Interaction of magnesium fluoride with copper(II) and vanadium(V) oxides

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Abstract

Copper(II) oxide and vanadium(V) oxide deposited on MgF_2 were studied by IR and EPR methods. The results obtained indicated that on the surface of MO_x/MgF_2 systems (M = Cu, V) the surface cations are coordinated by oxygen ions as well as the fluoride anions of the support lattice. It is supposed that the incorporation of fluoride ions from the surface of MgF_2 into the structure of the latter two complexes is hindered.   © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Among catalytic studies much attention has been paid to systems containing transition metal oxides deposited on a support. They may be supported on the oxides of main group metals as well as transition metal oxides. Thermal treatment induces many phenomena originating from the oxide-support interaction. The type of interaction depends on the chemical and crystal chemical properties of each, their surface energy, preparation method and calcination temperature [1,2]. In spite of studies on transition metal oxide/oxidic support systems, the nature of the interaction between the support and the active phase is not yet clear. Under normal pre-treatment conditions at high temperatures, dehydration of the surface of the catalyst takes place and oxide species are formed, whose structure and behaviour in elementary catalytic transformations are not understood so far. One of the difficulties is that oxygen ions of the transition metal–oxygen polyhedra are indistinguishable from those of the oxide support. We attempted to resolve this problem using systems with transition metal oxides deposited on a support that does not contain lattice oxygen — magnesium fluoride.

This study was undertaken to characterize MO_x/MgF_2 (M = Cu, V) surface complexes. MgF_2 was used previously as a support for transition metal oxides [3–8] because of its thermal stability and resistance to annealing in oxygen.

2. Experimental

2.1. Preparation of catalysts

All samples were prepared by the precipitation-deposition method. The CuO/MgF_2 preparations were obtained by introducing an aqueous solution of copper nitrate into a suspension of freshly precipitated magnesium fluoride. The suspension was then evaporated until dry. Thus, all the copper nitrate was introduced into the microporous MgF_2 particles. Magnesium fluoride was obtained by adding small portions of $MgCO_3 \cdot 3H_2O$ to an aqueous solution of hydrofluoric acid until neutralisation, and acidifying by introducing a few additional drops of the acid [3]. The solutions of $Cu(NO_3)_2$ taken for impregnation contained the amounts of copper nitrate that corresponded to surface coverage of MgF_2 equals to Cu/Mg atomic ratios between 0.01 to 0.250. The preparations were then dried first at 323 K under frequent stirring, then at 378 K for 24 h and finally annealed at 423–673 K for 4 h. Such conditions of thermal treatment ensure total decomposition of copper(II) nitrate to CuO. The samples were denoted with symbols CuX where X is the percentage atomic ratio Cu/Mg multiplied by 100. For example, the sample with the atomic ratio Cu/Mg = 0.01 has the symbol Cu1.

V_2O_5/MgF_2 was prepared by introducing an aqueous solution of ammonium metavanadate (NH_4VO_3) into freshly precipitated MgF_2 at pH = 4. Further steps were as for the CuO/MgF_2 samples. The samples of V_2O_5/MgF_2 will be denoted by the symbols VX.

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Table 1 summarises the chemical composition of the samples and their surface areas

2.2. Surface area

The surface area was determined by the BET method from the adsorption isotherms of nitrogen at liquid nitrogen temperature with the help of a Sartorius Gravimat.

2.3. X-ray study

X-ray examination was carried out with M-62 diffractometer in conjunction with a HZG-3 powder goniometer, CuKα radiation was used.

2.4. Infrared spectra

IR spectra were recorded on a Bruker IFS 113 V spectrometer. The samples were prepared by grinding 2 mg of the catalyst with 0.2 g of dried KBr and pressing the mixture into thin discs at 8 ton/m^2.

2.5. EPR spectra

The EPR spectroscopic studies were carried out with a X-band spectrometer type SE/X-2542 made by Radiopan. DPPH, a stable free radical with the g-factor 2.0036 was used as an external standard. Other details of the experimental procedure are described in Ref. [8].

3. Results and discussion

3.1. Surface area

Table 1 gives the chemical composition and surface areas of examined samples. In the case of CuO/MgF_2 preparations a distinct decrease of surface area is observed with increasing amount of introduced copper(II) nitrate. The surface area of the samples with the atomic ratio $Cu/Mg \geq 0.05$ was 30% smaller when compared with that of pure MgF_2. This can be explained by a greater contribution of the surface area of CuO in the total surface area: CuO has a poorly developed micropore system and its surface area equals 1 m^2/g (Table 1). On the other hand, the introduction of NH_4VO_3 onto MgF_2 results in an increase of the surface area, reaching a maximum value of 94 m^2/g for the sample with the V/Mg atomic ratio equal to 0.10 — sample V10. Increase of the surface area can be explained as an effect of peptisation of freshly precipitated MgF_2, which consisted of agglomerated tiny particles of poorly crystallised fluoride. On increasing the concentration of impregnated solution the ionic strength rose and the peptisation effect diminished resulting in the decrease of the surface area at higher V/Mg atomic ratio.

X-ray analysis revealed the presence of MgF_2 and CuO in the CuO/MgF_2 samples and MgF_2 and V_2O_5 in the $V_2O_5/$

Table 1
Characteristics of CuO/MgF_2 and V_2O_5/MgF_2 preparations

Sample	Atomic ratio (Cu/Mg or V/Mg)	Surface area ($m^2 g^{-1}$)
MF	0.00	30
CuO	–	1
Cu1	0.01	28
Cu5	0.05	21
Cu10	0.10	18
Cu25	0.25	19
V_2O_5	–	9
V2	0.02	33
V5	0.05	55
V10	0.10	94
V20	0.20	80

MgF_2 samples. The lines characteristic of the other copper and vanadium compound links were not observed. The lack of differences in the crystalline structure and lattice distances of magnesium fluoride after introduction of the active phase excluded the formation of solid solution and indicated that the copper and vanadium species were located on the surface of MgF_2.

3.2. Infrared spectra

Fig. 1 shows the IR spectra of CuO/MgF_2 samples. In these spectra IR bands at 703–707 cm^{-1} and 751–757 cm^{-1} were detected (spectra 3–6). These bands are characteristic of Cu–F bond vibrations in structures similar to $CuF_2 \cdot 2H_2O$ [9] and indicate the presence of the copper complexes surrounded by both oxygen and fluoride ligands. Another interesting observation was a shift of the band at 458 cm^{-1} characteristic of MgF_2 (spectrum 1) to higher frequencies (463 cm^{-1}) with increasing Cu/Mg atomic ratio (spectra 3–6). Change of shape of this band and appearance of a shoulder characteristic of CuO structures (spectrum 2) at 504 cm^{-1} was detected.

The IR spectra of V_2O_5/MgF_2 catalysts are presented in Fig. 2. The bands observed at 830, 880, 960 and 1010 cm^{-1} are typical of bond vibrations in vanadium–oxygen complexes. The band at 960 cm^{-1} seems to be characteristic of V=O bond vibrations, shifted relative to this band in V_2O_5 (1010 cm^{-1}). This shift indicates the formation of V–O–F complexes and results from the influence of fluoride ligands on the V=O bond vibrations [10]. For the samples containing a higher amount of vanadium the band at 880 cm^{-1} disappeared and simultaneously a new band appeared at 1010 cm^{-1}, whose relative intensity increased with vanadium content, as also the case for the bands at 830 and 960 cm^{-1}. The bands at 820 and 1020 cm^{-1} (spectrum 5) are characteristic of the bulk V_2O_5 phase [10], which was formed at higher concentrations, when islands of surface vanadium oxide species grow in thickness. At a very small surface coverage, apparently isolated vanadium complexes are formed (880
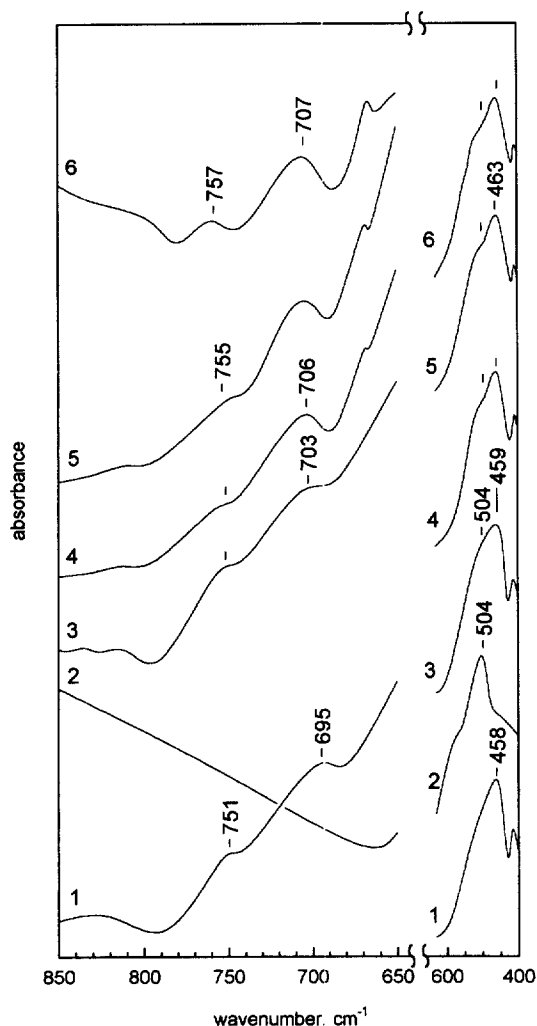
Fig. 1. IR spectra of CuO/MgF$_2$ samples: (1) MgF$_2$, (2) CuO, (3) Cu1, (4) Cu5, (5) Cu10, (6) Cu25.

Fig. 2. IR spectra of V$_2$O$_5$/MgF$_2$ samples: (1) MgF$_2$, (2) V2, (3) V5, (4) V10, (5) V20.

cm^{-1}), which then polymerize into chains or islands (830 and 1010 cm^{-1}) [11].

Concluding, the surface of CuO/MgF$_2$ and V$_2$O$_5$/MgF$_2$ samples was covered with two kinds of complexes of copper or vanadium: those in the coordination of both oxide and fluoride ligands and the ones in the coordination of oxide ligands only. The conclusion that these species were located on the surface was drawn from the X-ray studies, which show no change in the main phase peak.

3.3. EPR spectroscopy

The presence of two kinds of complexes on the surface of CuO/MgF$_2$ and V$_2$O$_5$/MgF$_2$ samples was confirmed by the EPR study. The EPR spectrum of the sample Cu1 (spectrum 1, Fig. 3) is a superposition of the lines of two kinds of copper complexes. The first one characterized by the parameters $g_{\parallel} = 2.350$ and $g_{\perp} = 2.051$ originates from a tetragonally distorted octahedral [CuO$_6$] complex [12]. This type of complex is dominant for the samples with higher copper content (spectrum 3). The second one described by the parameters
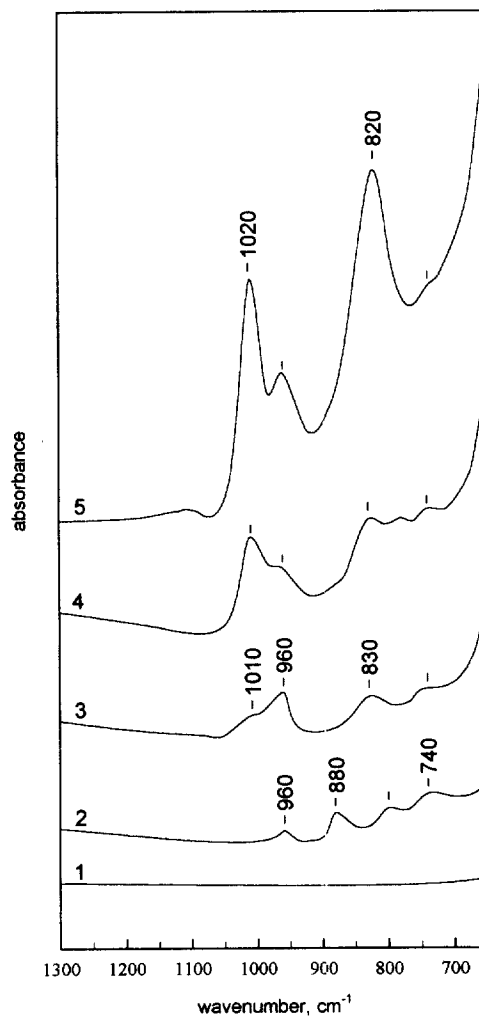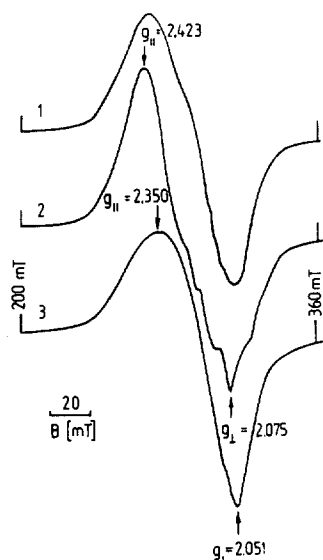

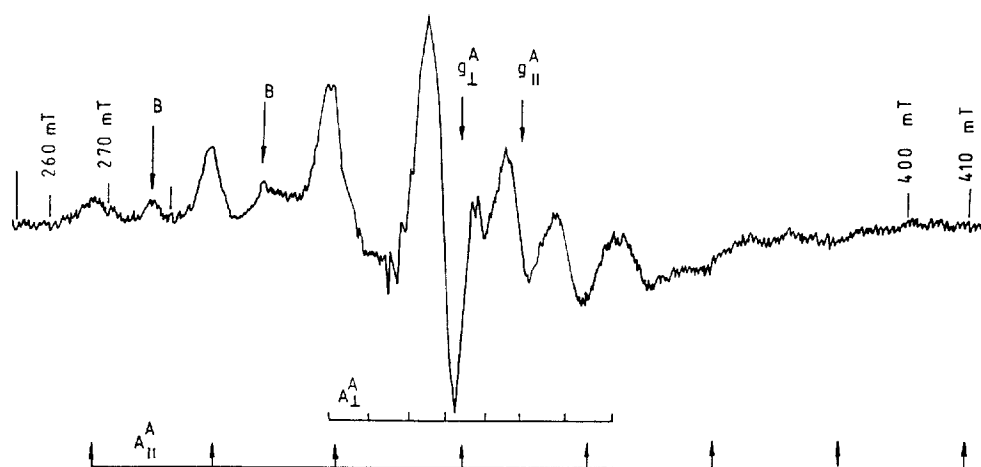Fig. 3. EPR spectrum of Cu1 samples treated at 423 K (1), 573 K (2) and Cu5 treated at 423 K (3) recorded at 77 K.

Fig. 4. EPR spectrum of reduced (vacuum treatment at 673 K for 3 h) V2 sample recorded at 77 K.

$g_{\parallel} = 2.423$ and $g_{\perp} = 2.075$ characteristic of octahedral copper (II) complex in which Cu^{2+} ion is surrounded by fluoride and oxygen ligands as in $CuF_2 \cdot 2H_2O$ [13]. This complex was dominant in the samples heated at 573 K (spectrum 2, Fig. 3). The superhyperfine structure, with splitting of about 60 Gs, was observed on the perpendicular peak of this spectrum is due to the superhyperfine interaction of the unpaired electron of copper(II) ions with the fluorine nucleus ($I = 1/2$). To sum up, in the first stages of the thermal treatment (423 K), on the surface of CuO/MgF_2 preparations, copper complexes may be present and Cu^{2+} ions are coordinated to oxygen ligands of the H_2O molecules, whereas after treatment at higher temperature the copper(II) ions are coordinated to oxygen or fluorine ligands.

The EPR spectra of V_2O_5/MgF_2 samples performed after the reduction of the catalyst by evacuation (vacuum treatment at 673 K for 3 h) indicated the presence of paramagnetic V^{4+} ions. During this procedure oxygen ion is assumed to be removed from the coordination sphere of V^{5+} ion and as a result the V^{4+} ion was produced in square pyramidal coordination with multiple-bonded oxygen in the apex as detected by EPR. The unpaired electron of V^{4+} ($3d^1$) interacting with the nuclear magnetic moment of ^{51}V ($I = 7/2$) gives a spectrum composed of two sets of 8 parallel and perpendicular lines of the hyperfine structure (Fig. 4). The observed spectra indicate the existence of two kinds of V^{4+} complexes. The parameters of a complex which gave the lines of higher intensity: $g_{\parallel}^A = 1.931$, $g_{\perp}^A = 1.987$ and $A_{\parallel} = 205$ Gs, $A_{\perp} = 64$ Gs were the same as in [VOF_5] complexes [14]. In the spectrum particularly on the central line, small lines of superhyperfine structure originating from the interactions of unpaired electrons with a fluorine nucleus ($I = 1/2$) were observed. The splitting constant for such a structure was established to be ~ 16 Gs. Since the line characteristic of $(V=O)^{2+}$ appeared after the reduction of the sample it can be concluded, that in the case of oxidized preparations vanadium complexes located on the interface of magnesium fluoride form species composed of $(V=O)^{3+}$ groups bonded to fluoride ligands. The second type of complexes were monovanadyl $(V=O)^{2+}$

species in a crystal field of oxide ions in square pyramidal symmetry, similar to those detected for reduced V_2O_5/SiO_2 catalysts [15,16]. Such a complex was characterized by EPR lines centered around $g_{\parallel}^B = 1.937$, $g_{\perp}^B = 1.977$ with hyperfine splitting constants of $A_{\parallel} = 197.4$ Gs and $A_{\perp} = 69.9$ Gs respectively.

3.4. Surface location of the copper and vanadium complexes

MgF_2 crystalizes in the rutile structure, where each Mg^{2+} ion is surrounded by six F^- ions, and each F^- ion is surrounded by three Mg^{2+} ions. Its cleavage plane, along which the smallest number of bonds is broken, is (110). In the coordination sphere of each Mg^{2+} ion located in this plane, two F^- ions are missing in every other row (Mg^{2+} ions with coordination number $= 4$) and the fluoride ions have fully filled their coordination sphere. The positive charge of such magnesium ions is not compensated by the surrounding fluoride ions and equals 2/3 unit. During the preparation of magnesium fluoride, or when it is contacted with water vapour, water dipoles interact with coordinatively unsaturated Mg ions and fill their coordination sphere. This leads to the formation of three types of surface hydroxyls — this model of the surface of MgF_2 was proposed by Wojciechowska [17].

Introduction of transition metal ions onto the surface of an oxide can proceed as a result of three processes: simple adsorption, ionic exchange or substitution. XPS results have shown [11] that the surface of MgF_2 is partly covered by OH groups, the concentration of which remains almost constant despite the amount of vanadium introduced onto the surface of MgF_2. This suggests that the deposition of vanadium proceeds via simple adsorption (the amount of surface OH groups characteristic of MgF_2 was not diminished). Thus these OH groups are neither basic nor acidic enough to react with the solution of NH_4VO_3 [11]. Preparation of the samples was carried out at pH 4. As indicated by the distribution of vanadium ions in aqueous solution in the concentration —

pH diagram [18] in the pH range 6–2, the VO_2^+ cations coexist with $H_2VO_4^-$ anions, which are adsorbed at the surface of MgF_2 at sites carrying positive charge, VO_2^+ becomes hydrated to form $VO(OH)_2^+$, from which in the presence of protons at the surface of MgF_2 the OH groups can be removed to give VO^{3+} species. One can expect, these cations to be adsorbed on the surface of MgF_2 at the sites with excess negative charge. In Fig. 5b such a complex is presented, where 5 fluoride ions surround a square pyramidal vacancy. Two of the fluoride ions have uncompensated charge of $-1/2$ and other two $-2/3$ unit. This vacancy shows the total charge of -3 unit and can easily adsorb a $(V{=}O)^{3+}$ cation forming an octahedron. The presence of such surface species on the surface of magnesium fluoride are consistent with the EPR studies and are responsible for the IR band at 960 cm^{-1}, originating from the V=O bond stretching vibrations, which are shifted by 60 cm^{-1} in respect to the position of this band in V_2O_5, owing to the lower order of the V=O bond in fluoride complexes which have higher electronegativity than oxygen complexes. However the $H_2VO_4^-$ ions are adsorbed at the surface of MgF_2 at the sites carrying uncompensated positive charge (Fig. 5b).
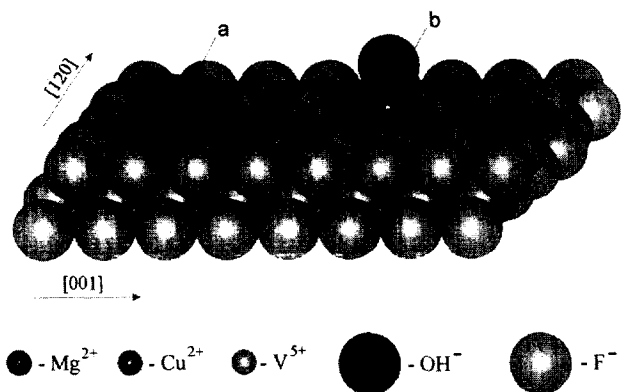
The presence of fluoride complexes on the surface of CuO/MgF_2 samples can be explained by the interaction of a copper nitrate with the surface of the support. As a result, copper–fluoride species of a structure similar to $CuF_2{\cdot}2H_2O$ are formed [19], where 4 fluoride ions and 2 water molecules (or OH groups) surround the Cu^{2+} ion. Such sites exist in the (210) crystal plane (Fig. 5a).

On the other hand, copper–oxygen or vanadium–oxygen complexes may adsorb in the (110) plane. Their two oxygen atoms fill the coordination sphere of unsaturated, surface magnesium ions (Fig. 6) giving isolated octahedra [20] at low MO_x content.

4. Conclusions

Two kinds of complexes were detected on the surface of CuO/MgF_2 and V_2O_5/MgF_2: (1) Cu^{2+} or V^{5+} coordinated by both fluoride and oxidic ligands; (2) Cu^{2+} or V^{5+} coordinated by oxidic ligands. Detection of M–F links in the samples with transition metal oxides supported over MgF_2 indicates that in the case of very reactive oxide supports, their lattice oxygen gets incorporated in the coordination sphere of vanadium and copper species.

Fig. 5. Surface complexes of $CuF_2(H_2O)_2$ (a) and VOF_5 (b) at the (210) crystal plane of MgF_2.
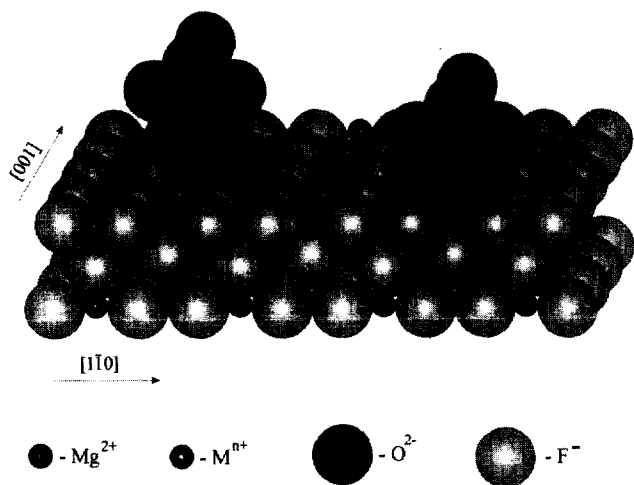
Fig. 6. The MO_x groups located on MgF_2 (110) crystal plane.

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