JOURNAL OF MATERIALS SCIENCE 25 (1990) 2513-2519

New $AlPO_4$-sepiolite systems as acid catalysts, I. Preparation, texture, surface-chemical properties and cyclohexene skeletal isomerization conversion

J. M. CAMPELO,* A. GARCIA, D. LUNA, J. M. MARINAS
Organic Chemistry Department, Cordoba University, S. Alberto Magno Av., E-14004 Cordoba, Spain

---

The effects of the addition of aluminium orthophosphate (Al/P = 1) to sepiolite were investigated with respect to texture, porosity, surface chemistry and catalytic performance. The $AlPO_4$-sepiolite catalysts, containing different weight compositions, were prepared by precipitation of $AlPO_4$ (Al/P = 1) with propylene oxide or aqueous ammonia on to commercial natural sepiolite. Sepiolite inhibits the $AlPO_4$ crystallization which is found when pure $AlPO_4$ is calcined at 873 K.

The surface acid–basic properties have been studied gas-chromatographically through the irreversible adsorption of organic acids and bases at temperatures in the range 473 to 673 K. In addition, the cyclohexene skeletal isomerization (CSI) acid catalysed test reaction to 1- and 3-methylcyclopentenes (1- and 3-MCP), was used to test catalyst performance. Catalytic activity, as an apparent rate constant, fits the Bassett-Habgood kinetic model for first-order processes. Marked changes were found in their catalytic properties as a function of the preparation method and the $AlPO_4$ to sepiolite ratio.

$AlPO_4$ addition induced acidity by increasing the strength of acid sites which resulted in a higher conversion which was accompanied by a greater selectivity for 1-MCP. The incorporation of $AlPO_4$ to sepiolite also inhibited the loss of activity with the prolonged use of the catalyst which was found for reference pure natural sepiolite.

---

1. Introduction

Aluminum orthophosphate (Al/P = 1) has been reported to exhibit a variety of catalytic behaviours, with activity for reactions such as alcohol dehydration, alkene isomerization, phenol and toluene alkylation, Beckman rearrangement, etc. [1-5]. Catalytic properties are sensitive to the method of sample synthesis, aluminium starting salt and calcination temperature [3-5]. The differences in catalytic activity with different preparation procedures may be related to variations in surface geometric structure, porous texture and bifunctional acid–base character. Its activity can be improved by the addition of foreign anions, such as F^- [6] and SO_4^{2-} [7], or by the preparation of $AlPO_4$ metal oxide systems, like $AlPO_4$-Al_2O_3 [8-10], $AlPO_4$-TiO_2 [11-13] and $AlPO_4$-ZrO_2 [14]

Sepiolite, a hydrated magnesium silicate [15], is a fibrous clay which presents the highest absorbent capacity of any mineral clay, as well as a high adsorptive capacity [16]. Its advantages over other minerals, due especially to its low density and high specific surface area, have long been accepted, and they account for most of the current uses of sepiolite [17] including enzyme immobilization [18]. Furthermore, surface acidity on natural sepiolite has been found although it is reported to be negligible [19-24] and thus is able to efficiently catalyse carbenium ion reactions that need low surface acidity [19]. However, recent work carried out in this laboratory [25] has shown that natural sepiolites are indeed acidic with surface acid sites that can catalyse the cyclohexene skeletal isomerization (CSI), a reaction that is known to be catalysed only by strong acid sites [26] and which is frequently used to study the behaviour of solid acid catalysts. At all pretreatment temperatures studied (573 to 873 K), regardless of the sepiolite type, there was a strong inhibition of isomerization capacity with the prolonged use of natural sepiolite catalysts due to coke deposition.

Consequently, modification of natural sepiolite through chemical or other means is really essential in order to develop solid acid catalysts. Thus, the activation of sepiolite is usually carried out by either acid treatment [27-32] or by partial exchange of border Mg^{2+} (in octahedral sheets) by Al^{3+} [33, 34]. The effect of the acid treatment was found to be the leaching out of Mg^{2+} cations while leaving the SiO_4 groups largely intact. The extent of these changes is found to vary with the acid strength, temperature and length of exposure.

---

*Author to whom correspondence should be addressed.

0022-2461/90 $03.00 + .12

In order to help in the development of improved activation of sepiolite, the present paper introduces a new class of porous, high surface area materials of potential interest as catalysts and adsorbents found by the preparation of $AlPO_4$–sepiolite systems. These systems were studied for the purpose of strengthening the solid acidity of natural sepiolite even after treatment at high temperature. Thus, the present work is devoted to the effects of the preparation method and $AlPO_4$ loading on physicochemical, surface and catalytic properties of $AlPO_4$–sepiolite catalysts. This paper also reports the use of the gas-chromatographic pulse technique for studying the acid strength distribution (through the adsorption, at several temperatures, of nitrogenous bases with different pKα) and the cyclohexene skeletal isomerization as test reaction for the strong surface acid sites.

The results revealed that the addition of sepiolite to $AlPO_4$ increased the catalytic activity (apparent rate constant) and selectivity to 1-methylcyclopentene (1–MCP) of the synthesized solid for CSI, also exhibiting lower deactivation when compared to the reference sepiolite catalyst. The activity was also found to increase with an increase in the amount of sepiolite. The sepiolite inhibits $AlPO_4$ crystallization when the system is heated to 873 K.

2. Experimental

2.1. Materials

The sepiolite originally from Vallecas-Madrid (Spain), was provided by Tolsa S.A. It is pure (85 wt %), natural and mechanically micronized in a dry medium whose chemical analysis is SiO_2 62.0, MgO 23.9, Al_2O_3 1.7, Fe_2O_3 0.5, CaO 0.5, K_2O 0.6 and Na_2O 0.3%; weight loss from 293 to 1273 K, 10.5%. The presence of smectite, quartz and dolomite as impurities was detected. The sample calcined at 873 K for 3 h was taken as the reference sample (PS).

$AlPO_4$–sepiolite systems were obtained by adding natural sepiolite to a reaction medium where the precipitation of $AlPO_4$ (Al/P = 1), from $AlCl_3 \cdot 6H_2O$ and H_3PO_4 (85 wt %) aqueous solutions, was initiated by the addition of aqueous ammonia (N) or propylene oxide (P). Then, the total precipitation of $AlPO_4$ was carried out by a further addition of aqueous ammonia or propylene oxide. The pH value of the precipitation "end-point" was 6.1. The precipitates were allowed to stand at room temperature for 24 h. After filtration they were washed several times with 2-propanol, dried at 393 K for 24 h, and then calcined at 873 K for 3 h in an electric muffle furnace and stored in a desiccator. Thus we prepared $AlPO_4$–sepiolite systems with weight relation of $AlPO_4$ to sepiolite of 3 and 1.

The samples are designated by APPS followed by the weight ratio of $AlPO_4$ to sepiolite and a letter that indicates the precipitation medium: APPS–3–P, APPS-3–N and APPS–1–N.

Also, pure $AlPO_4$ precipitated with aqueous ammonia (AP–N) and propylene oxide (AP–P) were taken as reference samples [4, 5].

2.2. X-ray diffraction analysis

The X-ray powder diffraction patterns of different samples were carried out with a Philips X-ray diffractometer with iron-filtered CoKα radiation (λ = 0.179 026 nm) and a scanning speed of 2° $\min^{-1}$ for 2θ from 2 to 50°. The time constant was 4 sec.

2.3. Textural properties

The nitrogen adsorption–desorption isotherms of different APPS systems were carried out at 77 K in a classic volumetric apparatus, The samples were outgassed overnight at room temperature and the reproducibility of most of the isotherms was checked. The nitrogen was 99.999% pure. Helium (99.999% pure) was used for the dead space measurements. Surface areas and porosity analysis were carried out by applying the BET [35] and Barret [36] methods and Lecloux criterion [37].

2.4. Surface chemical properties

The surface acidity was measured, at different temperatures, by means of the adsorption of pyridine (PY) and aniline (AN) vapour while the basicity was measured by means of the adsorption of acrylic acid (AA) and phenol (PH) vapour.

A number of pulses (maintaining the same pulse size) of a given probe molecule–cyclohexane solution (approximately 1 M) were injected one after another into the catalyst bed in order to saturate the irreversible adsorption sites on the catalyst with the adsorbate. The peak of the probe molecule in the chromatogram was not observed upon the initial injections, but the peak was gradually observed on successive injections and finally reached a constant area which indicated that the catalyst surface was saturated with irreversibly adsorbed adsorbate. In this sense, the pulse size was in the range corresponding to 0.1 to 0.5 monolayers in order to avoid difficulties if the adsorption was not rapid as well as for a more precise detection of effluent peaks. After saturation, different amounts of titrant were injected to calibrate the FID response. The detector (FID) response was found to be linear over the whole injection range (correlation coefficients above 0.998) employed in the pulse experiments.

The amount of strongly and irreversibly bound titrant, C_p, was calculated from the total amount of titrant added by subsequent pulses and the detected areas of successive effluent peaks according to:

$$C_p = \left(\sum_{i=0}^{n} (C_{in} - C_{out}) \right) \Big/ m$$

where n is the number of pulses; C_{in} the mmole of probe molecule injected in each pulse; C_{out} the mmole of probe molecule remaining in each pulse after adsorption; m the mass of catalyst (g). Integration of the signal was accomplished with a Varian 4270 integrator.

The amount of titrant irreversibly adsorbed, C_p, is assumed to be the number of surface acid or basic sites.

The adsorption of the probe molecule was determined in the temperature range corresponding to the reaction conditions of cyclohexene skeletal isomerization on $AlPO_4$–sepiolite catalysts. The catalyst (100 to 200 mg, $\leqslant$0.07 mm) was held by small plugs of Pyrex glass wool in the 4 mm diameter stainless steel microreactor tube and, before each run, the catalyst samples were standardized in a stream of $12\,ml\,min^{-1}$ of dehydrated and deoxygenated nitrogen (99.999% pure) at 473 K for 1 h. It was also confirmed that the contribution of glass wool is negligible.

2.5. Catalytic measurements

The CSI process was carried out in a microcatalytic pulse reactor. The schematic details of the reaction system as well as the operation conditons have been described previously [4, 5]. Depending upon the activity, between 50 and 200 mg catalyst was charged into the microreactor. The reaction was studied under the following conditions: hydrocarbon pulse, 0.2 to $2\,\mu l$; temperature, 523 to 673 K (at 50 K intervals) and nitrogen as the carrier gas (30 to $60\,ml\,min^{-1}$).

Cyclohexene (Merck, p.a.) was purified by passage through alumina (activated at 673 K in flowing nitrogen and then degassed by evacuation under reduced pressure) at room temperature to remove oxygen and peroxides, and later on distilled in nitrogen.

The reaction products (1-, 3- and 4-methylcyclopentenes) were identified by use of a Varian Mat 711 GC-MS (Organic Chemistry Department, Complutense University, Madrid, Spain).

3. Results and Discussion

3.1. XRD studies

XRD powder patterns of $AlPO_4$–sepiolite systems are shown in Fig. 1 together with that of natural sepiolite subjected to the same thermal treatment (3 h at 873 K). Regardless of the weight composition and preparation method, $AlPO_4$ maintained its amorphous nature and so sepiolite retarded the crystallization of the $AlPO_4$–N catalyst which was observed in the absence of sepiolite [5]. A similar observation had been previously found for $AlPO_4$–Al_2O_3 [10] and $AlPO_4$–TiO_2 [11, 13] catalysts in which both components mutually interacted leading to a retardation of $AlPO_4$ crystallization together with an inhibition in phase transformation (γ-Al_2O_3 to α-Al_2O_3 or TiO_2-anatase to TiO_2-rutile).

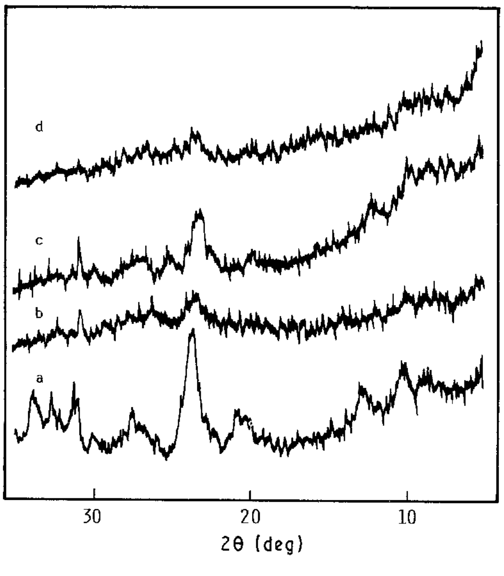

Figure 1 X-ray powder diffraction patterns of $AlPO_4$–sepiolite systems. CuKα radiation. (a) PS; (b) APPS-3–N; (c) APPS-1–N; (d) APPS-3–P.

The sepiolite remained in the same state as when treated at 873 K in the absence of $AlPO_4$, i.e. the folding in the structure and subsequent changes in surface topography [15, 38] were also found.

3.2. Textural properties

All $AlPO_4$–sepiolite nitrogen isotherms have closed and well defined hysteresis loops which correspond to Type H1 in the BDDT classification and are characteristic of mesoporous materials [39]. Also, the similarity in shape of the hysteresis loop associated with each isotherm indicates that the type of mesoporosity generated in the solid remains unchanged.

The nitrogen adsorption results were analysed by the n-method described by Lecloux [37]. For all samples a straight line passing through the origin was obtained at low relative pressure. All n-plots showed an upward trend corresponding to capillary condensation which strengthened the absence of microporosity. The total surface area, S_n calculated by the n-method was found to be in good agreement with that obtained by the BET equation, S_{BET}.

On the other hand, as the adsorption and desorption branches of isotherms follow parallel paths in a whole range of relative pressures, and capillary condensation starts at pressures similar to the corresponding H1 hysteresis loops, we can assume cylindrical idealization for the textural analysis. Thus, pore size distributions have been made by application of the Barret *et al.* method developed for the analysis of mesopores [36] by using the adsorption branch of the isotherm and the cylindrical idealization. Cumulative pore volume, ΣV_p, and cumulative surface area, ΣS_p, in the mesopore range tally with the total pore volume, V_p and surface area, S_{BET}, respectively. All these parameters are summarized in Table I. Table I also includes the same values, selected for comparison, of pure $AlPO_4$ [4, 5] and natural sepiolite [25].

As shown in Table I, the incorporation of sepiolite to $AlPO_4$ obtained in propylene oxide (AP–P) leads simultaneously to a decrease in surface area and pore volume and an increase in the most frequently occurring pore radius. However, the greatest differences are found when sepiolite is added to $AlPO_4$ gelified in aqueous ammonia, $AlPO_4$–sepiolite (APPS–N) catalysts, which results in a large increase in surface area and pore volume (almost 50%). An increase in sepiolite loading also leads simultaneously to a slight decrease in surface area and an increase in pore radius, although the pore volume remains unaltered. Pore size distribution (Table II) is also slightly displaced upwards towards the larger pores; this is demonstrated by the shift towards higher relative pressures which the hysteresis loop of the isotherm undergoes. This can be accounted for by the retardation of $AlPO_4$ crystallization.

Thus the most striking feature of the results shown in Tables I and II is that sepiolite increases the thermal stability of the $AlPO_4$–N catalyst which results in higher textural properties. This increase is accom-

TABLE I Textural properties of $AlPO_4$–sepiolite catalysts

Catalyst	S_{BET} ($m^2 g^{-1}$)	S_n ($m^2 g^{-1}$)	V_p ($ml g^{-1}$)	r_p (nm)	ΣV_p^* ($ml g^{-1}$)	ΣS_p^* ($m^2 g^{-1}$)
APPS–3–P	162	166	0.71	8.7	0.72	167
APPS–3–N	158	167	0.70	8.8	0.71	167
APPS–1–N	134	135	0.71	10.6	0.71	118
AP–P	228	236	0.75	6.6	0.76	229
AP–N	109	102	0.48	8.8	0.49	102
PS	100	99	0.39	7.8	0.40	107

*From the adsorption branch of the isotherms using the modelless method and cylindrical idealization.

panied by an increase in surface acidity and activity in the CSI process (see below).

3.3. Surface chemical properties

In the present adsorption studies, the gas-chromatographic pulse technique is used for the first time, in the measurement of the surface acid-base properties of $AlPO_4$, sepiolite and $AlPO_4$–sepiolite systems. This is done, not only because of the simplicity and rapidity with which requisite data can be obtained, but also due to a particularly attractive feature of the gas-chromatographic technique, which is that the measurements can be made on a large and representative sample of catalyst at temperatures used in the catalytic process.

In this sense, gas-chromatographic techniques have been used extensively in a number of adsorption studies showing great promise in the measurement of adsorption species on solid catalysts in catalytic conditions [40–42].

The distribution of acid–basic sites (sum of Lewis and Bronsted) in $AlPO_4$ (AP–P and AP–N), sepiolite and APPS systems is given in Table III as the amount of probe molecule adsorbed at saturation at a given temperature. The amount of stronger base remaining adsorbed at relatively low temperature (473 K) was taken as a measure of the total number of acid sites, that is, weak, medium and strong acid sites. As expected, upon increasing the temperature (or pK_b of the base) the surface acidity gradually decreased since only the strongest acid sites retain the adsorbed base and thus, the chemisorption of PY was greater than that of AN at every adsorption temperature. The amount of AN adsorbed at 673 K was thus taken as a measure of the strongest acid sites. Besides, the amount of base retained at different temperatures measured the acid strength distribution of a given catalyst. The same applied for the surface basic sites.

As compared to AP–P, the APPS–P catalyst exhibited almost the same total number of acid sites (against PY) although it displayed a higher number of strong acid sites (against AN) at all increasingly higher temperatures. The situation was somewhat different when AP–N and APPS–N catalysts were compared, since these latter always exhibited a higher number of acid sites especially when titrated against AN. The use of aqueous ammonia also developed APPS–N systems with a higher number of strong acid sites than APPS–P systems. All APPS systems displayed a higher number of strong surface acid sites than the parent sepiolite calcined at the same temperature.

Thus, the preparation of APPS systems strengthen the solid acidity of $AlPO_4$ and natural sepiolite after treatment at a high temperature (873 K) and so, these APPS systems catalyse more efficiently those reactions that require the presence of strong acid sites, which occurs with CSI (see below).

On the other hand, APPS systems remained bifunctional in character since they also possessed surface basic sites, although a smaller number of basic sites (measured against AA and PH) was observed for the APPS–P system. However, APPS–N systems exhibited a higher number of basic sites, especially when the $AlPO_4$ to sepiolite weight ratio was 3 (APPS–3–N).

3.4. Catalytic activity

The CSI process is used to test the strong surface acidity of APPS systems and hence to test their potential use of acid catalysts. The results show that acid sites on APPS systems are strong enough to produce skeletal isomerization more efficiently than both natural sepiolite or pure $AlPO_4$ catalysts.

The catalytic runs have been carried out in the absence of diffusional influences (boundary layer, internal and external mass transfer processes) through the choice of the suitable operating variables, especially space velocity (changing the catalyst weight and the carrier gas flow) and particle size. Furthermore, the amount of catalyst corresponded to a similar area loaded in the reactor. The catalytic runs have also been carried out at different weight ratios of catalyst from the CH introduced, showing that the fractional

TABLE II Pore size distributions of $AlPO_4$–sepiolite catalysts

Catalyst	Distribution (vol %)					
	> 30 nm	20–30 nm	10–20 nm	5–10 nm	2–5 nm	< 2 nm
APPS–3–P	11.8	10.0	18.8	39.0	19.8	0.6
APPS–3–N	14.1	10.5	19.2	37.0	17.5	1.7
APPS–1–N	25.3	13.0	22.6	30.2	7.9	0.9
AP–P	3.2	3.9	6.1	18.1	54.7	13.9
AP–N	1.3	3.3	8.1	32.6	50.2	4.6
PS	45.3	15.6	9.1	13.8	9.5	6.6

TABLE III Acid and basic properties of $AlPO_4$–sepiolite catalysts

Catalyst	Acidity[a]							Basicity[a]	
	PY		AN					AA	PH
	473 K	573 K	473 K	523 K	573 K	623 K	673 K	473 K	473 K
APPS-3-P	168	45	67	48	36	15	5	457	102
APPS-3-N	105	33	46	31	18	5	3	524	217
APPS-1-N	112	47	69	53	39	15	5	540	147
AP-P	185	23	63	17	9	2	1	528	255
AP-N	81	23	21	7	2	1	< 1	495	186
PS	83	38	48	14	7	2	1	363	92

[a]All values in $\mu mol\,g^{-1}$.

conversion of reactant to products was independent of the pressure, which determined the first-order reaction process. This behaviour also ensured linear chromatography in the pulse mode, i.e. ensuring equilibrium chromatography.

Side reactions such as dehydrogenation, cracking or thermal isomerization were not observed. No significant change in either isomerization activity or selectivity was observed with pulse number.

In the absence of mass transfer processes, the conversion of CH to 1-, 3- and 4-MCP (which was maintained below 10% level) followed the requirements of Bassett–Habgood kinetic treatment [43] for first-order kinetic processes in which the rate determining step is the surface reaction

$$\ln\left[1/(1 - X)\right] = RT\,kK\,(W/F)$$

where X is the total conversion, k the rate constant of surface process, K the adsorption constant of CH on the catalyst, W the catalyst weight and F the flow rate of carrier gas.

For all $AlPO_4$–sepiolite catalysts, Table IV compiles apparent rate constants, kK, at a reaction temperature of 673 K from linear plots of $\ln\left[1/(1 - X)\right]$ against F^{-1}, apparent activation energies, E_a, and preexponential factors, $\ln A$, from linear plots $\ln kK$ against T^{-1} and kinetic selectivity factor, σ, to 1-MCP. Table IV also includes activation enthalpies, $\Delta H^{\neq}$ and activation entropies, $\Delta S^{\neq}$, obtained through the Eyring equation by plotting $\ln kK/T$ against T^{-1}. Apparent rate constants and activation parameters previously obtained for untreated sepiolite [25] and $AlPO_4$ [4, 5] catalysts are also included in Table IV.

A least squares regression analysis shows, in all cases, correlation coefficients over 0.99. A t-test of significance, performed on the regression coefficients, shows that these are significant at levels over 1%. This is a measurement of data fit, in all experimental conditions, by the linear plots of $\ln\left[1/(1 - X)\right]$ against F^{-1}, $\ln kK$ against T^{-1} and $\ln kK/T$ against T^{-1}. All values are reproducible to within about 8%.

The results of the catalytic tests shows a considerable increase in activity for APPS catalysts in relation to $AlPO_4$ or natural sepiolite. Thus, preparation of APPS–P systems results in an increase in the activity to isomerize CH, about three times higher than that for the starting AP–P catalyst. However, the preparation of APPS–N systems results in a greater increase in activity. Thus, when the $AlPO_4$ to sepiolite weight ratio is 3, the activity of the APPS-3-N catalyst surpasses the AP–N one by a factor of five while, when the $AlPO_4$ to sepiolite weight ratio is 1, this factor becomes nine times higher.

Unlike natural sepiolite, with APPS catalysts there was a negligible loss of activity with prolonged use of the catalyst. Dehydrogenation at benzene and cyclohexadienes was also not found.

As CSI needs strong acidity, the APPS-1-N system must be the most active catalyst which is what really occurs through the adsorption (at every different temperature) of the strongest organic base used (AN) and thus, the changes in activity are similar to the changes in the acidic characteristics shown in Table III. The catalytic activity of APPS catalysts thus correlates well with the surface acidity measured gas-chromatographically.

On the other hand, as significant changes in the apparent rate constants do not result in changes in the activation energy, the nature of the active sites involved in the CSI on $AlPO_4$–sepiolite catalysts is the

TABLE IV Apparent rate constants at 673 K (kK), activation parameters (E_a, $\ln A$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$) and selectivities to 1-MCP (σ) for cyclohexene skeletal isomerization on $AlPO_4$, sepiolite and $AlPO_4$–sepiolite catalysts

Catalyst	$kK\ 10^6$ ($mol\,atm^{-1}\,g^{-1}\,sec^{-1}$)	Arrhenius equation		Eyring equation		σ^b
		E_a ($K\,cal\,mol^{-1}$)	$\ln A^a$	$\Delta H^{\neq}$ ($K\,cal\,mol^{-1}$)	$\Delta S^{\neq}$ ($cal\,mol^{-1}\,K^{-1}$)	
APPS-3-P	32.9	13.5	−0.2	12.4	−62.3	2.6
APPS-3-N	16.6	14.2	−0.4	13.0	−62.8	2.7
APPS-1-N	28.9	14.8	0.6	13.6	−60.8	2.7
AP-P	10.9	11.7	−2.6	10.6	−67.2	1.9
AP-N	3.1	14.6	−1.7	13.4	−65.5	1.4
PS	7.3	15.4	−0.3	14.2	−62.6	1.9

[a]A is expressed in $mol\,atm^{-1}\,g^{-1}\,sec^{-1}$.

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

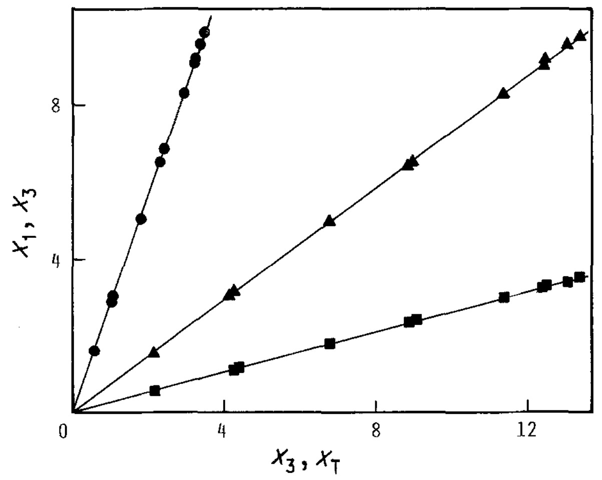

Figure 2 OPE curves [X_1 (▲) and X_3 (■) plotted against X_T] and Wheeler selectivity X_1 against X_3 (●) for the APPS-1-N catalyst.

same. The differences observed in activity are, therefore, due to differences in the total number of active sites.

This implies that only a small fraction of the acid sites is active in the CSI reaction, since a wide range of acid sites of varying strengths can be seen by the titration method.

Furthermore, the negative values of $\Delta S^{\neq}$ indicate that, on going from the ground state to the transition state, an extensive restriction must be considered. This highly ordered transition state is consistent with a reaction mechanism whose slowest step is the stabilization and immobilization of reactant molecules on catalyst acid active sites. In Table IV we can also see that $\Delta S^{\neq}$ changes slightly with respect to the catalyst. The reaction on AP-P, AP-N, PS, APPS-P and APPS-N catalysts can be considered entropy controlled since $T\Delta S^{\neq}$ is always higher than $\Delta H^{\neq}$. An approximately constant $\Delta G^{\neq}$ value is found in all cases.

3.4.1. Selectivity

With regard to the selectivity of the reaction, the amount of 1-MCP was always higher than that of 3-MCP and, unlike natural sepiolite, slight amounts of 4-MCP were found. Furthermore, the main reaction products (1- and 3-MCP) are primary stable competitive products coming from CH through parallel reactions since straight lines passing through the origin are obtained from the optimum performance envelope (OPE) curves [44, 45] (which describe the selectivity behaviour of products) as well as from the application of the Wheeler criterion [46] on the kinetic selectivity factor, σ, as shown in Fig. 2.

As reaction products are primary and competitive, they are formed at a constant rate in relation to feed conversion, and neither disappear nor accumulate due to secondary products. A primary product is defined as that which is produced from the reactant no matter how many intermediates are involved in its formation.

The selective factors, σ, obtained from the slopes of the plots X_1 against X_3, appeared in column seven of Table IV. As can be seen, the selectivity factors also increase with APPS catalysts, although no one difference between APPS-P and APPS-N is found. These changes in σ (two times higher), however, are smaller than those for activity.

As activities at different temperatures adjust to the same Wheeler's plot for every catalyst and, despite the differences in surface area of the catalysts, the virtually identical values of apparent activation energy of the test reaction and the trends of the dependence of the catalytic activity on the catalyst acidity indicated that in all cases the reaction proceeds on catalytic centres of the same kind. So, different σ values are due to the different A_1 to A_3 ratios according to

$$\sigma = K_1/K_3 = X_1/X_3$$
$$= [A_1 \exp(E_a/RT)]/[A_3 \exp(E_a/RT)] = A_1/A_3$$

3.4.2. Reaction network

The primary products (1- and 3-MCP) observed can be accounted for by initial formation of the cyclohexyl carbenium ion (through the chemisorption of CH on the catalyst acidic sites) that further rearranges to the 1- and 2-methycyclopentyl carbenium ions which then desorb as 1- and 3-MCP, as has been described elsewhere for $AlPO_4$ [4, 5] and sepiolite [25] catalysts.

However, the existence of a carbocationic character of the carbenium ion intermediates for APPS catalysts higher than for either pure $AlPO_4$ or natural sepiolite accounts for the experimental results.

The relative proportion of two isomers (1- and 3-MCP) is a reflection of the relative stabilities of the parent ions: 1-methylcyclopentyl is a tertiary ion, whereas 2-methylcyclopentyl is secondary. In this sense, Viruela-Martin *el al.* [47] optimize the tertiary 1-methylcyclopentyl carbeniun ion by MINDO/3 and its energy is 15.2 kcal mol^{-1} below the 2-methylcyclopentyl carbeniun ion.

The scope of the reactions that can be catalysed by these solid acids are currently under investigation. Thus, they act as catalysts in the alkylaromatic (α-series) cracking as well as in the alkylation of toluene with methanol [48].

4. Conclusions

In summary, our results have shown that $AlPO_4$ can be used as a promoter of natural sepiolite. Thus, the addition of sepiolite to $AlPO_4$ results in an increase in surface area, pore volume and the main pore radius of those systems obtained in aqueous ammonia (APPS-N), due to the inhibition of $AlPO_4$ crystallization which is observed, in the absence of sepiolite, for calcination temperatures of 873 K.

The preparation of any APPS catalyst also strengthens the solid acidity of both $AlPO_4$ and natural sepiolite. So, APPS-P and APPS-N catalysts show an increased catalytic activity and selectivity to 1-MCP for the CSI process, also exhibiting lower deactivation by coke deposition. The strongest differences are observed for systems obtained in aqueous ammonia and containing an $AlPO_4$ to sepiolite weight ratio of 1.

Furthermore, it can be concluded that activity and selectivity in the CSI process can be relatively well interpreted in terms of the acid properties of the catalysts determined gas-chromatographically through adsorption of organic bases at different temperatures.

The gas-chromatographic technique allows the determination of acidity distributions under conditions close to those employed in catalytic processes, making it possible to relate acidity to the catalytic activity.

Acknowledgements

The authors would like to gratefully acknowledge TOLSA S.A., for providing the sepiolite sample. Thanks are also due to Direccion General de Investigacion Cientifica y Tecnica, Ministerio de Educacion y Ciencia, España (Grant-in-aid for Scientific Research, project PA86-0065). The authors also wish to acknowledge the grammatical revision of the manuscript carried out by Professor M. Sullivan.

References

1. M. A. ARAMENDIA, J. M. CAMPELO, S. ESTEBAN, C. JIMENEZ, J. M. MARINAS and J. V. SINISTERRA, *Rev. Mex. Petrol.* **12** (1980) 61.
2. J. M. CAMPELO, A. GARCIA, D. LUNA and J. M. MARINAS, *Can. J. Chem.* **61** (1983) 2567.
3. J. M. CAMPELO, J. M. MARINAS, S. MENDIOROZ and J. PAJARES, *J. Catal.* **101** (1986) 484.
4. J. M. CAMPELO, A. GARCIA, J. M. GUTIERREZ, D. LUNA and J. M. MARINAS, *J. Colloid Interface Sci.* **95** (1983) 544.
5. J. M. CAMPELO, A. GARCIA, D. LUNA and J. M. MARINAS, *J. Catal.* **111** (1988) 106.
6. *Idem*,, *ibid.* **102** (1986) 299.
7. *Idem.*, in "Preparation of Catalysts IV" (Elsevier, Amsterdam, 1987) p. 199.
8. J. M. CAMPELO, J. M. MARINAS and R. PEREZ-OSSORIO, *An. Quim.* **74** (1978) 86.
9. J. M. CAMPELO and J. M. MARINAS, *Afinidad* **38** (1981) 333.
10. J. M. CAMPELO, A. GARCIA, D. LUNA and J. M. MARINAS, *Mater. Phys.* **24** (1989) 51.
11. *Idem., J. Colloid Interface Sci.* **118** (1987) 98.
12. *Idem., Bull. Soc. Chim. Fr.* (1988) 283.
13. *Idem., J. Chem. Soc., Faraday Trans I* **85** (1989) 2535.
14. A. BLANCO, J. M. CAMPELO, A. GARCIA, D. LUNA, J. M. MARINAS and M. S. MORENO, *Appl. Catal.* **53** (1989) 135.
15. K. BRAUNER and A. PREISINGER, *Tschermaks Miner. Petrog. Mitt.* **6** (1956) 120.
16. R. H. S. ROBERTSON, *Chem. Ind.* (1957) 1492.
17. *Idem., Silicates Industriels* **38** (1973) 33.
18. J. M. GARCIA-SEGURA, C. CID, J. MARTIN DE LLANO and J. G. GAVILANES, *British Polym J.* **19** (1987) 517.
19. A. J. DANDY and M. S. NADIYE-TABBIRUKA, *Clays Clay Miner.* **30** (1982) 347.
20. M. N. FERNANDEZ-HERNANDEZ and T. FERNANDEZ-ALVAREZ, *An. Quim.* **79** (1983) 342.
21. F. REY-BUENO, M. VILLAFRANCA-SANCHEZ, E. GONZALEZ-PRADAS and J. D. LOPEZ-GONZALEZ, *ibid.* **81B** (1985) 18.
22. M. VILLAFRANCA-SANCHEZ, E. GONZALEZ-PRADAS, J. D. LOPEZ-GONZALEZ and F. REY-BUENO, *ibid.* **81B** (1985) 158.
23. M. VILLAFRANCA-SANCHEZ, A. VALVERDE-GARCIA, E. GONZALEZ-PRADAS and F. REY-BUENO, *ibid.* **83B** (1987) 151.
24. E. GONZALEZ-PRADAS, A. VALVERDE-GARCIA, M. VILLAFRANCA-SANCHEZ and F. REY-BUENO, *ibid.* **83B** (1987) 162.
25. J. M. CAMPELO, A. GARCIA, D. LUNA and J. M. MARINAS, *Reactiv. Solids* **3** (1987) 263.
26. H. PINES, in "The Chemistry of Catalytic Hydrocarbon Conversions" (Academic Press, New York, 1981) p. 9.
27. J. D. LOPEZ-GONZALEZ, A. RAMIREZ-SAENZ, F. RODRIGUEZ-REINOSO, C. VALENZUELA-CALAHORRO and L. ZURITA-HERRERA, *Clay Miner.* **16** (1981) 103.
28. J. L. BONILLA, J. D. LOPEZ-GONZALEZ, A. RAMIREZ-SAENZ, F. RODRIGUEZ-REINOSO and C. VALENZUELA-CALAHORRO, *ibid.* **16** (1981) 173.
29. F. RODRIGUEZ-REINOSO, A. RAMIREZ-SAENZ, J. D. LOPEZ-GONZALEZ, C. VALENZUELA-CALAHORRO and L. ZURITA-HERRERA, *ibid.* **16** (1981) 315.
30. L. GONZALEZ-HERNANDEZ, L. IBARRA-RUEDA, A. RODRIGUEZ-DIAZ and C. CHAMORRO-ANTON, *Angew. Makromol. Chem.* **103** (1982) 51.
31. L. GONZALEZ-HERNANDEZ, L. IBARRA-RUEDA, A. RODRIGUEZ-DIAZ, J. S. MOYA and F. J. VALLE, *Clay Miner.* **19** (1984) 93.
32. L. GONZALEZ-HERNANDEZ, L. IBARRA-RUEDA, A. RODRIGUEZ-DIAZ and C. CHAMORRO-ANTON, *J. Colloid Interface Sci.* **109** (1986) 150.
33. A. CORMA, J. PEREZ-PARIENTE, V. FORNES and A. MIFSUD, *Clay Miner.* **19** (1984) 673.
34. A. CORMA and J. PEREZ-PARIENTE, *Clay Miner.* **22** (1987) 423.
35. S. BRUNAUER, P. H. EMMETT and E. TELLER, *J. Amer. Chem. Soc*, **60** (1938) 309.
36. E. P. BARRET, L. G. JOYNER and P. HALENDA, *ibid.* **73** (1951) 373.
37. A. LECLOUX and J. PIRARD, *J. Colloid Interface Sci.* **70** (1979) 265.
38. A. PREISINGER, *Clays Clay Miner.* **10** (1963) 365.
39. S. BRUNAUER, L. S. DEMING, W. S. DEMING and E. TELLER, *J. Amer. Chem. Soc.* **62** (1940) 1723.
40. A. V. KISELEV and Y. I. YASHIN, in "Gas Adsorption Chromatography" (Plenum, New York, 1969).
41. V. R. CHOUDHARY and L. K. DORAISWAMY, *Ind. Eng. Chem. Prod. Res. Dev.* **10** (1971) 218.
42. A. K. GOSH and G. CURTHOYS, *J. Chem. Soc., Faraday Trans I*, **79** (1983) 2569.
43. D. BASSETT and H. W. HABGOOD, *J. Phys. Chem.* **64** (1960) 769.
44. D. BEST and H. W. WOJCIECHOWSKI, *ibid.* **47** (1977) 11.
45. A. N. KO and H. W. WOJCIECHOWSKI, *Int. J. Chem. Kinet.* **15** (1983) 1249.
46. A. WHEELER, *Adv. Catal.* **3** (1951) 250.
47. P. M. VIRUELA-MARTIN, I. NEBOT, R. VIRUELA-MARTIN and J. PLANELLES, *J. Chem. Soc., Perkin Trans* **II** (1986) 1053.

Received 20 March
and accepted 4 September 1989