Mixed alumina chromia pillared layered α-zirconium phosphate materials: acidity and catalytic behaviour for isopropyl alcohol decomposition

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Abstract

The surface acidity and the catalytic behaviour of a series of mixed alumina chromia pillared α-zirconium phosphates have been studied. The acid properties of these catalysts have been evaluated by measurements of the NH_3 thermal programmed desorption, pyridine adsorption and dehydration of isopropyl alcohol at 220°C. Both surface acidity and catalytic activity show a marked dependence on the Al/Cr ratio, but they are not a monotonic function of the catalyst composition. The most acid materials were those with Al/Cr ratios between 20/80 and 40/60. From this ratio, the acidity is gradually reduced with increasing Al concentration. The activity of the mixed alumina chromia pillared materials for isopropyl alcohol decomposition is considerably enhanced with respect to the analogous chromia pillared compounds of the order of 20 times for maximum activity. The most active materials were those with the highest micropore volumes. All catalysts show selectivities higher than 99% for the dehydration of isopropyl alcohol.

1. Introduction

Since the pioneer works by Vaughan et al. [1] much effort has been spent towards the synthesis and applications of pillared layered compounds. In these materials, oxide nanostructures, originated by thermal transformation of interlayer oligomers, prop apart the layers creating a bidimensional pore framework with high surface area [2]. The early studies were almost exclusively focused on pillared clays which, although not appropriate for cracking of oil heavy fractions, have been used successfully as acid catalysts in many different reactions [3], as selective adsorbents [4] and ion exchangers [5]. Indeed, some pillared clays show activities and selectivities comparable to those of zeolites [6].

More recently, the preparation of porous materials by pillaring has been extended to include many others layered compounds [7]. Among these, α-layered M(IV) hydrogen phosphates of

general formula $M(IV)(HPO_4)_2H_2O$ with M = Zr, Ti, Sn, are interesting hosts because they are acid solids with high cation exchange capacity and chemical stability. For this reason, the layered phosphates are mainly used as acid catalysts [8], although, under certain conditions, they may also develop redox sites [9]. However, upon thermal treatment the layer structure collapses, so that only a few residual –OH groups and deficiently coordinated metal ions located on the surface are responsible for the catalytic properties.

On the other hand, permanent porosity can be induced in these phosphates by pillaring with different metal oxides, such as chromia, alumina and mixed alumina chromia [10–12]. The pillared phosphate materials have high surface areas and the active sites of the internal surface become accessible to adsorption. In other words, the catalytic activity may be considerably enhanced by this mechanism.

In a recent study on the reaction of decomposition of isopropyl alcohol, we have found that the incorporation of chromia pillars into α-ZrP and α-SnP substantially modifies the catalytic properties of such phosphates, by increasing extensively Brønsted and Lewis acidity. Studies carried out by Stone et al. [13] using oxide solid solutions, of α-$Cr_xAl_{2-x}O_3$, revealed that the incorporation of Cr(III) ions into the corundum phase α-Al_2O_3 introduces significant changes in activity and selectivity with respect to the pure oxides. For the reaction of isopropyl alcohol decomposition, they found that amounts of only 0.1% of Cr transform α-Al_2O_3 from a dehydrogenating to a dehydrating catalyst. Moreover, the activity was not a monotonic function of solute concentration. With these antecedents in mind, we have prepared a series of mixed alumina chromia pillared α-zirconium phosphate materials [12] in order to investigate their catalytic properties. In this paper, we report the acidity and the catalytic behaviour of mixed alumina chromia pillared α-zirconium phosphate materials for isopropyl alcohol decomposition.

2. Experimental

2.1. Materials

α-Zirconium phosphate (α-ZrP) was prepared by the sol–gel method [14] and the mixed alumina chromia pillared α-zirconium phosphate materials were prepared by intercalation of mixed oligomers into the colloidal phosphate and further calcination under nitrogen at 400°C as described elsewhere [12].

2.2. Catalyst characterization

The total acidity of the samples was determined by thermo programmed desorption of ammonia (NH_3-TPD). Before the adsorption of ammonia at 100°C, the samples were heated at 400°C in He flow. The NH_3-TPD was performed between 100°C and 400°C, at 10 K min^{-1}, and analysed by on line gas chromatography (Shimadzu GC-14A) provided with a thermal conductivity detector.

For the adsorption–desorption of pyridine, self supported wafers of the samples with weight-to-surface ratios of about 12 mg cm^{-2} were placed in a vacuum cell assembled with greaseless stopcocks and CaF_2 windows. Pretreatments were carried out with an in site furnace. The samples were evacuated (300°C, 10^{-4} Torr overnight), exposed to pyridine vapour at room temperature and then outgassed between R.T. and 400°C. The IR spectra were recorded at room temperature using a Perkin Elmer 883 apparatus.

2.3. Activity measurements

The catalysts were tested in a fixed-bed tubular glass reactor working at atmospheric pressure and with a catalyst charge of 25 mg without dilution. The isopropyl alcohol was fed into the reactor by bubbling a flow of Helium of 25 cm^3 min^{-1} through a saturator–condenser at 30°C, which allowed a constant isopropyl alcohol flow of 8.9 vol.-%. Prior to the catalytic

test, the samples were pretreated at different temperatures in a helium flow for 12 h. The reaction products were analysed by an on-line gas chromatograph provided with a FID and a fused silica capillary column SPB1. The helium carrier was passed through a molecular sieve before it was saturated with isopropyl alcohol. In some cases the reaction was carried out using a flow of synthetic air (25 cm^3 min^{-1}) saturated with isopropyl alcohol (8.9 vol.-%).

3. Results and discussion

The main characteristics of the studied catalysts are listed in Table 1. Accordingly, these materials can be classified in three groups: In group I, barely porous materials, with high Al/Cr ratios ($\geq$ 70/30) and low surface area and micropore volume, are included. In these compounds stuffed structures are formed as a consequence of the high concentration of aluminium on the external surface [12]. In group II are materials with intermediate Al/Cr ratios, 40/60–60/40. They are highly porous solids with very high contribution of micropores (> 0.15 cm^3 g^{-1}) and surface area > 400 m^2 g^{-1}. In these compounds, a very narrow pore size distribution is found in the upper limit range of micropores. Finally, the Group III corresponds to low Al/Cr ratios (< 30/70) mesoporous solids with a significant contribution of microp-
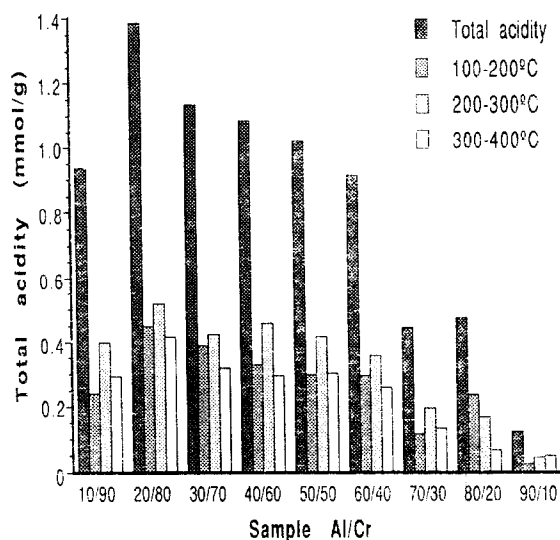

Fig. 1. Acidity of mixed alumina–chromia pillared α-zirconium phosphate materials from NH$_3$-TPD.

ores (> 0.1 cm^3 g^{-1}) and relatively high surface area (340–360 m^2 g^{-1}).

Fig. 1 shows the total and partial acidity for the different samples as measured by NH$_3$-TPD between 100–400°C. From an Al/Cr ratio 20/80 the number of acid sites decreases with increasing Al content, the acidity of the catalysts of Groups II and III is quite high, (> 0.8 mmol g^{-1}) and it is comparable with those of zeolites. While, for the catalysts of group I the acidity is below 0.5 mmol g^{-1}. This strong decreasing of acidity in materials of the group I is well correlated with the presence of high

Table 1
Chemical composition, interlayer distances (d_{001}) and textural parameters of mixed alumina chromia pillared α-zirconium phosphate catalysts

AlCr added	Metal ion taken up (meq/g)			d_{001} (Å)		S_L	V_{micro}
	Cr^{3+}	Al^{3+}	Total M^{3+}	at RT	at 400°C	(m^2/g)	(cm^3/g)
10:90	10.7	3.0	13.7	24.3	20.0	340	0.125
20:80	10.4	5.8	16.2	23.0	amorphous	360	0.131
30:70	10.1	8.4	18.5	27.0	amorphous	338	0.119
40:60	9.2	8.5	17.7	35.8	31.1	888	0.267
50:50	8.1	10.4	18.5	32.1	28.3	532	0.175
60:40	6.9	12.7	19.6	27.0	24.0	431	0.156
70:30	5.8	14.4	20.0	25.0	23.0	218	0.072
80:20	4.1	15.3	19.4	23.0	amorphous	151	0.030
90:10	1.7	14.6	16.3	25.2	amorphous	55	0.016

amounts of Al^{3+} adsorbed preferentially on the catalyst surface [15], which reduces the access to the internal surface. Strong acidity (T > 200°C) is predominant in practically all materials, with 2/3 or more of total acidity.

Pyridine adsorption studies were undertaken to evaluate the nature of the acid sites and their relative concentration on the pillared phosphate surface. Fig. 2 shows the IR spectra of three representative samples of groups I, II and III. In all the studied samples, the characteristic bands of Brønsted (1550 cm^{-1}) and Lewis (1445 cm^{-1}) acid sites were observed. The mixed pillared phosphates show a marked enhance-

ment of the acidity with respect to the original phosphates, a behaviour which seems to be general for pillared compounds [16]. The Brønsted acidity comes from P–OH groups in the phosphate surface some of which are regenerated during the thermal transformation of the interlayer oligomers to oxide pillars. In addition, remaining OH groups in the oxide pillars also contribute to this Brønsted acidity. The Lewis acidity is due to the intercalated pillars [17]. Aluminium does not adopt an exclusively octahedral coordination in the pillared phosphates, but on the contrary, it is preferentially penta-coordinated (or in distorted tetrahedral coordina-
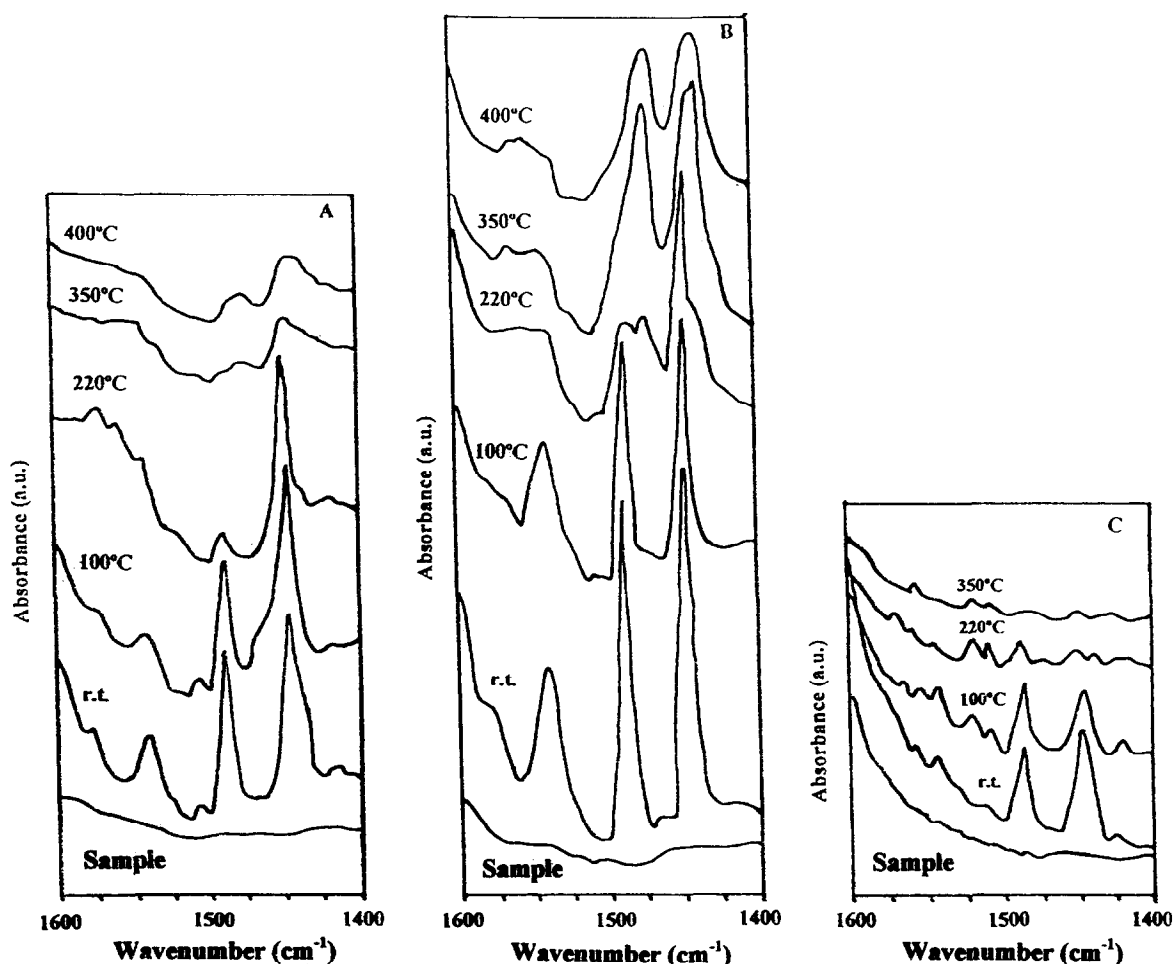

Fig. 2. IR spectra of pillared phosphates exposed to pyridine vapours and outgassed at different temperatures: (A) sample 30/70, (B) sample 40/60 and (C) sample 70/30.

tion) when directly linked to the phosphate layer [15]. On the other hand, Cr^{3+} ions may adopt a six-coordination at the expense of the oxygen ion coordinated to Al^{3+} ions, as described by Stone [13] for α-$Cr_xAl_{2-x}O_3$ solid solutions. This low coordination of aluminium may give rise to a substantial increase of the Lewis acidity.

The concentration of Brønsted (C_B) and Lewis (C_L) acid sites was determined from the integrated absorbances and the integrated absorption intensities of the PyH^+ and PyL bands [18]. As an approach and in order to compare with data reported in literature, we have used the extinction coefficient values obtained by Datka and Wachs [19] which are 1.11 and 0.73 cm μmol^{-1} for the PyL and PyH^+ respectively. Calculated values were: $C_L = 212$ $\mu mol/g$ and $C_B = 152$ $\mu mol/g$ ($C_L/C_B = 1.39$) for sample 30/70; $C_L = 363$ $\mu mol/g$ and $C_B = 376$ $\mu mol/g$, ($C_L/C_B = 0.97$) for sample

40/60 and $C_L = 77$ $\mu mol/g$ and $C_B = 44\mu mol/g$ ($C_L/C_B = 1.74$) for sample 70/30. The highest porous material (sample 40/60) presents the maximum acidity and the minimum relative concentration C_L/C_B. In samples with high aluminium content the acidity is markedly decreased due the formation of stuffed structures which impedes the access of the pyridine molecules to the internal pores. Interestingly, the acidity found in sample 40/60 is considerably greater than those of alumina pillared clays [17] and alumina [19]. Although the acidity measured by NH_3-TPD gives similar values for samples 30/70 and 40/60, the study of pyridine adsorption indicates a higher acidity for sample 40/60. This is attributed to the sample 40/60 which has a more open pore structure [12] and, consequently, is more accessible to pyridine molecules. The materials with an intermediate Al/Cr ratio, are even more acid than certain zeolites [20] and mixed oxides [13].
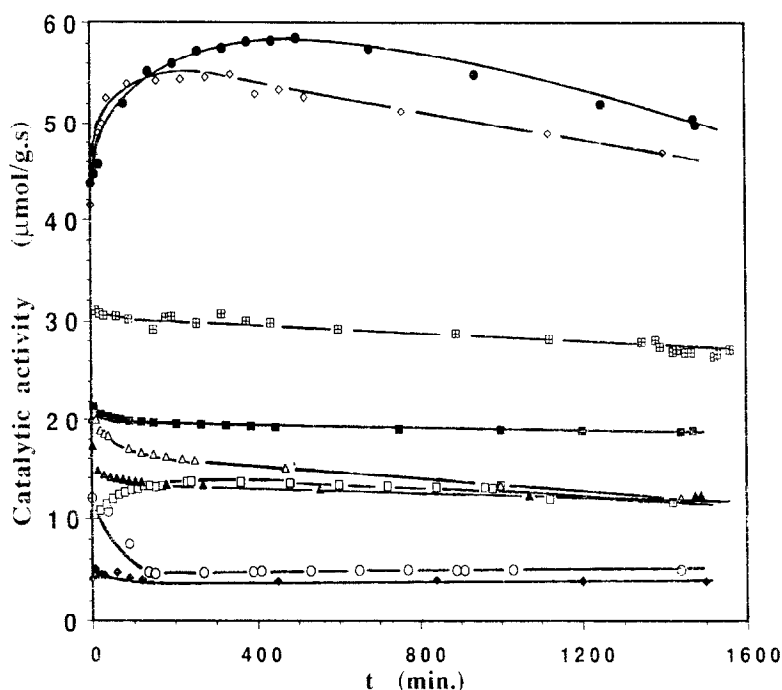

Fig. 3. Catalytic activity of pillared phosphates catalysts as a function of time on-stream (♦ sample 10/90, △ sample 20/80, crossed open square sample 30/70, ● sample 40/60, ◇ sample 50/50, ■ sample 60/40, ▲ sample 70/30, □ sample 80/20, and ○ sample 90/10.).

3.1. Catalytic activity

The activity of the catalysts in the reaction of decomposition of isopropyl alcohol as a function of the time on-stream is plotted in Fig. 3. In general, the stationary regime is reached in about three hours, except for the most active materials, 40/60 and 50/50, for which, initially, the activity increases very rapidly and after eight hours gradually decreases, but still maintaining a very high value. The stationary regime remains for at least 24 h, with a decreasing in activity, as much, of only 10% for samples with maximum activity.

The activity of the different catalysts in the reaction of decomposition of isopropyl alcohol in helium at 220°C is listed in Table 2. The most significant finding is that propylene is the only product formed (acetone and isopropyl ether < 1%) in both inert and oxidizing atmospheres. This fact, not reported hitherto in literature, precludes the presence of basic and/or redox sites on the catalysts, which are responsi-

Table 2

Activity of mixed alumina chromia pillared materials for isopropyl alcohol decomposition

Sample (Al/Cr)	Activity (μmol g^{-1} s^{-1})	Sample[a]	Activity (μmol g^{-1} s^{-1})
10/90	3.91	α-ZrP	0.04
20/80	11.5	α-SnP	1.2
30/70	27.2	CrSnP	2.7
40/60	50.9	CrZrP	2.1
50/50	47.0		
60/40	18.9		
70/30	12.4		
80/20	11.7		
90/10	5.0		

[a] From [21].

ble for the dehydrogenation reaction. All catalysts, including those with low acidity and surface area, present high activity as compared with the pristine phosphate and their analogous chromia pillared α-zirconium and α-tin phosphates [21]. The activity sharply increases with the Al content up to an Al/Cr ratio of 40/60, with a maximum value of 50.93 μmol g^{-1} s^{-1}, i.e. maximum activities correspond to materials
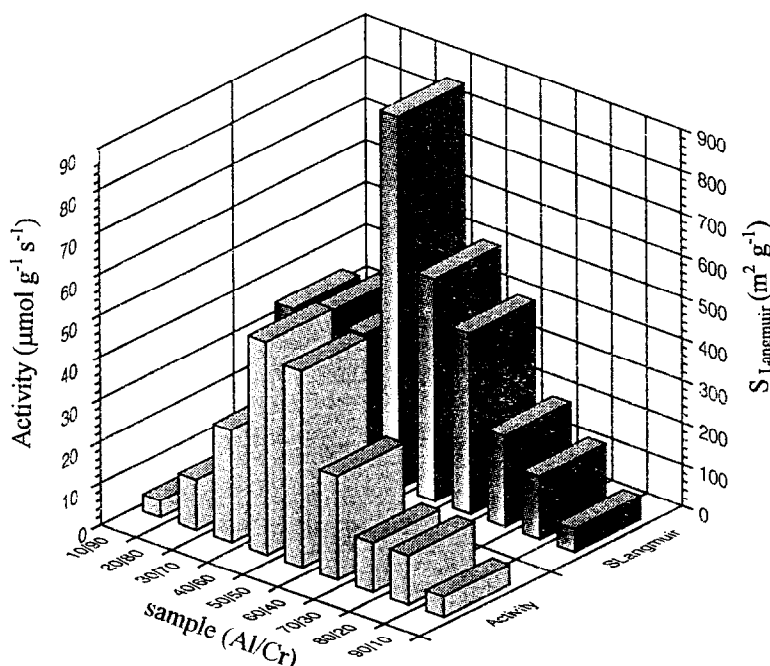

Fig. 4. Comparison between isopropyl alcohol decomposition activity and surface area for the studied catalysts.

of the Group II. From the Al/Cr ratio 50/50, the activity decreases abruptly up to a value of 5 μmol g^{-1} s^{-1}, for sample 90/10. The maximum activity is about 25 times higher than that obtained for chromia pillared α-zirconium phosphate and 40 times the activity of α-SnP, which is the most active layered phosphate. This high value contrast with the extremely low activity of α-ZrP for the dehydration reaction. Of course, the activity of the mixed pillared materials is also much higher than those of α-Cr$_x$Al$_{2-x}$O$_3$ [13] and ZrP$_2$O$_7$ [8], both with very low surface areas and acidities.

In Fig. 4, the activity and the surface area (S_{Langmuir}) as a function of the Al/Cr ratio are compared. Direct correlation exists between Al/Cr ratios 40/60–90/10, i.e. the higher the surface area the higher the activity.

On the other hand, there is good correlation between activity and micropore volume for catalysts with Al/Cr ratios of 30/70 to 70/30, i.e., activity increases with micropore volume. However, samples 10/90 and 20/80 present similar activities to those of samples 90/10 and 80/20 respectively, even though micropore volumes are quite different. This fact suggests that the dehydration reaction occurs, to a great extent, in micropores with adequate size to allow the access of the isopropyl alcohol molecules. This also means that not necessarily should exist a linear correlation between activity and surface acidity. Thus, maximum surface acidity is observed for sample 20/80, whereas maximum activity corresponds to sample 40/60. This sample presents a unique pore size centred at 18 Å, almost in the limit between micropore and mesopore, so that the isopropyl alcohol molecules can enter easily into the porous structure of this catalyst.

Interestingly, even though the decomposition of isopropyl alcohol is performed in air flow, the only product of the reaction is propene. This behaviour is very different from that observed for α-ZrP and their chromia pillared derivatives, which in similar conditions, gave propene and acetone, the latter due to the presence of redox
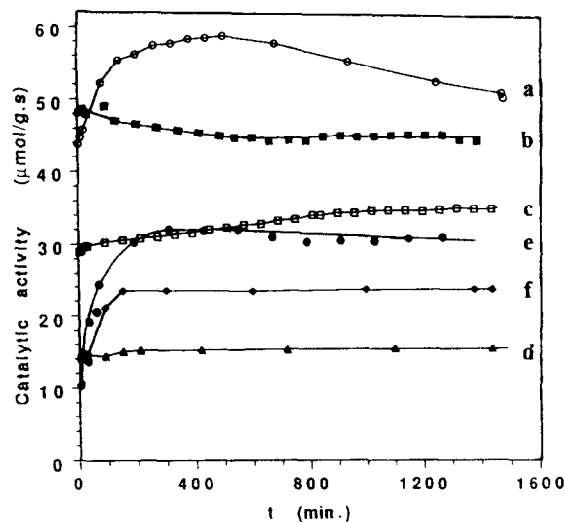

Fig. 5. Catalytic activity of sample 40/60 under different conditions. Catalysis in He: (a) material calcined in N$_2$, (b) K$^+$-exchanged sample in (a), (c) sample in (a) doped with NH$_3$, (d) material calcined in air. Catalysis in air: (e) sample in (a), (f) sample in (d).

sites [21]. It may be that the stronger linkage of aluminium with the external surface of the phosphate, together with the presence of larger amounts of metal oxide in the mixed pillared materials, make possible redox sites inaccessible to isopropyl alcohol molecules.

3.2. Pretreatments

Sample 40/60, with maximum activity has been chosen to study the influence of different variables on the catalytic behaviour. The activity in He is drastically reduced if the catalyst is calcined in air during its preparation (Fig. 5d). In these conditions, Cr(III) is oxidized to Cr(VI), which is then segregated as CrO$_3$ and reduced again at higher temperature. This triple process gives rise to the formation of partially collapsed structures, which hinder accessibility to internal active sites [22]. The activity is slightly increased if the reaction is then carried out in air (Fig. 5f). It is possible that in these conditions some Cr(VI) oxide centers might develop on the surface of the catalyst in the course of catalytic

reaction, a small amount would be enough to increase the dehydration activity.

Catalysis in air also considerably reduces the activity of the catalyst prepared in N_2 atmosphere (about 40%) (Fig. 5e). A possible explanation for such reduction is that, in this case, the predominant effect of oxygen is to increase the binding ability of metal ions with low coordination on the surface of the catalyst, which otherwise should act as Lewis acid centers.

Exchange with K^+ also reduces the activity of the catalyst (Fig. 5b), due to a partial elimination of Brønsted acid centres. In addition this bulky cation restricts the access of the isopropyl alcohol molecules to the internal acid sites. In fact, we have observed that when hydrated Cu^{2+} ions occupy exchange positions the surface area of pillared phosphates is reduced to one third part [23]. Poisoning with NH_3 prior to the reaction with isopropyl alcohol, causes a reduction of the activity of 40% (Fig. 5c), as a consequence of the neutralization of a high percentage of acid sites, but given that the remaining activity is still quite high, it seems that the weak acid sites are involved in the reaction.

4. Conclusions

Ammonia and pyridine adsorption studies and the isopropyl alcohol decomposition test have revealed the remarkable acidity of mixed alumina–chromia pillared phosphate materials. Both acidity and catalytic activity are dependent on the Al/Cr ratio in the catalyst, but there is not a linear correlation with composition. The most highly porous materials, those with intermediate Al/Cr ratios (40/60 and 50/50) were the most active catalysts, with activities higher than 45 mmol g^{-1} s^{-1} after 24 h. From this, it is inferred that the decomposition of isopropyl alcohol occurs predominantly inside large micropores. All materials, independently of their composition, were exclusively dehydrating catalysts with selectivities toward propylene higher than 99%.

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