Acidic properties of vanadium oxide on magnesium fluoride

M. Wojciechowska *, W. Gut and M. Grunwald-Wyspiańska

Faculty of Chemistry, A. Mickiewicz University, Poznań, Poland

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Vanadium oxides supported on magnesium fluoride obtained by the impregnation and the precipitation–deposition method have been studied by IR spectroscopy. The adsorption of pyridine indicated the presence of Lewis acid centers on the impregnated samples, whereas on the samples prepared by precipitation both Lewis and Brønsted centers have been observed. From the adsorption coefficients of the 1540 cm^{-1} (Brønsted site) and 1445 cm^{-1} (Lewis site) bands the numbers of both sites have been estimated. The hydroxyl groups bound in the chains of the $(VO_3)_n$ tetrahedra or those in the trigonal pyramids VO_5 are believed to be responsible for the protonic centers, whereas the aprotonic centers occur at the ionic vanadium with coordinatively unsaturated spheres.

Keywords: Vanadium oxide; magnesium fluoride; acidic properties; IR spectroscopy

1. Introduction

We have recently published data on the surface structure of monolayer vanadium catalysts deposited onto magnesium fluoride [1]. The results of the study revealed that at low concentration of the vanadium oxides VOF_5 complexes and isolated VO_4 tetrahedra were present. The latter polymerized forming chains of $(VO_3)_n$ tetrahedra of the metavanadate type, or some kind of islands composed of trigonal bipiramids. At higher vanadium concentrations, polyvanadate species of octahedrally coordinated vanadia covered the surface of MgF_2. Introduction of V–O polyhedra onto magnesium fluoride resulted in high catalytic activity. V_2O_5/MgF_2 preparations have been found to be active not only in redox but also in acid–base reactions [2]. They were active in the decomposition of isopropanol to propylene as well as in the butene double bond isomerization. These reactions require the presence of both weak and medium strength acid centers, so that such centers must have been present on the

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* To whom correspondence should be addressed.

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surface of the V_2O_5/MgF_2 preparations. Vanadium oxides supported on alumina have also been mentioned in the literature [3,4] as catalysts taking part in acid–base reactions.

We have become interested in investigating the nature of the acid centers existing on the surface of the V_2O_5/MgF_2 system. IR spectroscopy was used and the acidic properties of the preparations were discussed on the basis of the experimental results of pyridine adsorption. In addition, the changes occurring in the hydroxyl coating of MgF_2 after introduction of the vanadia complexes are studied. One should point out that OH groups in the other supported vanadium systems are rare.

2. Experimental

2.1. PREPARATION OF CATALYSTS

Two preparation methods were used: impregnation (I) and precipitation–deposition (P). Impregnated samples of V_2O_5/MgF_2 were obtained by mixing MgF_2 (0.25–0.5 mm) previously heated (at 673 K for 5 h) with an aqueous solution of ammonium metavanadate. The preparations were dried at 378 K for 24 h and then calcinated at 673 K for 5 h. By using solutions of ammonium metavanadate of two different concentrations, the obtained preparations were characterized by V/Mg atomic ratios of 0.007 and 0.015, which corresponded to surface coverages of MgF_2 equal to 0.5 and 1.0 monolayer of V_2O_5.

Precipitated samples of V_2O_5/MgF_2 were prepared by precipitation from the solution of ammonium metavanadate onto the suspension of freshly precipitated magnesium fluoride [5]. The preparations were characterized by V/Mg atomic ratios of 0.02 and 0.05.

Table 1 summarizes the chemical composition of the samples and their surface areas as determined by the BET method from the adsorption isotherms of nitrogen at liquid nitrogen temperature. Results of structural studies of these catalysts by XRD, XPS and EPR are described in ref. [1].

Table 1
Characteristics of V_2O_5/MgF_2 preparations

Catalyst	Preparation method	Atomic ratio V/Mg	Surface area ($m^2\ g^{-1}$)
MF		0.000	29
I-MFV$_{0.7}$	impregnation	0.007	29
I-MFV$_{1.5}$	impregnation	0.015	29
P-MFV$_2$	precipitation–deposition	0.020	33
P-MFV$_5$	precipitation–deposition	0.050	55
V_2O_5		1.00	9

2.2. INFRARED SPECTRA

The IR spectra were recorded by a Brucker IFS 113v spectrometer in the range of free lattice vibrations and in the range of stretching vibrations of OH groups, as well as in the region of the stretching and deformation vibrations of adsorbed pyridine. For examination within the range of 700–1200 cm^{-1} the samples were prepared by grinding of 2 mg of the catalyst with 0.2 g KBr and pressing into thin discs at 8 ton cm^{-2}.

The spectra in the range of 1400–4000 cm^{-1} were studied using a vacuum cell equipped with sodium chloride windows. The samples were prepared in the form of self-supporting thin wafers which were outgassed under a pressure of 10^{-3} Pa at 623 K for 3 h. Several portions of oxygen were introduced successively during this period. The samples were cooled to room temperature and their IR spectra were registered. Pyridine was then introduced into the cell at temperatures of 293, 423, 523 and 623 K for 0.5 h. The sample was again cooled to room temperature, outgassed for 5 min and the spectrum was registered.

3. Results and discussion

Fig. 1 shows the results of the spectroscopic analysis of the V_2O_5/MgF_2 preparations, series I and P, respectively, referred to the spectra of pure MgF_2 and V_2O_5. The IR bands of the I series are observed in the 957–962 cm^{-1} range and near 1000 cm^{-1}. In addition to the bands at 969 and 1010 cm^{-1}, the preparations of the P series exhibited bands at 817 and 851 cm^{-1}, and the preparation MFV_2 showed an additional band at 880 cm^{-1}. In the IR spectra of both series the catalysts with higher vanadium content produce bands of higher intensity (with the exception of the 880 cm^{-1} band).

A small coverage of the MgF_2 surface with vanadium ions results in the creation of $(V{=}O)^{3+}$ species bound to fluoride ions [1]. Analysis of the IR spectra of the oxovanadate complexes VOL_5 [6] has shown that the band near 960 cm^{-1} can be assigned to stretching vibrations of the V=O bond in the environment of the fluoride ions. In addition, there are isolated vanadate complexes (band at 880 cm^{-1}) present in the MFV_2 preparation (spectrum 4, fig. 1) which polymerize gradually in chains or islands of monolayers with IR bands assigned at 817, 851 and 1010 cm^{-1}. The polyvanadate complexes could only be identified in the P-series preparations. On the other hand, formation of VO_5 species prevailed on the impregnated catalysts.

Figs. 2 and 3 present the results of the IR study in the range 4000–1400 cm^{-1} of the impregnated preparations. On the surface of pure MgF_2, evacuated at the temperature 673 K, three kinds of OH groups can occur, to which are assigned the bands at 3400, 3615 and 3770 cm^{-1} respectively (see spectrum 1 in fig. 2A), each with a different geometrical configuration and a different electric charge

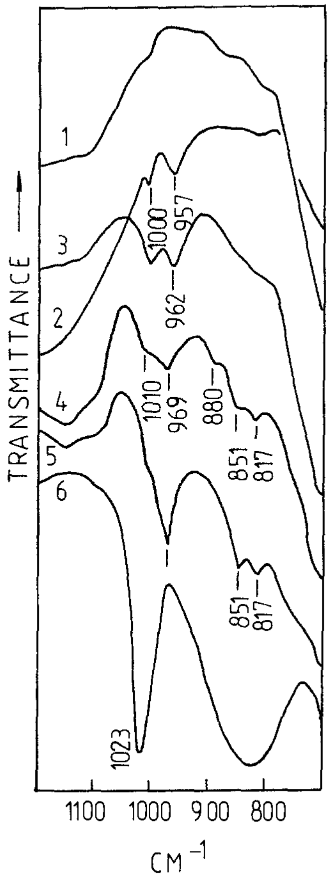

Fig. 1. IR spectra of I-MFV preparations: (2) $MFV_{0.7}$; (3) $MFV_{1.5}$; P-MFV preparations: (4) MFV_2; (5) MFV_5 and (1) MgF_2; (6) V_2O_5.

[7]. By contrast, the hydroxyls occurring on the surface of the room temperature evacuated MgF_2 yield spectrum 2 of fig. 2A. Introduction of the ammonium vanadate onto the surface of magnesium fluoride, followed by evacuation at room temperature, does not modify the OH groups present on MgF_2: only the intensities of the IR bands at 3230, 3516 and 3591 cm^{-1} increase relative to those at 3400 cm^{-1} (spectrum 3, fig. 2A). This result is in accord with our previous data obtained with the XPS method [1], supporting the conclusion that OH groups are linked to surface Mg^{2+} ions of the magnesium fluoride surface which remains uncovered by the vanadate species.

Exposing the samples to pyridine vapour at room temperature does not effect substantial modifications in the surface structure of the hydroxyl coating on $MFV_{0.7}$ (spectrum 4, fig. 2A); following the evacuation at temperature 523 K, only those hydroxyl groups with IR bands at 3230, 3591 cm^{-1} are removed (spectrum 5). Two bands, at 1667 and 1636 cm^{-1}, originating from the adsorbed

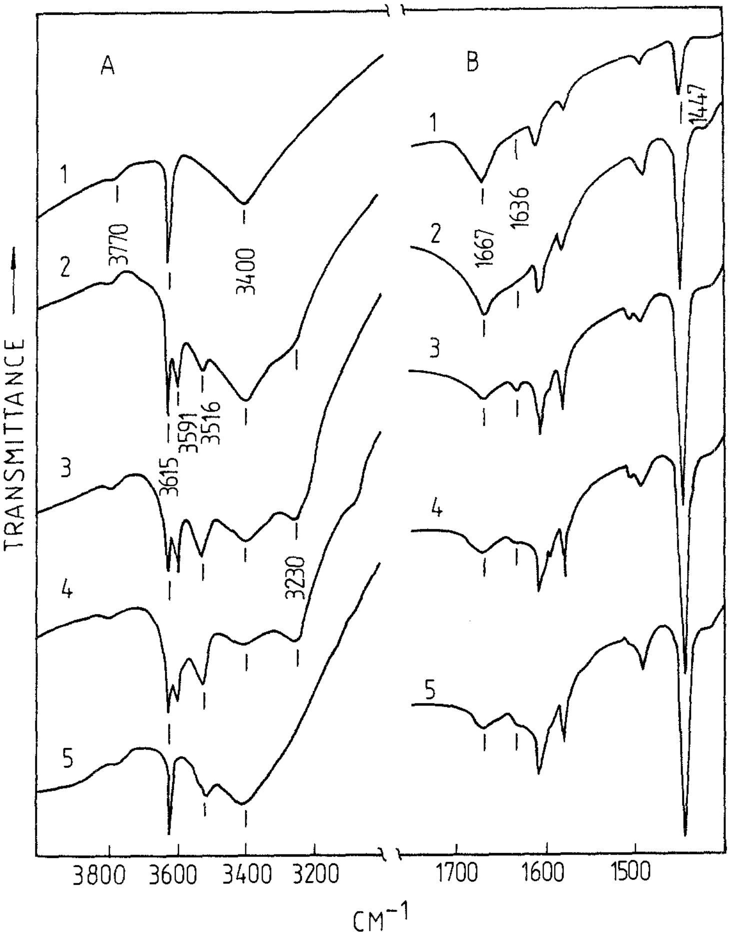

Fig. 2. (A) IR spectra of MgF_2: (1) 673 K; (2) 293 K; and I-$MFV_{0.7}$ before pyridine adsorption: (3) 293 K; after pyridine adsorption: (4) 293 K; (5) 523 K. (B) IR spectra of MgF_2 after pyridine adsorption: (1) 423 K; and I-$MFV_{0.7}$ (2) 293 K.; (3) 423 K; (4) 523 K; (5) 623 K.

molecular water, are also evident in the spectra collected in fig. 2B. They are assigned to hydrogen-bonded molecules and water molecules which are not linked by hydrogen bonds but interact with magnesium ions on the MgF_2 itself, respectively. Their intensity decreases as the temperature of the vacuum treatment of these preparations is increased. Introduction of pyridine vapours on the surface of the catalyst resulted in the appearing of bands which are indicative of the presence of acid sites on the surface. Namely, the band at 1447 cm^{-1} referred to pyridine coordinatively bound to Lewis acid centers [8]. The intensity of the 1447 cm^{-1} band of the $MFV_{0.7}$ preparation increased markedly compared with its intensity on pure MgF_2 (spectra 1–3, fig. 2B). Hence, the vanadium ions introduced onto the surface of the fluoride originated new Lewis-acid centers. In the temperature range from 423 to 623 K the pyridine yields the IR band of

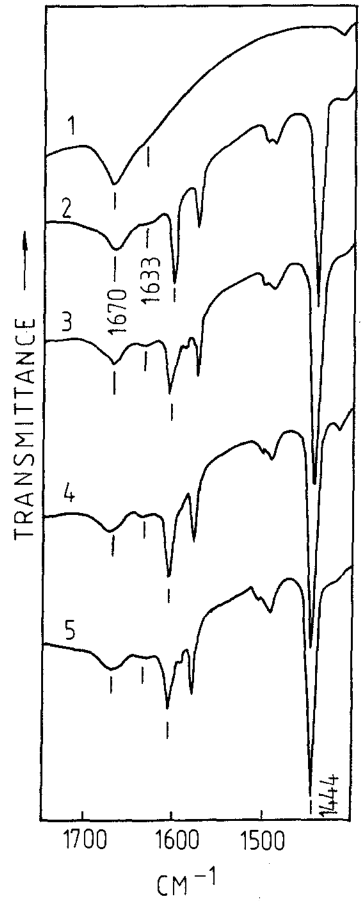

Fig. 3. IR spectra of I-$MFV_{1.5}$ before pyridine adsorption: (1) 293 K. After pyridine adsorption: (2) 293 K; (3) 423 K; (4) 523 K; (5) 623 K.

unchanged intensity at 1447 cm^{-1} (spectra 3–5). Evidently, the energy required for the pyridine removal remains constant in this temperature range, indicating the existence of relatively strong acid centers on the surface of the preparation. IR results obtained for the preparation $MFV_{1.5}$ (fig. 3) have confirmed the presence of this kind of Lewis acid centers on the impregnated catalysts. (The spectra in the range from 4000 to 3000 cm^{-1} of the preparations $MFV_{0.7}$ and $MFV_{1.5}$ as well as MFV_2 and MFV_5 are very similar, hence only the representative examples are published here.)

Figs. 4 and 5 present the results of the investigations of the precipitation–deposition preparations. Introduction of ammonium vanadate effects a new, distinct band at 3790 cm^{-1} (spectrum 1, in fig. 4A) and causes the increase of the intensity of the adsorbed molecular water bands at 1667 and 1636 cm^{-1} as compared to those of MgF_2 (spectra 1, figs. 4B and 2B). The latter is due to the increase in the surface area of the MFV_5 preparation. The new band at 3790

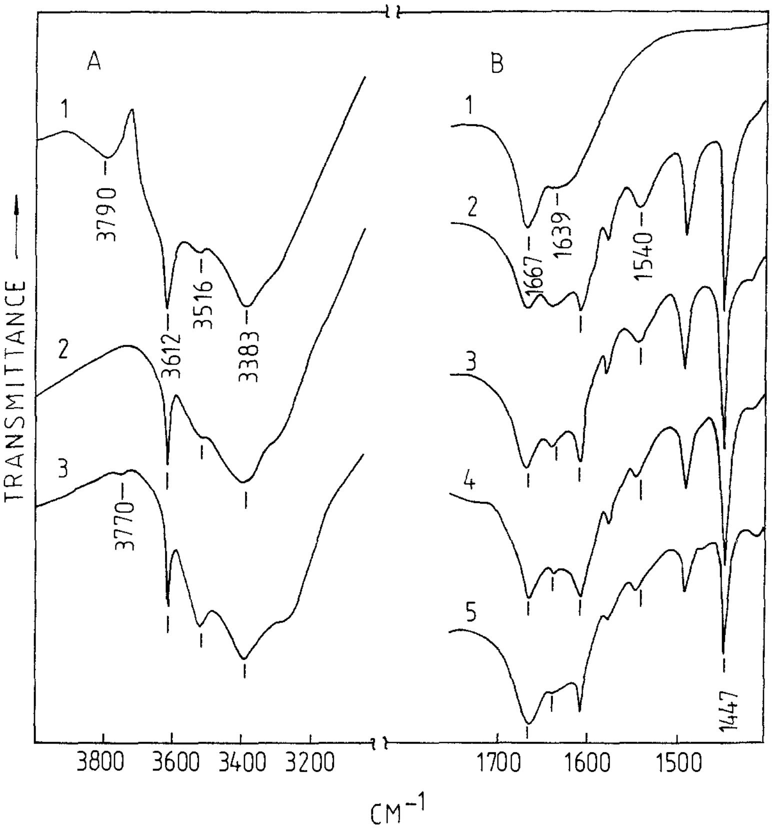

Fig. 4. IR spectra of P-MFV$_5$ before pyridine adsorption: (A) and (B) – (1) 293 K. After pyridine adsorption: (A) and (B) – (2) 293 K; (3) 423 K and (B) – (4) 523 K; (5) 623 K.

cm^{-1} has to be attributed to the vanadium species created on the catalyst surface. Exposure of the catalyst to pyridine brought about the 1540 cm^{-1} band associated with the pyridinium ion resulting from the interaction of Brønsted acid sites on the surface of the preparation with pyridine molecules [8]. The disappearance of the band at 3790 cm^{-1} during the interaction of the sample with pyridine evidenced that the hydroxyls responsible for this band had an acidic character (spectrum 2, figs. 4B and 5). At the same time, bands at 1447 cm^{-1} indicating the occurrence of Lewis-acid centers have been detected. Their intensity could be lowered by increasing the temperature of pyridine desorption (spectra 2–5 in fig. 4B and spectra 2–4 in fig. 5): depending on their strength, the acid centers are gradually removed. In conclusion, the preparations obtained by precipitation exhibited both Lewis and Brønsted acid centers. The centers varied in strength, thus differing from the properties of the impregnated catalysts, where one observes only relatively strong Lewis acid sites.

The variation of the number of acid sites per surface area unit of the catalyst as a function of the temperature of pyridine desorption of the P-series catalysts

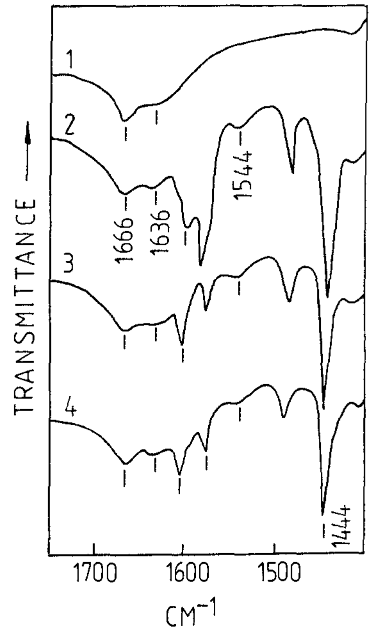

Fig. 5. IR spectra of P-MFV_2 before pyridine adsorption: (1) 293 K. After pyridine adsorption: (2) 293 K; (3) 423 K; (4) 523 K.

is shown in fig. 6. The Lewis and Brønsted acidity were both much higher for the MFV_5 preparation than for MFV_2; a fact which results from the higher concentration of vanadium in MFV_5. The highest number of acid centers was maintained on the surface of the samples exposed to pyridine at 293 K.

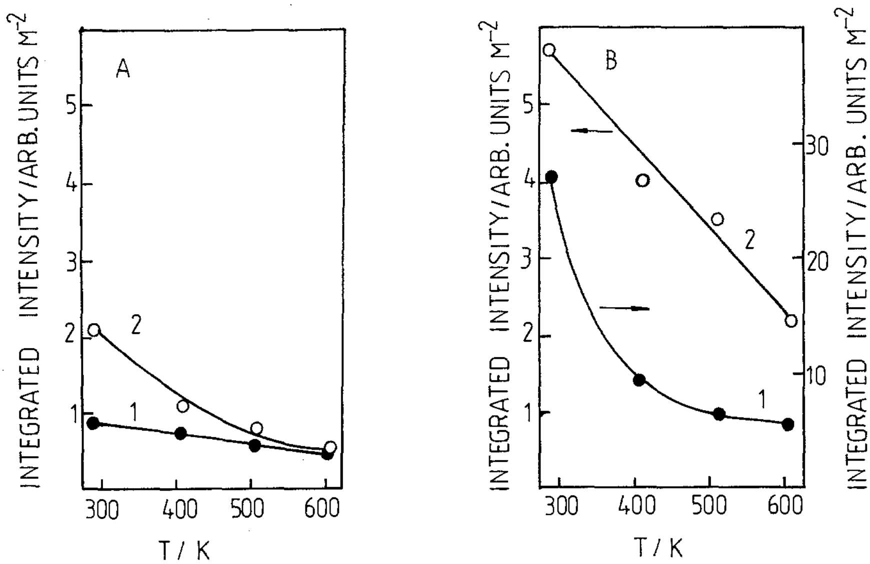

Fig. 6. Integrated intensity of BPy band (1540 cm^{-1}) (A) and LPy band (1445 cm^{-1}) (B) on P-MFV_2 (1) and P-MFV_5 (2).

With the results of IR spectroscopy (fig. 1) one can explain the presence of the protonic centers on V_2O_5/MgF_2 catalysts as originating from hydroxyl groups linked to chains of $(VO_3)_n$ tetrahedra of metavanadate type (bands at 817, 851 and 1010 cm^{-1}) similar to those appearing in, for example, potassium or ammonium metavanadates [9], or chains of distorted VO_5 trigonal bipiramids known from the structure of calcium or strontium metavanadate [10]. These structures can be thought of as resulting from polymerization of isolated VO_4 tetrahedra. At higher vanadium concentration, the hydroxyls bound to the polyvanadate species of the octahedrally coordinated vanadium will be responsible for the Brønsted acidity. In a similar way, the protonic acidity of V_2O_5/TiO_2 has previously been related to the vanadia on V–Ti oxide [11,12]. On the other hand, Lewis acidity may originate from the coordinatively unsaturated vanadium or magnesium ions. Such ions can form after removal of the OH groups from the vanadium species located on MgF_2. These ions, mainly vanadium with not completed coordination sphere, constitute the acceptor sites. But, the Lewis acid centers present on the MgF_2 surface could also contribute to the Lewis acidity. The strength of these centers may be affected as the result of a shift of the electron density towards vanadium, i.e. the acidity of the adjacent magnesium ions with unsaturated coordination sphere can increase.

On the basis of the published data, V_2O_5 alone exhibits both weak Brønsted centers and somewhat stronger Lewis centers [13], whereas MgF_2 has very weak aprotonic centers only [7]. On the other hand, V_2O_5/MgF_2 preparations obtained by precipitation exhibited Lewis acid centers of varying strength as well as quite strong protonic centers, capable of forming the pyridinium ion. Hence, the newly created binary system V_2O_5/MgF_2 covered with polyvanadate species, acquires acidic properties which are not the sum of the acidities of its components but are formed in the process of interaction between the vanadium species and the support.

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