SURFACE CHEMISTRY OF POROUS MAGNESIUM FLUORIDE

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SUMMARY

Porous preparations of magnesium fluoride were obtained from magnesium sulphate and magnesium carbonate and their surface properties have been studied. It has been shown that pure magnesium fluoride has a weak surface acidity of the Lewis type and no protonic sites stronger than $H_R \leq 0.82$. Base properties of MgF₂ surfaces are more pronounced than acid ones, but the base strength is low. Surfaces of MgF₂ also bear oxidizing and reducing centres capable of forming ion radicals with adsorbed perylene and tetracyanoethylene. The low catalytic activity of magnesium fluoride for acid catalysed reactions suggests the application of MgF₂ as a catalyst support rather than as a catalyst.

INTRODUCTION

Most studies in heterogeneous catalysis are devoted to oxide and metallic catalysts. Recently, however, a significant amount of work on metal fluorides and fluorinated metal oxide catalysts has been reported. Particular emphasis has been given to fluorinated surfaces of alumina. This is the subject of a large review (243 references) by Choudhary [1]. Different combinations and modifications of AlF₃ and Al₂O₃ have been patented for acidcatalysed reactions. The β -AlF₃/Al₂O₃ is especially active [2].

Contrary to aluminum fluoride-containing catalysts, surface properties of magnesium fluoride and catalysts where MgF_2 is used as a support or a promoter are a subject of only a small

number of papers [3-13]. The lack of interest in magnesium fluoride as a support or as a catalyst seems to be unjustified since MgF, has good thermal stability, relatively high hardness and resistance to calcination in oxygen. These properties are necessary for catalytic processes requiring regeneration of the catalyst by compustion of the coke deposited on the surface. The fact that alkaline earth metal fluorides with well-developed pore structures, i.e. with high surface areas, are not as easy to obtain as oxide catalysts, explains to some extent why only a small number of studies were devoted to their surface properties. We have found in our earlier studies [13] that the preparation of porous MgF_{2} with surface area about 100 m²/g, stable at high temperatures (essential for catalytic applications) is possible. However, all the magnesium fluoride preparations studied by us previously were obtained from magnesium sulphate and hydrofluoric acid as starting materials. Sometime additional substances were introduced as stabilizers and modifiers of surface properties. We have proved that magnesium fluoride is active for acid-catalysed reactions, but we suspected that the surface acidity of MgF2, which is a decisive factor for its activity for the above reactions, originates from the presence in the pores of this catalyst of unwashed sulphuric acid [12]. (Sulphuric acid is a reaction product of the preparation of magnesium fluoride).

The present study is aimed at comparing the properties of a MgF_2 catalyst obtained from the starting compounds mentioned above (designated as S) and that prepared by action of hydrofluoric acid on magnesium carbonate (designated as C). In the latter case no acid molecules remain on the surface after the preparation procedure (including washing, drying and calcinating of the MgF_2) is completed. Therefore, information concerning the surface chemistry of pure MgF_2 can be obtained.

RESULTS AND DISCUSSION

The MgF₂ preparations S and C have quite similar surface areas (46 and 39 m²/g, respectively), therefore one can suppose that their microporous structure is also similar. In spite of this similarity in physical nature of their surfaces, the chemical properties of these surface are different as shown in Table 1. High-temperature adsorption of pyridine, which is a measure of surface acidity, appeared to be several times higher on 'sulphate' preparation S than on 'carbonate' preparation C (see Table 1) Also the acid strength of the surface of preparation $C(H_0=3.3)$ is considerably lower than that of the 'sulphate' preparation $(H_0=1.5)$. Detection of the above acid sites was only possible

TABLE 1

Acid-base and redox properties of magnesium fluoride surface

Property	Preparation	Preparation	
	S	C	
Amount of pyridine adsorbed		······································	
in meq/g	0.066	0,012	
in µeq/m ²	1.43	0.31	
Amount of acetic acid adsorbed			
in meq/g	0.229	0.227	
in µeq/m ²	4.98	5.82	
Acid strength, H	1.5	3.3	
Base strength, H_	9.3	9.3	
Concentration of Pet (a)			
spins/g	1.2×10^{16}	0.4×10^{16}	
spins/m ²	2.6×10^{14}	1.0×10^{14}	
Concentration of TCNE (b)	16	10	
spins/g	0.6×10^{10}	0.7×10^{10}	
spins/m ²	1.3×10^{14}	1.8×10^{14}	

(a) Pe⁺ - perylenium cation radicals

(b) TCNE - tetracyanoethylene anion radicals

after thermo-vacuum pretreatment of the MgF_2 samples prior to acid strength estimation by an indicator technique. Such a pretreatment removes chemisorbed water which is a poison both for acidic and basic centres of higher strength. Determinations carried out by the conventional indicator technique (without thermovacuum pretreatment) gave significantly lower acid strength values (H_0 =4.6 in both cases) .The results indicate that magnesium fluoride itself (*i.e.* free of surface modifying admixtures) possesses some surface acidity which most likely originates from coordinatively unsaturated (c.u.s.) magnesium ions forming pair centres as well as single defects on the surface. Such a conception of c.u.s. ions has also been applied in the case of magnesia [14], chromia [15], alumina [16] and titania [17]. In the case of the 'sulphate' preparation, even after thorough washing, the possibility cannot be ruled out that the acidic properties observed are, to some extent, due to small amounts of sulphuric acid which at the temperature of calcination of MgF_2 samples partially decomposes to SO_3 . This SO_3 is stabilized in the form of a surface complex with the basic centres of MgF_2 [13]. However, this cannot be the case for the 'carbonate' preparation.

The base properties of both preparations under study are not significantly different. In terms of the c.u.s. concept of acid and base centre formation, they should be ascribed to coordinatively unsaturated anions. The amounts of acetic acid adsorbed per 1 g of the catalyst are approximately equal for preparations S and C. whereas the density of population of the sites (adsorption per unit area) capable of adsorbing acetic acid is higher for the 'carbonate' preparation (Table 1). It is known that acetic acid can also be partially adsorbed on acid centres [17. 18]. In spite of this fact, one can conclude that the 'carbonate' preparation has a larger concentration of basic sites since its acetic acid adsorption capacity is higher whereas its concentration of acid sites is lower. The maximum base strength is the same for both catalyst preparations; $H_{=} 9.3$ for samples subjected to thermo-vacuum pretreatment and H = 7.15 for samples without such pretreatment.

ESR studies on MgF_2 preparations with adsorbed perylene and tetracyancethylene have shown that surfaces of both preparations possess redox properties. The 'sulphate' preparation has a higher capability for perylene oxidation (converting this hydrocarbon into the perylenium cation radical). The reducing properties of surfaces of both preparations, as shown by the conversion of tetracyanoethylene into a corresponding anion radical, are similar (slightly higher electron-donating ability for the 'carbonate' sample). The parallel between the redox and acid-base properties of the investigated MgF₂ preparations suggests that in the case of magnesium fluoride the oxidizing sites exhibit Lewis acid character and the reducing sites act as basic centres. This is analogous to the observations of Ghorbel *et al.* [19] on alumina. Both preparations appeared to be inactive for the skeletal isomerization of cyclohexene to methylcyclopentenes, which requires strong acid centres. This result is in agreement with indicator tests (Table 1) which have proved the absence of strong acid sites on the MgF_2 surfaces.

TABLE 2

Catalytic activity of 'sulphate' preparation of magnesium fluoride for different acid-catalysed reactions.

	Temperature	
Reaction	320 ⁰ C	370°C
Dehydration of 2-propanol, kK, mol g ⁻¹ s ⁻¹ atm ⁻¹	0.19×10^{-3}	0.86×10^{-3}
KK, MOI M S AUM	0.41 x 10	
Skeletal isomerization of	• • • • • • • • • •	
cyclohexene	inactive	inactive
Isomerization of 1-butene, mol %	11.4	<u>+</u>
Ratio of cis 2-butene/trans 2-butene	1.15	N.I.
Cracking of cumene	inactive	inactive

* N.I. - not investigated at 370°C but a measurement has been carried out at 200°C in addition to that at 320°C. Catalytic activity for double bond isomerization of butene appeared to be zero at 200°C.

Activity for butene double bond isomerization was observed only in the case of 'sulphate' preparation. This reaction is known to occur both on moderate strength acid centres (carbonium ion mechanism) and on base centres (carbanion mechanism). In the former case the cis/trans ratio is generally 1-2 [20], while in the case when the reaction proceeds through a π -allyl carbanion the ratio is much higher. Data shown in Table 2 suggest that MgF, surface behaves as a solid acid since the measured cis/trans ratio is low, i.e. the reaction goes via butyl carbonium ions. The rate of 2-butene formation, however, is not high. This leads to conclusion that the concentration of moderate strength acid centres necessary for this reaction is low. There are no centres of sufficient strength to catalyse this reaction on the surface of the 'carbonate' preparation. This fact is also in agreement with indicator observations (Table 1). Both preparations are inactive for cumene cracking which requires the presence of Broensted acid centres. Tests with arylmethanol indicators (not reported in Table 1), which are selective for Broensted acid sites [21] , have shown the absence of coloured carbonium ion in the case of all arylcarbinols used (see Experimental). This result proves the lack of Broensted acid centres with the strength $H_{\rm R} \leq 0.82$, i.e. corresponding to $pK_{\rm R}$ + of 4. 4', 4" - trimethoxytriphenylmethanol which is capable of reacting even with weak protonic sites. Thus again the results of catalytic measurements and the indicator tests for the presence of a given type of acid centres are in good agreement.

On the other hand, both preparations possess weak Lewis acid sites, as shown by results of the tests with p-dimethylaminoazobenzene ($pK_a = 3.3$). In the case of 'sulphate' preparation moderate strength centres capable of reacting with benzeneazodiphenylamine (pK = 1.5) are present. A model reaction catalysed even by very weak acid centres is the dehydration of isopropyl alcohol. Data presented in Table 2 indicate that preparation S is quite active for this reaction, whereas preparation C only yielded traces of propylene in the reaction product. Such a result is to some extent a surprise since active centres of strength sufficient to catalyse the alcohol dehydration are present on the surface of 'carbonate' preparation as shown in Table 1. However, the indicator test is only a qualitative measure and the appearance of red colour (acid form of p-dimethylaminoazobenzene, $pK_a = 3.3$) on the surface of preparation C indicates only the presence of acid centres with $H_{o} \leqslant 3.3$ but does not give information on their concentration. The amount of adsorbed pyridine also cannot give such information because pyridine is capable of chemisorbing even on acid centres weaker

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than those corresponding to $H_0 = 3.3$. Thus a juxtaposition of the result of indicator base for a diffuse acidity and the result of the catalytic test for activity in 2-propanol dehydration leads to the conclusion that acid sites with Hammett acid function value $H_0 \leq 3.3$ are present on the surface of "carbonate" preparation of magnesium fluoride but their concentration is very low. It is worthwhile to mention that the only products of isopropanol decomposition on MgF₂ were propylene and water, thus this surface has no dehydrogenating centres capable of forming acetone.

We therefore have to conclude that MgF_2 possess some surface acidity. This is contrary to our earlier suggestion [12] which ascribed the surface acidity of MgF_2 to residual sulphuric acid. The higher acidity of preparation 5 may be due to some residual sulphuric acid but it may also be due to the different method of proparation.

Magnesium fluoride clearly possesses surface basicity, however its strength is not high ($H_{\perp} = 9.3$). This is probably the reason why the base centres of MgF₂ do not catalyse double bond isomerization of butenes. The surface of magnesium fluoride also has sites capable of oxidizing polynuclear hydrocarbons such as perylene and of reducing molecules with high electron affinity such as tetracyanoethylene. Concentrations (per unit surface area) of these redox centres on MgF₂ are one or two orders of magnitude lower than on zeolites, silica-alumina and alumina [22, 23].

On the grounds of the above surface properties, magnesium fluoride can be classified as a acid-base catalyst, however, the amount of the acid-base properties is low in the case of admixture-free MgF_2 . Therefore, catalytic applications of porous magnesium fluoride should be sought in its use a catalyst support rather than as a catalyst by itself.

EXPERIMENTAL

Preparation of catalysts

A 35% solution of hydrofluoric acid and magnesium sulphate solution saturated at 40° C were used for preparation of sample S At this temperature the acid was poured slowly into the MgSO₄

solution with vigorous stiring. The precipitate of magnesium fluoride was washed with distilled water until pH 5 was reached, then dried at 105 $^{\circ}$ C for 24 h and calcined at 400 $^{\circ}$ C for 5 h. Sulphur content in the calcinated sample amounted to 0.58 % and its surface area was 46 m²/g.

Sample C of magnesium fluoride was prepared by addition of small portions of $MgCO_3 \cdot 3H_2O$ powder to 17 % solution of hydro-fluoric acid until neutralization followed by acidification with a few drops of hydrofluoric acid. The precipitate was thoroughly washed and then dried and calcinated under the same conditions as sample S. The surface area of sample S was 39 m^2/g .

All reagents used for preparation of samples S and C were of A.R. grade.

Determination of surface area of porous magnesium fluoride

The surface areas were determined by measurement of low temperature (-195 $^{\circ}$ C) nitrogen adsorption, using sorptometer Gravimat, Sartorius (Göttingen, W.Germany).

Adsorption of pyridine and acetic acid

Magnesium fluoride samples were evacuated (10^{-5} Torr) at 350 °C for 3 h and then they were contacted with vapours of either pyridine or acetic acid at 200 °C for 1 h. Afterwards the samples were evacuated at temperature of 200 °C for 2 h. The amounts of chemisorbed C_5H_5N or CH_3COOH remaining on the surface after evacuation were determined using a Perkin-Elmer Elemental Analyzer Model 240.

Measurements of acid and base strength of surface centres

Magnesium fluoride samples were pretreated under vacuum (10^{-5} Torr) at 350 °C for 3 h in small glass ampoules connected to a vacuum line and then transferred to a dry-box where the glass seals were broken and benzene solutions of indicators were added to evaluate acid and base strength by the Walling technique [6]. All the H_o indicators (reacting with Broensted and Lewis acid sites) listed in a recent review by Benesi and

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Winquist [24] were used. Tests for the presence of Broensted acid sites were carried out with the H_R indicators: diphenylmethanol, triphenylmethanol and 4, 4', 4" -trimethoxytriphenylmethanol. Base strength was estimated using the same H_ indicators as applied in a study by Take *et al.*[25].

Determination of redox properties of MgF, surface

ESR studies on MgF_2 samples with chemisorbed perylene and tetracyanoethylene were carried out at room temperature using a Polish made spectrometer SE - 25/71 Å, at a clystron frequency of 9.6 GHz and a magnetic field modulation of 100 kHz. An ultramarine sample having a spin concentration of 1.1 x 10¹⁷ was used as a standard for estimating Pe⁺ and TCNE⁻ concentration. The samples for the ESR study were prepared as follows: the sample of magnesium fluoride was placed in a quartz tube and evacuated at 350 °C and 10⁻⁵ Torr for 3 h. The solution of 0.005 M perylene or of 0.1 M tetracyanoethylene in dry benzene, was introduced to the catalyst sample by breaking a thin glass seal. Both of these solutions were previously deaerated by several freeze-evacuate-thaw cycles. ESR spectra were recorded 75 h after the solution came into contact with the solid.

Catalytic tests

All measurements of catalytic activity were carried out by pulse techniques using a Perkin-Elmer Model 154 - 0502 Microreactor connected to a gas chromatograph for analysis of reaction products. The flow rate of helium carrier gas was 30 cm³/min and the amount of catalyst was 0.3 g. The tests were performed at 320 °C and 370° C in all cases with the exception of the butene isomerization where a measurement at 200 °C was made instead of that at 370 °C. The catalytic activity for 2-propanol dehydration was expressed in terms of the product kK of the Bassett-Habgood equation [26].

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