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Study on surface chemistry of porous NiF_2–MgF_2 system

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Abstract

Nickel carbonate and magnesium carbonate were used as precursors of NiF_2–MgF_2 samples of various percentage compositions. The preparations obtained were examined using X-ray spectroscopy, IR spectroscopy and catalytic tests. It was shown that NiF_2 and MgF_2 formed a common crystal lattice of the rutile type. New Lewis acid centres appeared on the surface of the NiF_2–MgF_2 system which originated from the coordinatively unsaturated Ni^{2+} ions. In addition, an increased number of redox or basic centres arising from the O^-, F^- or OH^- groups on the surface of the studied preparations was also detected. The low catalytic activity of the NiF_2–MgF_2 samples indicated the possibility of using this system as a support rather than a catalyst.

Keywords: IR spectroscopy; Surface chemistry; Nickel fluoride; Magnesium fluoride; Catalysis; 2-Propanol

1. Introduction

Most studies on heterogeneous catalysts have concentrated on oxides and metals. Much less attention has been paid to systems containing fluorine. Most of the works concerning fluorine heterogeneous catalyst have been devoted to fluorinated alumina and aluminium fluoride [1]. The properties of magnesium fluoride were also studied [2,3] and MgF_2 was shown to have a high thermal stability and hardness. These properties are necessary for catalytic processes requiring regeneration of the catalysts by combustion of the coke deposited on the surface. The surface of magnesium fluoride appeared to be inert. Hence, MgF_2 was applied as a catalytic support, first for inorganic acids [4–6] and then for various transition metal oxides such as MoO_3 [7–9], V_2O_5 [10–14], WO_3 [15–18], CuO [19,20] and Cr_2O_3 [21]. These catalysts proved to be very interesting systems, active in many acidic and redox reactions.

The properties of the active phase introduced on to a support depend on many factors. Among others, the type of support used and the active phase–support interaction are important. The aim of the present work was to prepare and study a new support composed of two fluoride compounds: MgF_2 and NiF_2. Both fluorides crystallize in the same structure (rutile-type), have a similar size of elementary cell and are stable in high temperatures. In this paper the effect of introducing nickel fluoride into magnesium fluoride on the structure and catalytic properties of the NiF_2–MgF_2 system is reported.

2. Experimental details

2.1. Preparation of NiF_2–MgF_2

The MgF_2–NiF_2 system was prepared by adding small portions of a $NiCO_3$ and $MgCO_3 \cdot 3H_2O$ mixture to a 20% aqueous solution of hydrofluoric acid until neutralization was achieved. Subsequently, the solution was acidified by the introduction of a few additional drops of acid. The composition of the MgF_2–NiF_2 mixture was chosen to obtain systems containing 5, 15, 25, 50, 75, 100 mol% NiF_2. The solution was then evaporated and the samples dried at 378 K for 24 h followed by annealing at 773 K for 5 h. The support obtained was ground and the fraction of 0.25–0.50 mm grain size collected. Samples are denoted by the symbols MNF_x, where x is the mol% NiF_2 in the system. The characteristics of the various preparations are presented in Table 1.

2.2. Surface area determination

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 instrument.

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Table 1
Characteristics of MgF_2–NiF_2 samples [a]

	Sample						
	MgF_2	MnF_5	MNF_{15}	MNF_{25}	MNF_{50}	MNF_{75}	NiF_2
Surface area ($m^2\,g^{-1}$)	31	30	35	41	33	29	26
NiF_2 content (mol%)	0	5	15	25	50	75	100

[a] For sample designation, see text.

2.3. X-Ray study

X-Ray examination was carried out with a M-62 diffractometer in conjunction with a HZG-3 powder goniometer employing Cu Kα radiation.

2.4. Infrared spectra

The IR spectra were taken using a Bruker IFS 113V spectrometer in the range 650–1100 cm^{-1} and in the OH group vibrations range employing the stretching and deformation frequencies of adsorbed pyridine. For examination within the range of free lattice vibrations, samples were prepared by pelleting the catalysts with KBr. The spectra in the 1300–1800 and 3000–4000 cm^{-1} ranges were studied with samples prepared as self-supporting thin wafers placed in a vacuum cell equipped with NaCl windows. The wafers were oxidized in oxygen at 673 K for 4 h, then outgassed under a pressure of 10^{-3} Pa at room temperature and their IR spectra recorded. Pyridine was then introduced into the cell at 473 K and the cell was then outgassed for 5 min at this temperature, cooled to room temperature and the IR spectrum of the adsorbed pyridine recorded.

2.5. Catalytic tests

The catalytic properties of the samples were determined by the pulse microreactor technique using the reaction of 2-propanol. The conditions for catalytic measurements were as follows: reaction temperature, 523 K; catalyst weight, 0.01 g; volume pulse size of 2-propanol, 0.1 μl; carrier gas, helium; flow rate, 30 $cm^3\,min^{-1}$; GC column length and filament, 1 m, Emulphor 0; GC column temperature, 338 K.

3. Results and discussion

The characteristics of the MgF_2–NiF_2 system of various percentage compositions are presented in Table 1. The data show that introduction of 25 mol% NiF_2 into MgF_2 causes a certain increase in the surface area of the system. However, the introduction of larger amounts of NiF_2 led to a decrease in the surface area. The reason for the enlargement in the surface area could be a 'fluffing' effect generated by the evolution of water vapour during thermal treatment. Since, in contrast to magnesium fluoride, nickel fluoride is soluble to a certain extent in water, it can be expected that NiF_2 will retain water molecules which will then be eliminated in the activation process. Thus, a larger surface area is observed in the case of MNF preparations of lower NiF_2 content (< 50 mol%), while a higher NiF_2 content in the support results in a decrease in the surface area (the surface area of pure NiF_2 is lower than that of pure MgF_2).

Fig. 1 depicts the results of the X-ray examinations of the MgF_2–NiF_2 system relative to the amounts of MgF_2 and NiF_2 present. X-Ray analysis in the small angle range did not permit determination of the structure of MgF_2–NiF_2 system, since both NiF_2 and MgF_2 have the same rutile-type structure and elementary cells of similar sizes. This is why peaks characteristic of MgF_2 and NiF_2 were present at nearly the same 2Θ angle value. Differences in the peak positions can be seen only for high values of 2Θ (> 30°). In this range a distinct shift of peaks was observed in the diffractograms for the MNF_{50} preparation relative to those of NiF_2 and MgF_2 (Fig. 1). These shifts indicate that a 'new phase' has been formed in the preparation obtained, i.e. MgF_2 and NiF_2 have formed a common crystal lattice, at least in part.

The IR results in the 400–1200 cm^{-1} range (Fig. 2) confirm that small changes have occurred in the structure of the MgF_2–NiF_2 system relative to the initial fluorides. Apart from the bands characteristic of NiF_2 (1048, ~820 cm^{-1}) and MgF_2 (455 cm^{-1}), a shift of the characteristic band for magnesium fluoride towards higher frequencies was observed (e.g. for the MNF_{75} preparation the band was at 470 cm^{-1}). The greater the amount of NiF_2 introduced into MgF_2, the greater the shift of the bands.

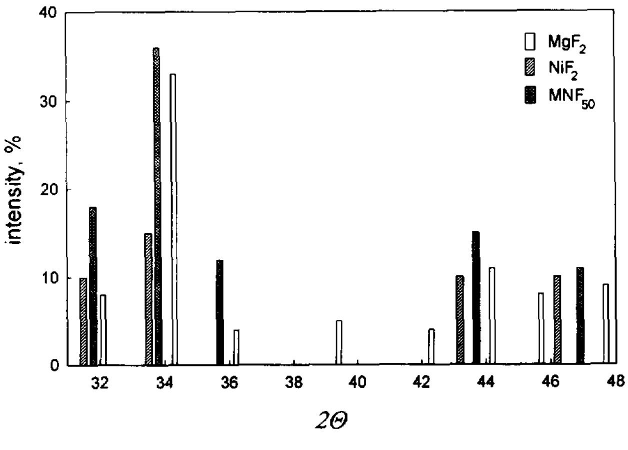

Fig. 1. Diffractograms for the MgF_2, NiF_2 and MNF_{50} preparations.

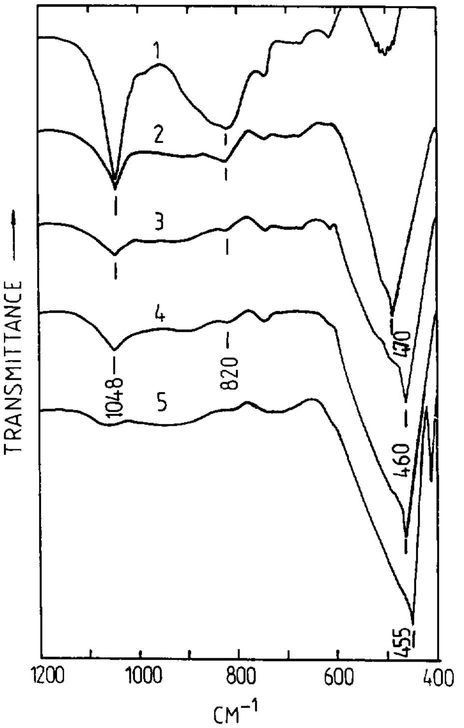

Fig. 2. IR spectra of the following preparations: (1) NiF_2; (2) MNF_{75}; (3) MNF_{50}; (4) MNF_{25}; (5) MgF_2.

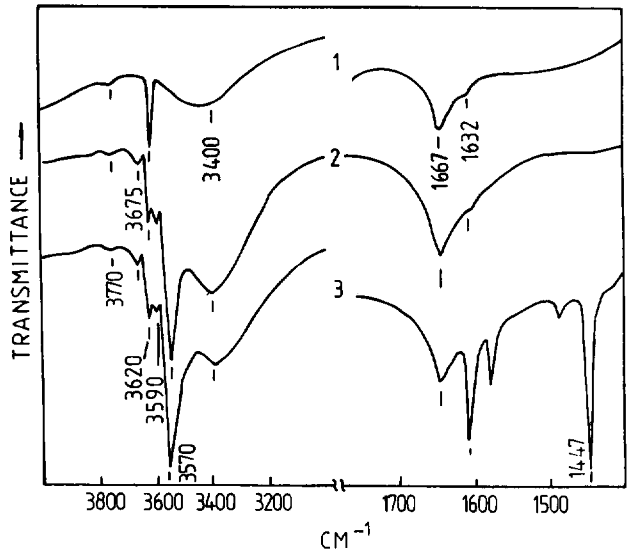

Fig. 3. IR spectra of (1) MgF_2 and (2) MNF_{50} before pyridine adsorption and (3) MNF_{50} after pyridine adsorption.

The IR studies in the 1400–4000 cm^{-1} range for the MgF_2–NiF_2 preparations allowed changes in the hydroxyl group vibrations relative to magnesium fluoride to be observed. Thus, apart from the bands recorded for MgF_2 (~ 3400, 3620 and 3770 cm^{-1}), a series of new bands was seen to appear: 3570, 3590 and 3675 cm^{-1} (Fig. 3). It is to be expected that these bands originate from the OH groups coordinated with the nickel ions. Also, bands related to the presence of molecular water were recorded: 1667, 1632 cm^{-1}. The introduction of pyridine vapours brought about the appearance of a band at 1447 cm^{-1}, indicating the formation of new Lewis acid centres on the surface of the support. The source of such centres could be unsaturated nickel or magnesium ions. The band at 1447 cm^{-1} was considerably more intense for MgF_2–NiF_2 preparations than for magnesium fluoride, indicating that the aprotic centres are mainly derived from coordinatively unsaturated nickel ions.

Catalytic tests were also performed to determine the character of the MgF_2–NiF_2 surface. Thus, the activity of prepared catalysts towards 2-propanol decomposition was studied. The elimination reaction of 2-propanol can proceed in two directions: dehydrogenation and dehydration:

$$C_3H_7OH \begin{array}{l} \nearrow C_3H_6 + H_2O \\ \searrow C_3H_6O + H_2 \end{array}$$

Dehydration occurs in the presence of acid centres, while dehydrogenation needs the presence of strong basic or redox centres on the surface of the catalyst [11]. Magnesium fluoride is inactive in this reaction; however, the introduction of NiF_2 into the system caused a linear increase of the activity towards acetone formation with increasing NiF_2 content (Fig. 4). Some activity was also observed towards propene (~ 1%). Thus, apart from the weak acid centres, basic or redox sites are also present on the surface of MgF_2–NiF_2 and are responsible for the dehydrogenation reaction. Such basic or redox sites may be fluoride or oxidic anions present as surface lattice defects and surface OH groups. The acid centres could be coordinatively unsaturated metal cations.

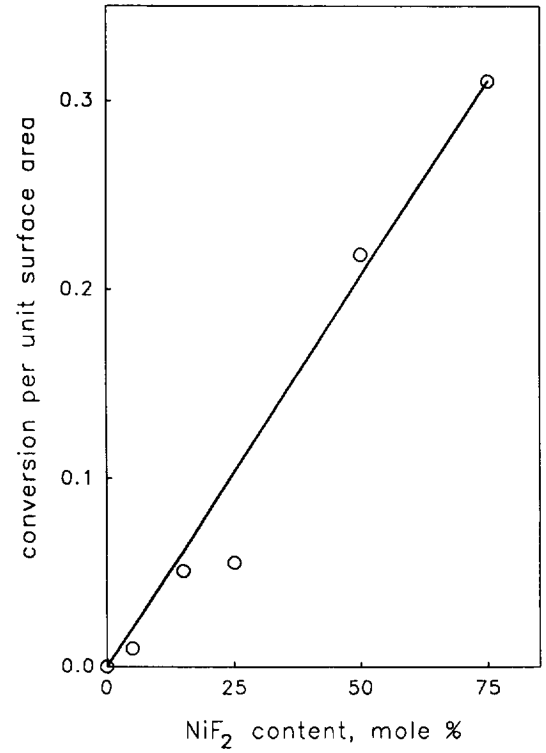

Fig. 4. Catalytic activity of MgF_2–NiF_2 preparations relative to acetone formation in the decomposition of 2-propanol as a function of the NiF_2 content.

Summing up, one can say that the introduction of NiF_2 into MgF_2 causes certain changes in the structure of magnesium fluoride. A consequence of these changes is the appearance of both new hydroxyls and Lewis acid centres. The presence of a small amount of redox or basic centres was also detected.

On the basis of the above results and the structural data for pure MgF_2 [7], we made an attempt to determine the surface structure of the NiF_2–MgF_2 system. Magnesium fluoride crystallizes in the rutile-type structure, where each Mg^{2+} ion is surrounded by six F^- ions and each fluorine ion is surrounded by three Mg^{2+} ions. The cation is in a deformed octahedral environment: two fluoride ions are located at a greater distance than the other four, i.e. 4(Mg–F), 1.94 Å; 2(Mg–F), 1.99 Å. A similar situation occurs in the case of nickel fluoride. It also has the rutile-type structure and its elementary cell size is close to that of MgF_2 (NiF_2: $a=b=4.65$ Å, $c=3.08$ Å; MgF_2: $a=b=4.64$ Å, $c=3.06$ Å).

One can assume that the most frequently appearing lattice planes in MgF_2 as well as in NiF_2–MgF_2 are close-packed ones occupied by both Mg^{2+} or Ni^{2+} and F^- ions, namely the (110) and (001) planes. The coordination shell of each Mg^{2+} or Ni^{2+} ions located in the (110) plane has one or two fluorine atoms missing (Mg^{2+} or Ni^{2+} ions with coordination number CN = 5 or 4, respectively), whereas in the (001) plane besides coordinatively unsaturated ions Mg_{cus} or Ni_{cus} (CN = 4), coordinatively saturated ions are also present. The electrical charges of such coordinatively unsaturated cations are not balanced by the surrounding negative ions and amount to +2/3 for Mg^{2+} or Ni^{2+} ions with CN = 4 to +1/3 for Mg^{2+} or Ni^{2+} ions with CN = 5 [7].

During the preparation of the NiF_2–MgF_2 system, the coordination shell of the surface unsaturated cations fills with H_2O molecules, resulting in the formation of surface hydroxyl groups during the process of calcination. The IR study revealed the presence of six bands in the spectra of the NiF_2–MgF_2 system which could be attributed to various hydroxyl groups. Three of these, i.e. the bands at 3400, 3620 and 3770 cm^{-1}, originate from the OH groups bonded to the Mg^{2+} ions [7]. The other three bands which appear directly adjacent to the former, i.e. at 3570, 3590 and 3675 cm^{-1}, respectively, were ascribed to OH groups bonded with Ni^{2+} ions. Thus, the spectra may be accounted for by assuming that all these bands originate from three kinds of hydroxyl groups:

Type I: OH group located directly over the Mg^{2+} or Ni^{2+} (M^{2+}) ion with CN = 5. The M^{2+}–OH bond is perpendicular to the lattice plane.

Type II: OH group located between two M^{2+} ions with CN = 4 (two fluorine ions are missing from the coordination shell of each).

Type III: OH group located directly over M^{2+} ion with CN = 4. The M^{2+}–OH bond is perpendicular to the lattice plane.

A perspective view of the surface of the NiF_2–MgF_2 system with OH groups located in these positions is shown in Fig. 5 for the (110) plane and in Fig. 6 for the (001) plane.

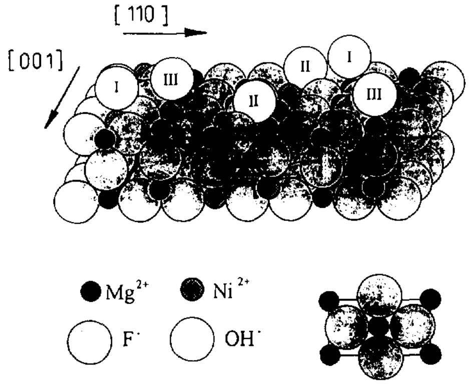

Fig. 5. The (110) crystal plane of the NiF_2–MgF_2 system with located OH groups.

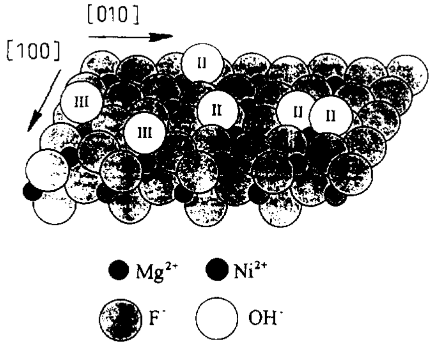

Fig. 6. The (001) crystal plane of the NiF_2–MgF_2 system with located OH groups.

The OH groups depicted differ from each other in terms of their electrical charge as well as their geometrical configurations. The charges on the OH groups were calculated on the basis of the simple ionic model, i.e. as the sum of the negative charges of the anion and the sum of the strength of the electrostatic bonds (which is equal to the cation charge divided by CN) between the anion and neighbouring cations [28]. Their values are as follows: −2/3 for type I, −1/5 for type II and −3/5 for type III. As a result, the OH groups also show different properties. Thus, from Kuözinger and Ratuasamy [28], we know that the Brønsted acidity of the OH groups decreases and their basicity increase as their charges become more negative. Thus, all three above-mentioned hydroxyl groups have a basic character.

4. Conclusions

1. Nickel fluoride and magnesium fluoride form a common crystal lattice.
2. A number of new OH groups relative to MgF_2 was found to be present on the surface of the NiF_2–MgF_2 system.
3. The introduction of nickel fluoride on to MgF_2 led to the appearance of new Lewis acid sites as well as new basic or redox centres on the surface of the NiF_2–MgF_2 system.

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