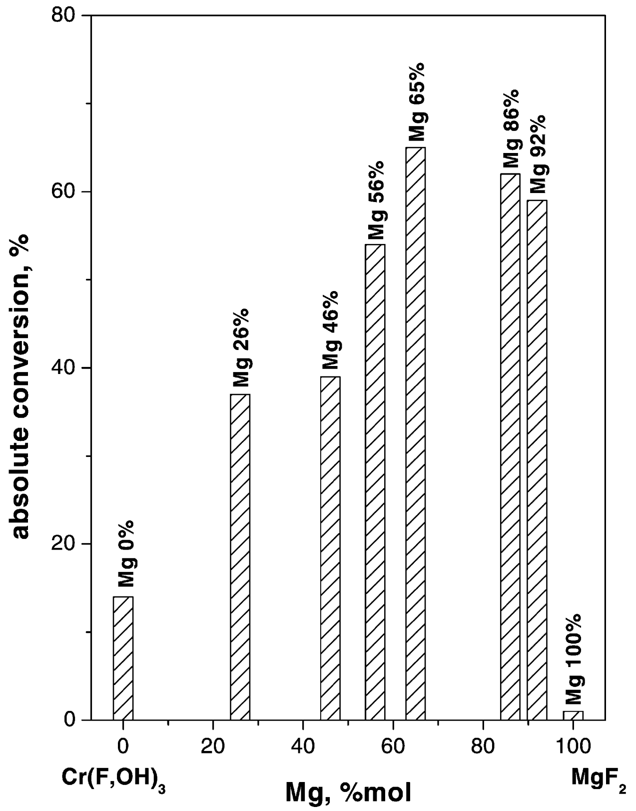


Fig. 8. Conversion of $CCl_2F_2$ vs. Mg content for various Mg-replaced α-$CrF_3 \cdot 3H_2O$ calcination products [16].

explained the increasing catalytic activity by the generation of new Lewis acid centers or enhancement of the earlier existing centers. A comparison of the performance of these two systems has shown that the $AlF_3$ doped with magnesium fluoride in the amounts as small as 3–10% results in a drastic increase in the CFCs conversion. When applying $CrF_3$, a 60% conversion was obtained only after introduction of Mg in over 56%. Taking into regard the results of [13] reporting the properties of a mixed system $CrF_3$/$MgF_2$-$AlF_3$, it is supposed that the decrease in the activity of $AlF_3$/$MgF_2$ [15], containing magnesium fluoride in the content of above 10% Mg, is related to the anti-synergy effect attributed to the formation of $MgAlF_5$.

The effect of magnesium fluoride in chromium-magnesium catalysts on the fluorination reaction of $CF_3CH_2Cl$ has also been studied by Lee et al. [13]. They concluded that $MgF_2$ plays an important role in extending the lifetime of the chromium catalysts, by suppressing the formation of undesired side products. In addition, $MgF_2$ enhances the activity and selectivity of the chromium catalysts through the electronic interaction with $CrF_3$. Lee et al. [14] have shown that the active centers in chromium-magnesium fluoride catalysts are coordinatively unsaturated chromium species. This species are easily hydrated and deactivated by coke formation.

Another process in which the catalysts with a metallic phase supported on $MgF_2$ were used was hydrodesulfurization (HDS). Analysis of literature data prompted us to try and use $RuS_2$ as the active component for a catalysts of HDS process. Ruthenium sulfide catalyst was found to be the most active hydrodesulfurization catalyst among the transition metal sulfides and exhibited very high activity [67]. The properties of the $RuS_2$ catalyst were found to be to a significant degree modified by the support used [68–70]. The modification is a consequence of the interaction between the metallic phase and the support, leading to a modification of the electronic state of the metal as a result of charge transfer between the metal and the support. The outcome of our further studies [21,71] were the catalysts $RuS_x$/$MgF_2$ characterized by very high activity in hydrodesulfurization of thiophene. Their activity was 20 times higher (expressed per active phase) than that of the commercially available cobalt-molybdenum catalyst (Fig. 9).

Magnesium fluoride has also been found useful as a support in interesting oxide catalysts showing high activity and selectivity in $NO_x$ reduction to $N_2$ in the presence of carbon oxide [19,72] and hydrocarbons [20]. Our earlier studies on reduction of nitrogen oxides with carbon monoxide on different oxides of transition metals supported on $MgF_2$ proved the best performance of CuO/$MgF_2$ catalysts. The results helped resolve the mechanism of this reaction and establish the reasons for the catalyst deactivation [72,73]. However, despite very high initial activity they undergo a rather fast deactivation with time-on-stream. Addition of dioxygen to the reaction gases significantly prolongs the lifetime of the catalysts. In the process of NO reduction also propene was used as a reducing agent.

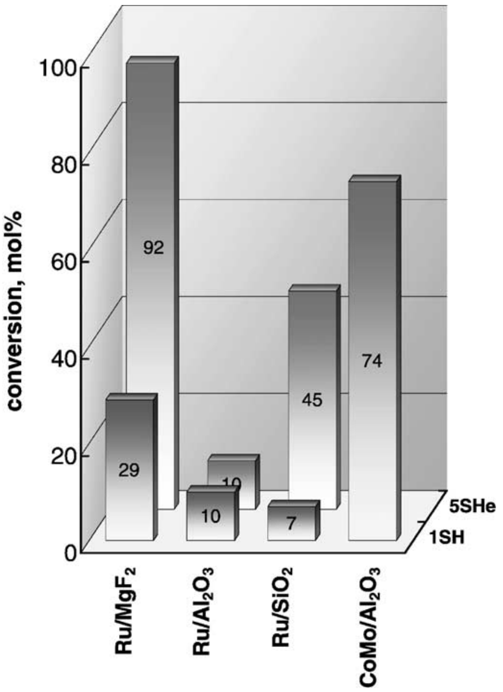


Fig. 9. Thiophene hydrodesulfurization on Ru/$MgF_2$, Ru/$Al_2O_3$, Ru/$SiO_2$ and commercial CoMo/$Al_2O_3$ catalysts after activation in 10% $H_2S$/$H_2$ (1SH) and 50% $H_2S$/He (5SHe).

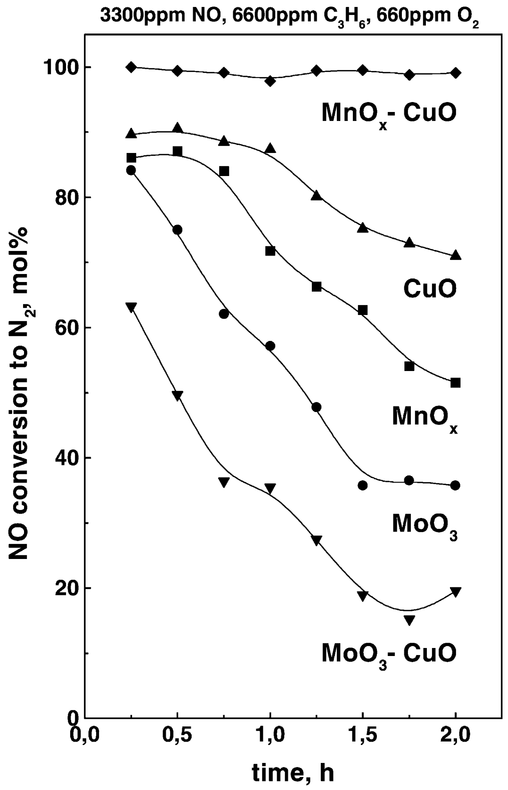


Fig. 10. Catalytic activity of various metal oxides supported on magnesium fluoride in the NO + $C_3H_6$ + $O_2$ reaction at 643 K.

Fig. 10 presents the activities of single oxides ($MnO_x/MgF_2$, $CuO/MgF_2$, $MoO_3/MgF_2$) and double oxide systems ($MnO_x$-$CuO/MgF_2$ and $MoO_3$-$CuO/MgF_2$) in the reaction:

$$4NO + 2C_3H_6 + 7O_2 \rightarrow 2N_2 + 6CO_2 + 6H_2O.$$

An exceptionally active and stable catalyst proved to be $MnO_x$-$CuO/MgF_2$ in the presence of dioxygen [74]. The other catalysts activities were lower and decreased with time.

## 4. Summary

1. Magnesium fluoride satisfies the criteria of a good catalyst support and can be successfully used in catalytic processes.
2. The absence of oxygen atoms in the crystalline lattice of $MgF_2$ makes it possible to analyze the structure of oxide phases (transition metal oxides, heteropolyacids) supported on magnesium fluoride in particular by IR spectroscopy, because $MgF_2$ does not have characteristic bands in the range ~1300–600 $cm^{-1}$.
3. $MgF_2$ support is resistant in hydrodechlorination of CFCs. The use of metal fluorides as supports allows better control of the selectivity of this process.
4. The use of fluorides of different metals as the active phase supports has permitted obtaining catalysts active in the processes important from the point of view of the natural environment protection, such as hydrodechlorination of CFCs ($AlF_3$, $CrF_3$, $AlF_3$-$MgF_2$, $Pd/MgF_2$), hydrodesulfurization of organic compounds ($Ru/MgF_2$), elimination of nitrogen oxides and CO oxidation ($CuO$-$MnO_x/MgF_2$).

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