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The Effect of the Fluoride Ion on the Catalytic Activity of $AlPO_4$ in the Cyclohexene Skeletal Isomerization

J. M. CAMPELO, A. GARCIA, D. LUNA, AND J. M. MARINAS

Department of Organic Chemistry, Faculty of Sciences, University of Cordoba, E-14004 Cordoba, Spain

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INTRODUCTION

The effect of the fluoride ion on surface acidity and the catalytic properties in organocationic reactions of solid acid carriers have been thoroughly investigated, especially in the case of Al_2O_3 (*1–16*).

The protonic acidity of the Al_2O_3 hydroxyl groups is very weak, but after partial substitution with fluorine strong Brønsted acidity was found. At the same time the small amount of fluoride ion enhances electron-acceptor properties as electron-donor properties decrease.

This surface modification strongly affects the catalytic activity of Al_2O_3 in many carbocation-type reactions such as double bond migration and skeletal isomerization of butenes and pentenes (*3, 5, 12, 13*), toluene disproportion (*4*), cracking of 2-methylpropane (*5*), cyclohexene (*8*), and 2-methylpropene (*9, 10*) isomerizations, and cumene cracking (*12, 13*).

The enhancement of the catalytic activity can be sought by the inductive effect of the electronegative fluorine atoms on adjacent OH groups resulting in the weakening of the O—H bonds, i.e., in the increase of acid strength. Thus, there is evidence that fluorination of Al_2O_3 mainly affects the distribution of sites with different strengths rather than the overall acidity of the surface (*14–16*).

Recently we have shown that $AlPO_4$ as the catalyst or the catalyst support finds multiple uses in several important industrial processes like dehydration, isomerization, cracking, polimerization, condensation, alkylation, hydrogenation, etc. (*17–19*).

In previous papers (*20–22*) significant differences were found in texture and mainly in the concentration of surface acid–basic and oxidizing–reducing centers, showing that the nature of the precipitating agent also plays an important role in the final properties of the $AlPO_4$ obtained. Therefore, the nature of the precipitating agent could be a new clue in the design of $AlPO_4$ catalysts with a required reactivity.

On the other hand, Moffat *et al.* (*23*), using semiempirical quantum chemical CNDO/2 calculations, have shown that phosphorus atoms function as the Lewis acid site in $AlPO_4$ and that Brønsted acidity is due to the protons attached to exposed oxygen. These are found to function as Lewis basis sites due to their having higher electronic density than bridged oxygen.

The presence of acid sites over $AlPO_4$ (where both the number of acid sites as well as their strength are important) has been found: by the irreversible adsorption of organic bases with different pK_a and steric hindrance through the application of a spectrophotometric method developed by us (*24*); or by the study of catalytic reactions promoted by such sites, especially cyclohexene skeletal isomerization (*20, 25, 26*) which is known to be catalyzed only by strong acid sites (*27*). Furthermore, the acidity of $AlPO_4$ changes with impregnation with alkali (*28*) or fluoride (*29*) ions as well as with calcination temperature (*28*). But little study has been done on the depen-

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dency of texture, catalytic activity, and selectivity on calcination temperature and fluoride impregnation.

For this reason, in this paper we study the texture of $AlPO_4$ treated at different temperatures (770–1270 K) and $AlPO_4$ impregnated with fluoride ions (1–3 wt%) as well as their catalytic activities for the cyclohexene skeletal isomerization (CSI). This is carried out since we have shown previously (*20*) that there is a linear correlation between catalytic activity and the strong acidity measured vs aniline.

EXPERIMENTAL

Materials. Aluminum orthophosphate (Al/P = 1) was prepared from aqueous solutions of $AlCl_3 \cdot 6H_2O$ and H_3PO_4 (85 wt%) by precipitation with propylene oxide (*28*). The solid was calcined at 770, 920, 1070, and 1270 K for 3 h.

The $AlPO_4$ including fluoride ions were prepared from $AlPO_4$-920 by impregnation until incipient wetness with aqueous solutions of ammonium fluoride, followed by drying at 393 K for 24 h and calcining at 573 K for 3 h. The content of fluoride ions was in the range 1–3 wt% (F1-$AlPO_4$ to F3-$AlPO_4$). A sample of $AlPO_4$-920 was soaked with the same volume of water as that used for the ammonium fluoride solution, dried, and calcined similarly. This was used as control $AlPO_4$-920.

Textural properties. The textural properties of $AlPO_4$ calcined at different temperatures and impregnated with fluoride ions were determined from the adsorption–desorption isotherms of nitrogen at its liquid temperature, using conventional volumetric apparatus.

X-Ray diffraction analysis. The X-ray powder diffraction patterns of different samples were measured with a Philips X-ray diffractometer with Fe-filtered Co$K\alpha$ radiation (λ = 1.79026 Å).

Infrared spectroscopy. Infrared spectra at room temperature were carried out in a Perkin–Elmer 599 double-beam grating spectrophotometer on 2% $AlPO_4$–KBr pressed disks (≈200 mg weight). Materials previously ground to 0.1 μm size, were pressed and stored in a desiccator. The samples were maintained in the desiccator until any difference in OH band intensity was observed after repetitive spectra were run.

Apparatus and procedure. The CSI was carried out in a microcatalytic pulse reactor as has been previously reported (*20*).

RESULTS AND DISCUSSION

Textural Properties

The isotherms, except for $AlPO_4$-1070 and $AlPO_4$-1270 samples, were found to be type IV in the BDDT's classification (*30*) and the hysteresis loops belong to de Boer classification type A (*31*), the hysteresis loops closing at some intermediate relative pressures. This, together with the nearly parallel aspect of the two branches over an appreciable range of relative pressures, indicates that in the texture analysis we are dealing essentially with a cylindrical pore system. Moreover, the isotherms of $AlPO_4$-1070 and $AlPO_4$-1270 samples are reversible exhibiting no hysteresis, a behavior which is expected for nonporous adsorbents.

Surface areas (S_{BET}, $m^2\ g^{-1}$) are collected in column 2 of Table 1.

Applying the criterion of Lecloux (*32*), V–n_3 plots of the adsorption branch of the isotherm were constructed for each one of the samples. From them a weak microporosity is patent in samples F2- and F3-$AlPO_4$ (almost null in F2-$AlPO_4$). Surface areas from V–n_3 plots (S_t, column 3 of Table 1) corresponds quite well to S_{BET} data.

Pore size distributions have been made by application of the "corrected modeless" method developed for the analysis of mesopores (*33*) using the cyclindrical pore model. The pore volume, V_P, and the most probable radius, r, for the samples are shown in columns 6 and 7 in Table 1. Table 2 shows the pore size distributions of the studied samples.

From these data, some differences in tex-

TABLE 1

Textural Properties of $AlPO_4$ Calcined at Different Temperatures and $AlPO_4$ Impregnated with Fluoride Ions

Catalyst	S_{BET} (m^2 g^{-1})	S_t (m^2 g^{-1})	$S_{\mu P}$ (m^2 g^{-1})	$V_{\mu P}$ 10^3 (ml g^{-1})	V_P (ml g^{-1})	r (nm)
$AlPO_4$-770	57	58	—	—	0.43	6.7
$AlPO_4$-920	79	81	—	—	0.51	6.7
$AlPO_4$-1070	10	—	—	—	0.02	—
$AlPO_4$-1270	8	—	—	—	—	—
F1-$AlPO_4$	64	65	—	—	0.47	8.9
F2-$AlPO_4$	64	66	7	6	0.47	8.9
F3-$AlPO_4$	64	66	16	8	0.47	8.9

tural parameters of samples are patent, especially when the solid is pretreated at temperatures higher than 923 K, which strongly decreases the surface area and porosity due to the crystallization of $AlPO_4$, as can be seen from X-ray diffraction. For F-$AlPO_4$ samples, the impregnation with fluorine simultaneously decreases surface area and pore volume slightly (independently of the fluorine content) but the pore radii spectrum is displaced toward ever increasing values. This fact is very important since the catalytic properties of $AlPO_4$ are strongly dependent on their textural and acid properties and thus fluoride impregnation is able to modify the latter (*29*) while the textural properties of the parent structure remain.

X-Ray Diffraction Analysis

X-Ray diffraction effects on the samples are given in Figs. 1 and 2 both before and after sintering in air at different temperatures up to 1270 K and after impregnation with ammonium fluoride up to 1–3 wt% fluorine.

From these it is clearly patent that crystallinity grows with treatment temperature becoming fully developed at 1070 K. After the treatment at 1270 K the sample shows patterns corresponding fairly well to that of ASTM synthetic $AlPO_4$ (*34*). The structure corresponds to the pseudohexagonal one of tridymite. The band at d = 4.31 A (2θ: 24.0°) may be related to the presence of structural defects (*34*). Thus, amorphous $AlPO_4$ is produced from materials calcined at temperatures lower than 1070 K while higher temperatures determine the $AlPO_4$ crystal phases.

The X-ray diffraction patterns given for $AlPO_4$ samples that contain 1–3 wt% F are practically identical to pure $AlPO_4$, thus

TABLE 2

Pore Size Distributions of $AlPO_4$ Calcined at Different Temperatures and $AlPO_4$ Impregnated with Fluoride Ions

Pore size (Å)	Distribution, vol%				
	$AlPO_4$-770	$AlPO_4$-920	F1-$AlPO_4$	F2-$AlPO_4$	F3-$AlPO_4$
>200	9.5	5.1	7.0	8.6	7.6
100–200	28.0	37.6	59.4	58.7	53.1
50–100	51.8	48.8	18.6	19.3	27.9
20– 50	10.7	8.5	14.3	13.2	11.4
<20	—	—	0.7	0.2	—

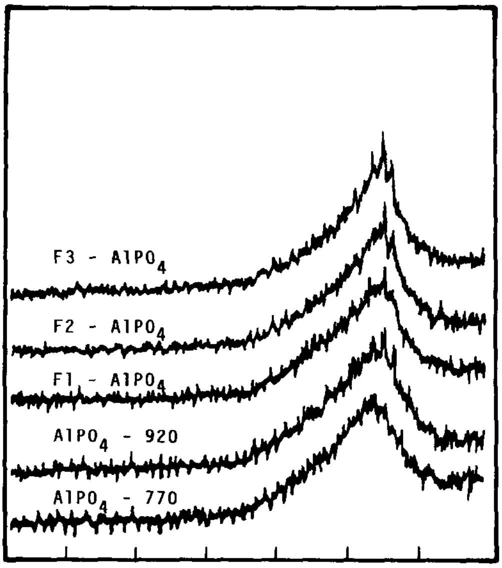


FIG. 1. X-Ray diffraction profiles for $AlPO_4$-770, $AlPO_4$-920, F1-, F2-, and F3-$AlPO_4$ samples.

maintaining the low degree of crystallinity of the samples and hence, their porous texture. Thus, we assume that the majority of the fluorine atoms are incorporated as surface groups, due to the low fluorine content.

Infrared Spectra

Figures 3 and 4 give IR spectra of $AlPO_4$ calcined at different temperatures and $AlPO_4$ impregnated with fluoride ions. Peaks are not well developed; only those corresponding to O—P—O (500, 630–640 cm^{-1}), Al—O cristobalite like (720–735 cm^{-1}), P—O (1140, 1245 cm^{-1}), and O—H ($\simeq$3450 cm^{-1}) are apparent (*35*).

Removal of OH groups at 1070 K suggests that they are held too close to other OH groups. The remaining OH groups at 1070 K can be ascribed, according to Peri (*36*), to isolated geminal O—H pairs attached to P or to single P—OH groups that are more difficult to remove. The OH groups are absent in the $AlPO_4$-1270 sample. Hydroxyl groups on the phosphorus atom are acidic and their acidity might be further enhanced by H-bonding to Al—OH groups, as has been stated by Moffat *et al.* (*23*).

Infrared spectra in the region of the stretching vibrations of OH groups show some decrease in OH band intensity after introducing up to 2 wt% fluorine (Fig. 5). A further increase up to 3 wt% does not affect the OH band intensity. Thus, the substitution of $AlPO_4$ hydroxyl groups with fluorine in the impregnation process is evident, as occurs on γ-Al_2O_3 (*37*) where the less acidic hydroxyl groups are first removed while hydroxyls of strong acidity are created.

Catalytic Activity

The CSI process yields a mixture of 1-, 3-, and 4-MCP although the fractional conversion to 4-MCP is almost negligible due to the short contact time in the reaction process. The $AlPO_4$-1070 and $AlPO_4$-1270 samples are inactive with respect to the isomerization process due to the absence of surface acid sites (*28*).

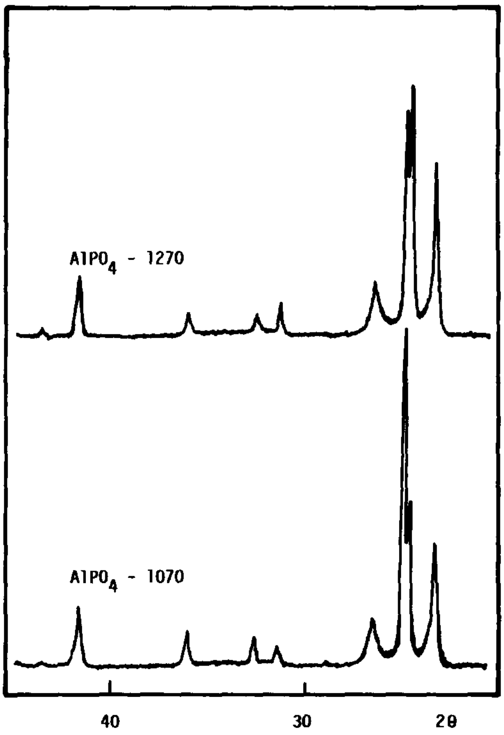


FIG. 2. X-Ray diffraction profiles for $AlPO_4$-1070 and $AlPO_4$-1270 samples.

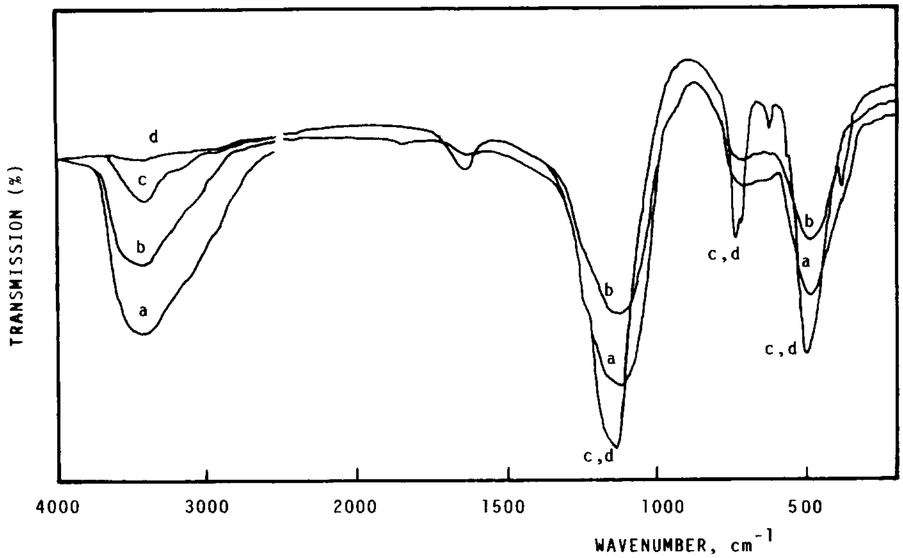


FIG. 3. Infrared spectra of calcined $AlPO_4$ catalysts. (a) $AlPO_4$-770, (b) $AlPO_4$-920, (c) $AlPO_4$-1070, (d) $AlPO_4$-1270.

Isomerization activity, expressed by the total conversion to 1-, 3-, and 4-MCP, is fitted to the Bassett–Habgood kinetic model (*38*) for first order processes in which the surface reaction is the controlling step and the partial pressure of the reactant is low

$$\ln[1/(1 - X)] = RTkK(W/Q)$$

where X is the total conversion to 1-, 3-, and 4-MCP, R the gas constant, T the reaction temperature, k the rate constant of the surface process, K the adsorption constant of CH on the catalyst, W the catalyst weight, and Q the flow rate of the carrier gas.

The apparent rate constants, kK, at a fixed temperature, from the linear plots

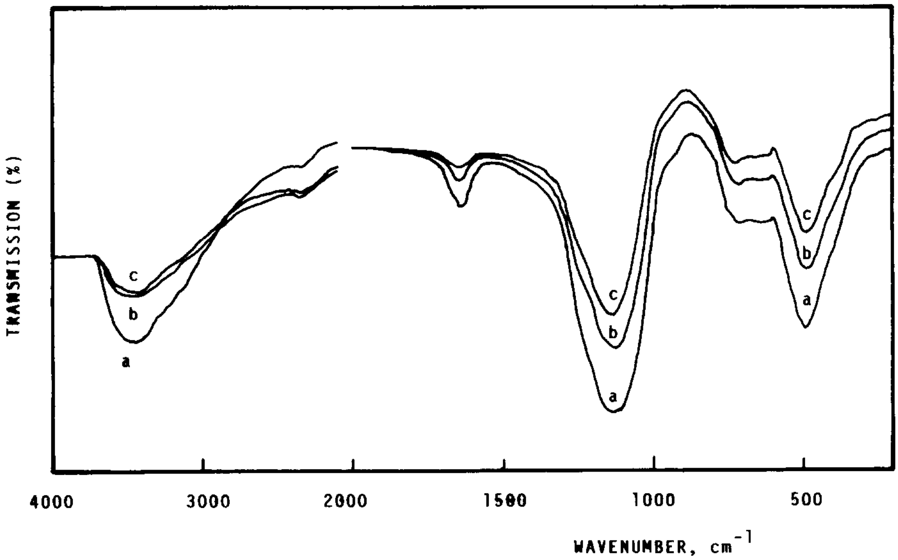


FIG. 4. Infrared spectra of F1- (a), F2- (b), and F3-$AlPO_4$ (c) samples.

$\ln[1/(1 - X)]$ vs W (Fig. 5) and the apparent activation energies, E_a, from $\ln X$ vs T^{-1} were obtained in each case and are collected in Table 3 together with the Arrhenius parameters, $\ln A$. All values were reproducible to within about 7%.

In Table 3 it is shown that the catalytic activity of pure $AlPO_4$ depends on its pretreatment temperature according to the surface acid sites determined spectrophotometrically (*24*). Thus, increasing the calcination temperature of $AlPO_4$ was found to decrease the isomerization activity, especially for temperatures over 920 K where the crystallization of $AlPO_4$ occurs. However, the most striking feature of the results shown in Table 3 is that the impregnation of $AlPO_4$ with fluoride ions greatly increases the catalytic activity for the CSI. Besides, the smallest fluoride content in $AlPO_4$ produces a significant enhancing effect on its ability to isomerize CH. An increase in the fluoride content above 1 wt% results in a lesser increase in the catalytic activity almost null in the F3-$AlPO_4$ sample.

Since the CSI is known to be a probe reaction for strong acid sites on catalyst surfaces (*27*), the impregnation of $AlPO_4$ with fluoride ions leads to the generation of stronger acid sites on the $AlPO_4$ surface as occurs with other solid acid catalysts such as Al_2O_3 (*1–16*), SiO_2 (*39*), Al_2O_3–SiO_2 (*40*), TiO_2 (*41*), SiO_2–TiO_2 (*41*), TiO_2–Al_2O_3 (*42*), TiO_2–SiO_2–Al_2O_3 (*42*), Al_2O_3–Cr_2O_3 (*43*), and zeolites (*44–47*).

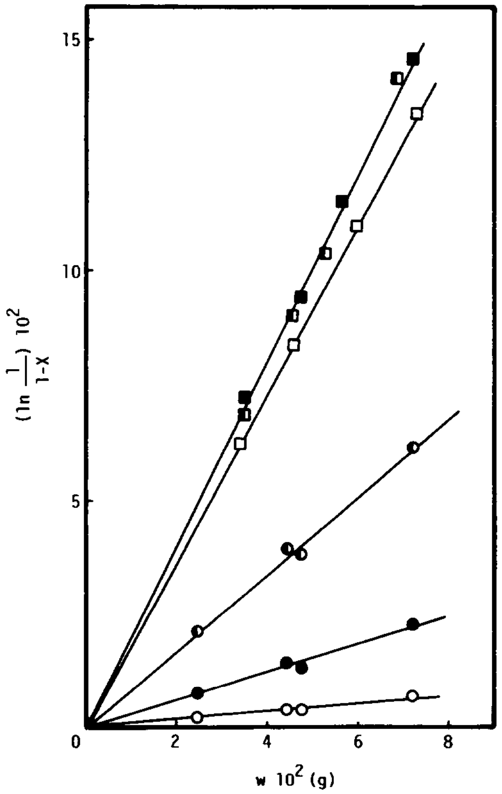


FIG. 5. Test of first order rate law for CH isomerization. F1-$AlPO_4$ (□) 673 K; F2-$AlPO_4$ (■) 673 K; F3-$AlPO_4$ (○) 523 K, (●) 573 K, (◐) 623 K, (◧) 673 K.

TABLE 3

Apparent Rate Constants, kK, Activation Energies, E_a, Preexponential Factors of the Arrhenius Equation, $\ln A$, for Cyclohexene Skeletal Isomerization on Pure $AlPO_4$ and Fluorided $AlPO_4$ Catalysts

Catalyst	T (°K)	$kK\ 10^6$ (mol atm^{-1} g^{-1} s^{-1})	E_a (kJ mol^{-1})	$\ln A$[a]
$AlPO_4$-770	523	0.11		
	573	0.33	61.2	6.81
	623	0.86		
	673	1.92		
$AlPO_4$-920	523	0.20		
	573	0.59	59.1	6.78
	623	1.47		
	673	3.18		
$AlPO_4$-1070[b]				
$AlPO_4$-1270[b]				
F1-$AlPO_4$	523	1.08		
	573	3.54	63.8	9.46
	623	9.59		
	673	22.25		
F2-$AlPO_4$	523	1.53		
	573	4.58	59.1	8.66
	623	11.44		
	673	24.79		
F3-$AlPO_4$	523	1.47		
	573	4.54	60.7	8.54
	623	11.66		
	673	25.82		

[a] A is expressed in mol atm^{-1} g^{-1} s^{-1}.

[b] The sample does not exhibit activity for the CSI process.

Thus, the effect of fluoride impregnation on the catalytic acitivity of $AlPO_4$ in the CSI is entirely consistent with the modification of surface acidity in the samples (*29*). The fluoride ion treatment modifies the surface acidity–basicity balance with a sharp loss of the surface basic properties leading to a surface with only surface acidity, although the number of acid sites is moderately lower than that of pure $AlPO_4$ and the surface acidity is rather similar in all fluorided-$AlPO_4$. However, the strength of acid sites is increased by inductive effects of highly electronegative fluorine on neighboring hydroxyls which enhance their protonic mobility through the weakening of the O—H bond. The whole effect is a reduction of the absolute number of OH groups and an increase in the acid strength of those remaining. The IR spectra confirm this assumption as has been stated above. Besides, the fluorine attached to Al or P polarizes the Al—O—P bonds increasing the Lewis acid strength of $AlPO_4$.

On the other hand, the apparent activation energies, E_a, are practically constant for all samples studied. This, together with the fact that we are dealing with first order kinetics, indicate that the transition state is of the same type for all catalysts. Thus, differences in catalytic activities can be accounted for the more or less developed carbocationic character of the reaction intermediates which is a function of the acid strength of the catalyst.

Selectivity Studies

As can be seen in Table 4 where the fractional conversion to 1- and 3-MCP (X_1 and X_3) appeared, the concentration of 1-MCP was always higher than 3-MCP for all catalysts studied.

TABLE 4

Fractional Conversion to 1- and 3-MCP (X_1 andX_3) and Selectivity Factors, σ, for Cyclohexene Isomerization on Pure $AlPO_4$ and Fluorided $AlPO_4$ Catalysts

Catalyst	T (°K)	W (mg)	$X_1 \times 10^2$	$X_3 \times 10^2$	σ^a
$AlPO_4$-770	523	96	0.034	0.032	
	573		0.117	0.109	1.07
	623		0.329	0.307	
	673		0.793	0.739	
$AlPO_4$-920	523	83	0.064	0.042	
	573		0.208	0.137	1.54
	623		0.564	0.373	
	673		1.319	0.871	
F1-$AlPO_4$	523	73	0.382	0.124	
	573		1.377	0.449	3.07
	623		4.051	1.322	
	673		10.152	3.312	
F2-$AlPO_4$	523	69	0.518	0.165	
	573		1.696	0.540	3.14
	623		4.608	1.469	
	673		10.781	3.435	
F3-$AlPO_4$	523	45	0.323	0.100	
	573		1.093	0.336	3.25
	623		3.050	0.938	
	673		7.298	2.245	

[a] Ratio of the fractional conversion of 1-MCP to 3-MCP (X_1/X_3).

The optimum performance envelope (OPE) curves, obtained by plotting the fractional conversion (X) of a particular product against the total conversion (X_T) for different weight ratios of catalyst to introduced CH (*48*), shown that, in the range of conversions studied, 1- and 3-MCP are stable primary reaction products coming from CH.

Besides, these isomerization products are really competitors, with a first order kinetic, since straight lines are obtained from the application of the Wheeler criterion (*49*) on the kinetic selectivity factor (σ). Thus, for a parallel process when a first order kinetics is followed, σ can be written as

$$\sigma = k_1/k_3 = X_1/X_3.$$

The selectivity is independent of the contact time and overall conversion. Thus, as in previous studies (*20, 24, 25*) the different σ values are due to the different A_1/A_3 ratios according to

$$\begin{aligned}\sigma &= k_1/k_3 \\ &= [A_1 \exp(-E_a/RT)]/[A_3 \exp(-E_a/RT)] \\ &= A_1/A_3.\end{aligned}$$

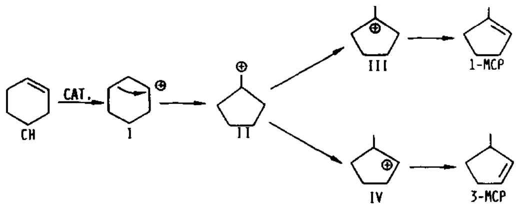
Since the preexponential factor is a function of the number of high strength acid sites and these are different on each catalyst, the selectivities on $AlPO_4$ and fluorided-$AlPO_4$ samples are different (column 6 in Table 4).

On the other hand, the selectivity to 1-MCP follows the same behavior as the catalytic activity, i.e., they increase by fluoride impregnation although the σ increase is only two times higher than those of the $AlPO_4$-920 sample. Besides, an increase in the fluoride content over 1 wt% did not result in an important change in the surface acid sites of high strength as shown by the similarity of the σ values.

Thus, Tables 3 and 4 showed that regardless of the fluoride content of the $AlPO_4$ up to 3 wt%, catalytic activities and selectivities remain almost the same as expected through the surface acidity of the samples. So, the impregnation with fluoride ions enhances the activity of $AlPO_4$ for CSI, i.e., acid-catalyzed reactions, although its activity was not as high as those of the sulfate-treated $AlPO_4$ catalysts (*50*). However, the anion affects the catalytic activity and surface acidity in a much stronger way than it does the textural properties.

Reaction Pathway

Reaction products are obtained by a carbocationic mechanism with subsequent Wagner–Meerwein type rearrangements of intermediates across parallel reactions as has been proposed previously (*20*).



In the first step of the reaction a carbenium ion I is formed through the chemisorption of CH on the acid sites of the catalyst. The unstable cyclohexyl carbenium ion I suffers skeletal isomerization (Wagner–Meerwein rearrangement) involving a less stable primary carbenium ion II, which rearranges to a more stable tertiary carbenium ion III. This then desorbs as 1-MCP. The rearrangement of the carbenium ion II to a secondary carbenium ion IV gives rise to 3-MCP.

In this sense, analysis of both kinetic energy release and collisional activation measurements (*51, 52*) proves that in gas phase the incipient cyclohexyl carbenium ion rearranges spontaneously to the most stable carbenium ion, i.e., 1-methylcyclopentyl cation (III).

Thus, the impregnation of $AlPO_4$ with fluoride ions increases the acid strength of the catalyst and hence produces intermediates with a more developed carbocationic character which in turn increases the conversion of both reaction products (1- and 3-MCP) with a rise in the selectivity factor, σ, due to the greater stability of tertiary carbenium ion III in relation to secondary one IV (*53*).

In conclusion, the principal finding of this research is that the treatment of $AlPO_4$ with aqueous ammonium fluoride, following by drying and calcination at 573 K, leads to the generation of strong acid sites as measured by CSI without an appreciable decrease in the textural properties of the solids. Thus, the fluorided $AlPO_4$ catalysts are expected to act as efficient catalysts in several acid-catalyzed reactions where the pure $AlPO_4$ is active, or even in other processes where pure $AlPO_4$ is not able to act as the catalyst. Besides, the fluoride treatment serves as a method to control the surface charge and hence the point of zero charge of solids used as metal supports, such as $AlPO_4$. This also provides a way of controlling the possible strong metal–support interaction (SMSI) effect in order to achieve the maximum adsorption of the required species.

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