$AlPO_4$-catalyzed Diels–Alder reaction of cyclopentadiene with (−)-menthyl acrylate. Influence of catalyst surface properties

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Different synthetic $AlPO_4$ systems are effective yet mild acid catalysts for the heterogeneous cycloaddition reaction of cyclopentadiene with (−)-menthyl acrylate. The reaction proceeds selectively under mild conditions and in a relatively short reaction time with an almost total conversion, a high endo/exo ratio, and a reasonable asymmetric induction. When the reactions are carried out without solvent, some correlations are obtained between the number of acid sites, titrated with pyridine, and reaction yields, endo/exo and diastereofacial selectivities. The positive influence of surface area of catalysts is also determined. However, the lack of good correlations between reaction results and surface properties of the catalysts indicates the influence of some other factors.

Keywords: $AlPO_4$ catalysts; Diels–Alder reaction; asymmetric induction; heterogeneous cycloaddition reaction

1. Introduction

In the last years considerable progress has been made in the asymmetric Diels–Alder cycloaddition reaction so that this reaction still remains one of the most common standard procedures for asymmetric six-membered ring formation [1–4]. Despite the increasing number of efficient asymmetric Diels–Alder reactions achieved between prochiral 1,3-dienes and several enantiomerically pure dienophiles catalyzed by Lewis acids, the disposal of environmentally hazardous residues generated by the use of this homogeneous catalysis methodology has its drawbacks. The use of solid acids as heterogeneous catalysts may be an interesting alternative to overcome these problems. Thus, magnesium silicate [5], silica gel [5,6], alumina [7–11], zeolites [12–15], and clays [16–29], and silica and alumina modified by Lewis acids [30,31] have been recently reported as good catalysts in Diels–Alder reactions.

Among the various chiral dienophiles studied in this field, acrylic acid derivatives have been shown to be an important key for the total synthesis of a variety of natural products [1–4]. In this respect, by using these heterogeneous catalysts [25–27], the best asymmetric inductions (about 55% diastereomeric excess, de) have been obtained in the clay-catalyzed (cation-exchanged K10 montmorillonites) reactions of (−)-menthyl acrylate and (R)-O-acryloyl pantolactone with cyclopentadiene. However, results very recently obtained [32] showed that amorphous $AlPO_4$ is a more efficient catalyst than clay. In particular, 74% de was obtained in the reaction of cyclopentadiene with (−)-8-phenylmenthyl acrylate which constitutes the highest asymmetric induction described to date for a solid-catalyzed Diels–Alder reaction of a chiral acrylate.

With regard to this, in a number of papers on $AlPO_4$ and $AlPO_4$–Al_2O_3 catalysts dealing with the relation between surface chemistry and catalytic properties, we have shown that they are bifunctional catalysts whose surface acid and basic sites enable them to be used in the field of selective organic synthesis. Thus, we have described their use for a number of organocationic reactions in gas phase such as cyclohexene skeletal isomerization (CHSI) [33,34] or in the field of selective synthetic chemistry which involves acid- and base-catalyzed reactions. Thus, we have previously reported their use as catalysts for base-catalyzed condensations: in Knoevenagel condensation in a dry medium [35] and in the liquid-phase retroaldolization of diacetone alcohol [36], as well as for the liquid-phase acid catalyzed tetrahydropyranylation of alcohols and phenols [37]. Regioselective ring-opening of 2,3-epoxy esters [38] was also described. Furthermore, synthetic $AlPO_4$ and $AlPO_4$–Al_2O_3 have also been used as metal supports in the liquid-phase hydrogenation of the double bond of olefins bearing a variety of organic functions [39–41].

The structural similarity between SiO_2 and $AlPO_4$ makes the latter useful as catalytic material where the surface Al^{3+} and phosphorous cations act as Lewis acid sites, Brønsted acidity is due to the protons attached to

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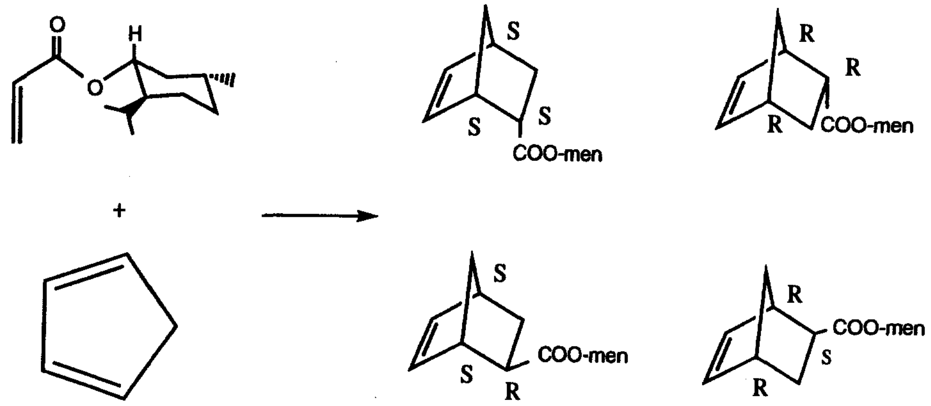


Scheme 1.

exposed oxygen and the basic sites are due to the surface O^{2-} groups produced by the dehydration reaction between adjacent OH groups [42,43]. Consequently, the surface concentration of acid-basic sites, and hence the catalytic activity of $AlPO_4$ systems, depend markedly on a number of variables such as preparation methods, here including the precipitation medium used (ammonia, ethylene or propylene oxide) [44] and starting aluminum salt [33], thermal treatments [33,45], doping ions [45–49], or different P : Al ratio obtained by preparing different $AlPO_4$–Al_2O_3 systems [34,50]. In this sense, Al_2O_3 is the most effective oxide to considerably improve thermal stability, surface acidity and, hence, the catalytic performance of $AlPO_4$ catalysts [34,51].

In order to get information about the nature of the surface active sites of catalysts in this synthetically important process, we report in this paper on the results obtained in the benchmark asymmetric Diels–Alder reaction of (−)-menthyl acrylate with cyclopentadiene (scheme 1). Reactions were carried out in methylene chloride as well as in the absence of solvent, using a number of different $AlPO_4$ and $AlPO_4$–Al_2O_3 catalysts, with widely varying acid site numbers and acid–base character.

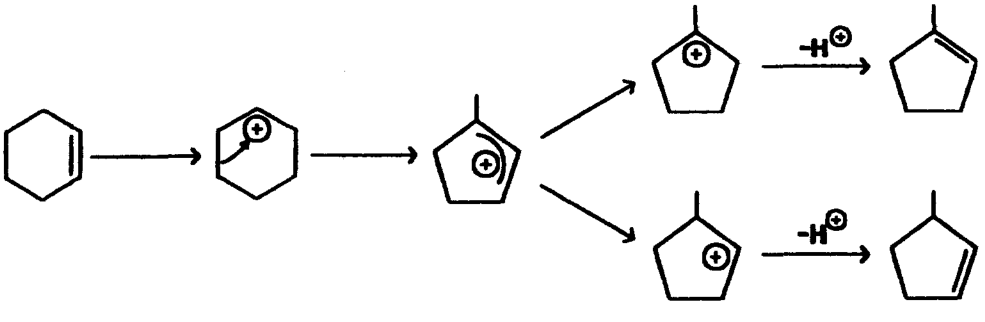
Acid–base properties of these catalysts are determined not only by titration with different molecules (pyridine and benzoic acid) using a spectrophotometric method [44,46,47], but also by using the gas-phase skeletal isomerization of cyclohexene to 1- and 3-methylcyclopentene [33,34,44–51], CHSI (scheme 2), one of the simplest model reactions recommended as the best method in studying stronger acid sites on solid catalysts [52,53].

The results obtained in the Diels–Alder reactions, carried out with and without a solvent, are analysed in the light of the properties of the catalysts. Some correlation between surface acid–base properties and results obtained in the Diels–Alder reaction will address the changes in surface physicochemical properties arising from changes in different preparation conditions, calcination temperature, doping ions or alumina content more adequately to enable the preparation of a tailored $AlPO_4$ catalyst with most appropriate activity and stereoselectivity in asymmetric Diels–Alder reactions.

2. Experimental

2.1. Catalysts

Seventeen different solids have been used as catalysts. Three amorphous $AlPO_4$ (Al/P molar ratio = 1) were prepared from aqueous solution of aluminum chloride ($AlCl_3 \cdot 6H_2O$) and phosphoric acid (aqueous solutions 85 wt%), by precipitation at 0°C to an "end point" pH value of 6.1, using ammonium hydroxide solution



Scheme 2.

($AlPO_4$-A), ethylene oxide ($AlPO_4$-E) and propylene oxide ($AlPO_4$-P). Three $AlPO_4$–Al_2O_3 (75 : 25 wt%) systems ($AlPO_4$–Al_2O_3-A, -E and -P, respectively) were similarly obtained. Catalysts $AlPO_4$-A-N and $AlPO_4$-A-S are obtained by changing aluminum chloride for another aluminum salt such as $Al(NO_3)_3{\cdot}9H_2O$ or $Al_2(SO_4)_3{\cdot}18H_2O$, and using aqueous ammonia as the precipitation agent. Following the procedure previously described [33,34,51], precipitated solids were repeatedly washed with distilled water to completely avoid the possibility of contamination with the anion (Cl^-, NO_3^- or SO_4^{2-}) of the used salt. The resulting powders screened to < 0.149 mm were calcined at 650°C for 3 h. A commercial aluminophosphate ($AlPO_4$-C, Probus) was subjected to the same calcination treatment. As well, $AlPO_4$-P and $AlPO_4$-A-S were calcined for 3 h at 500°C and $AlPO_4$-A-S and $AlPO_4$-A-N also at 800°C thus obtaining the $AlPO_4$-P5, $AlPO_4$-A-S5, $AlPO_4$-A-S8 and $AlPO_4$-A-N8 systems respectively. The amorphous $AlPO_4$ containing 2 wt% doping ions ($AlPO_4$-P-F, -Li, -Na and -K, respectively) were prepared [45–49] from $AlPO_4$-P by impregnation until incipient wetness with aqueous solutions of ammonium fluoride or the corresponding alkali hydroxide, followed by drying at 100°C for 24 h and calcining at 300°C for 3 h.

2.2. Surface physico-chemical properties

Surface areas (S_{BET} in $m^2\ g^{-1}$) were determined by the BET method [54] from the adsorption–desorption isotherms of nitrogen at its liquid temperature, using a conventional volumetric apparatus. Results obtained are summarized in table 1, where the surface acidity and basicity of catalysts (monolayer coverage X_m at equilibrium at 25°C, in $\mu mol\ g^{-1}$) are also collected. These values were determined by a spectrophotometric method described elsewhere [44,46,47], that allows titration of the amount of irreversibly adsorbed pyridine (PY, $pK_a = 5.25$) or benzoic acid (BA, $pK_a = 4.19$) employed as titrant agents of acid and basic sites, respectively.

2.3. Gas-phase cyclohexene skeletal isomerization as model acid-catalyzed reaction

The apparent rate constant values (kK in $\mu mol\ atm^{-1}\ g^{-1}\ s^{-1}$) of different catalysts are also collected in table 1, because these values are another way of measuring the stronger acid sites [52,53]. The CHSI reaction was carried out in a microcatalytic pulse reactor according to the method described elsewhere [33,34,44–51]. The catalyst (20–100 mg, < 0.07 mm) was held by small plugs of Pyrex glass wool in the 4 mm diameter stainless steel reactor tube. The experiments were conducted at 400°C in nitrogen as carrier gas (30–60 ml min^{-1}) and the hydrocarbon pulse varied between 0.2 and 2.0 μl. The reaction products (1-, 3- and 4-methylcyclopentene) were analyzed by GC with flame ionization detection using two columns in series packed with Chromosorb G AW-DMCS 80/100 treated with 5 wt% of polyphenyl ether and 5 wt% squalane, respectively.

2.4. Catalyzed cycloaddition reaction between cyclopentadiene and (−)-menthyl acrylate

Reactions were carried out in Schlenk flasks. To a suspension of catalyst (1.00 g) in methylene chloride (10 ml) under argon atmosphere at 20°C, (−)-menthyl acrylate prepared according to the literature [55] (0.42 g, 2 mmol) and freshly distilled cyclopentadiene (0.396 g, 6 mmol) were added via a syringe, the flask was shaken and the reaction monitored by gas chromatography (cross-linked methyl silicone column 25 m × 0.2 mm

Table 1

Surface area, S_{BET} , acid–base properties and apparent rate constants at 400°C (kK) in cyclohexene skeletal isomerization of the different catalysts

Catalyst	S_{BET} ($m^2\ g^{-1}$)	Acidity vs. PY ($\mu mol\ g^{-1}$)	Basicity vs. BA ($\mu mol\ g^{-1}$)	$kK \times 10^6$ ($mol/(atm\ m^2\ s)$)
$AlPO_4$-A	174	212	298	3.3
$AlPO_4$-E	242	267	266	5.0
$AlPO_4$-P	228	228	166	3.2
$AlPO_4$-P5	146	201	150	19.5
$AlPO_4$-C	20	42	104	0.1
$AlPO_4$–Al_2O_3-A	244	187	535	15.0
$AlPO_4$–Al_2O_3-E	242	208	577	13.0
$AlPO_4$–Al_2O_3-P	319	326	774	18.0
$AlPO_4$-P-F	64	163	62	24.8
$AlPO_4$-P-Li	205	130	160	0.9
$AlPO_4$-P-Na	200	172	207	0.7
$AlPO_4$-P-K	208	190	293	0.6
$AlPO_4$-A-N	183	–	–	6.3
$AlPO_4$-A-N8	9	–	–	6.7
$AlPO_4$-A-S5	37	–	–	144.8
$AlPO_4$-A-S	22	–	–	81.6
$AlPO_4$-A-S8	18	–	–	2.8

Table 2
Results obtained with different catalyts in the reaction of cyclopentadiene with (–)-menthyl acrylate in CH_2Cl_2 at different reaction times

Catalyst	1 h			24 h		
	yield [a] (%)	endo/exo [a]	de [a,b] (%)	yield [a] (%)	endo/exo [a]	de [a,b] (%)
none	–	–	–	36.0	3.8	6.0
$AlPO_4$-A	98.9	14.4	43.8	–	–	–
$AlPO_4$-E	27.2	11.0	43.8	84.7	8.7	39.6
$AlPO_4$-P	9.5	–	–	73.2	5.3	14.5
$AlPO_4$-P5	95.9	12.9	45.0	–	–	–
$AlPO_4$-C	3.1	–	–	38.6	3.8	7.9
$AlPO_4$–Al_2O_3-A	35.4	12.3	45.3	78.3	6.9	33.3
$AlPO_4$–Al_2O_3-E	6.2	–	–	60.3	5.3	23.4
$AlPO_4$–Al_2O_3-P	5.8	–	–	42.3	4.7	23.0
$AlPO_4$-P-F	3.7	–	–	42.9	4.6	16.6
$AlPO_4$-P-Li	5.8	–	–	53.1	4.4	13.0
$AlPO_4$-P-Na	2.7	–	–	36.2	4.5	13.0
$AlPO_4$-P-K	34.7	13.4	45.9	96.7	13.0	45.2
$AlPO_4$-A-N	68.9	12.0	43.8	91.6	11.9	43.5
$AlPO_4$-A-N8	2.1	–	–	30.7	3.9	9.1
$AlPO_4$-A-S5	2.1	–	–	40.2	3.9	9.1
$AlPO_4$-A-S	3.2	–	–	42.5	3.9	9.1
$AlPO_4$-A-S8	1.6	–	–	22.7	4.2	9.1

[a] Determined by GC.
[b] (1R,2R,4R)-bicyclo[2.2.1]hept-5en-2-carboxylate of (–)-menthol is the major cycloadduct.

× 0.33 μm, helium as carrier gas 19 psi and programmed oven temperature) using the previously described procedure [25,26], which also allows determination of the absolute configuration of the major cycloadduct (table 2).

In the reactions carried out in the absence of solvent the same amounts of reagents and 2 g of catalyst were used, the flask was shaken at 20°C for 24 h, the catalyst repeatedly washed with methylene chloride, and the reaction monitored in a similar way. The results obtained are collected in table 3.

3. Results and discussion

According to the results in table 1, the surface properties of $AlPO_4$ are largely influenced by the method of preparation (gelation agent and temperature of treatment further to preparation), the use of additives, such as cations (Li, Na or K), anions (F) or metal oxide (Al_2O_3) and the nature of the aluminum starting salt. Thus, aluminum nitrate and aluminum chloride yielded materials with higher surface area and low activity in CHSI than aluminum sulphate. Apparently the aluminum starting salt plays and important role in the final properties of catalysts.

Table 1 also shows that incorporation of Al_2O_3 or F anion to $AlPO_4$ systems is always accompanied by an increase in the number of strong acid sites in catalysts, according to the important increase in catalytic activity in the CHSI process. Besides, acid sites of moderate strength titrated with pyridine do not experience an appreciable change while basic sites increase in $AlPO_4$–Al_2O_3 systems and decrease in the $AlPO_4$-P-F. The presence of cations in $AlPO_4$ catalysts leads to a noticeable decrease in CHSI which indicates an important lowering in strong acid sites.

In this respect, these solids with very different surface acid–base properties lead to very different results in the reaction of cyclopentadiene with (–)-menthyl acrylate carried out in methylene chloride (table 2). The catalytic effects are not only related to changes in conversion,

Table 3
Results obtained with different catalyts in the reaction of cyclopentadiene with (–)-menthyl acrylate in the absence of solvent

Catalyst	Yield [a] (%)	Endo/exo [a]	de [a,b] (%)
none	72.5	3.0	4.1
$AlPO_4$-A	100.0	13.8	34.4
$AlPO_4$-E	98.9	14.1	37.5
$AlPO_4$-P	99.1	12.4	35.4
$AlPO_4$-P5	99.6	15.2	36.5
$AlPO_4$-C	67.3	4.0	18.0
$AlPO_4$–Al_2O_3-A	99.3	10.1	35.7
$AlPO_4$–Al_2O_3-E	98.9	7.7	28.6
$AlPO_4$–Al_2O_3-P	94.4	8.8	31.3
$AlPO_4$-P-F	99.4	10.3	28.3
$AlPO_4$-P-Li	73.9	6.5	24.5
$AlPO_4$-P-Na	100.0	9.4	33.3
$AlPO_4$-P-K	100.0	16.0	38.6
$AlPO_4$-A-N	100.0	15.2	38.5
$AlPO_4$-A-N8	61.4	3.2	11.1
$AlPO_4$-A-S5	58.7	2.1	14.5
$AlPO_4$-A-S	68.3	4.8	22.1
$AlPO_4$-A-S8	46.6	3.3	16.0

[a] Determined by GC at 24 h.
[b] (1R,2R,4R)-bicyclo[2.2.1]hept-5en-2-carboxylate of (–)-menthol is the major cycloadduct.

but mainly to endo/exo and diastereofacial selectivities. In fact, the non-catalyzed reaction takes place in a reasonable extent, but with very low selectivities. Therefore, the highest endo/exo and diastereofacial selectivities are obtained in the most active catalysts, although different catalytic sites may lead to different selectivities. This behaviour is mainly due to the competence of the less selective non-catalyzed reaction, whose participation in the overall result increases for the less active catalysts.

With regard to the influence of the nature of the catalysts, several general facts must be emphasized. First of all, solids with a low surface area (namely AlPO$_4$-C, AlPO$_4$-A-N8, AlPO$_4$-A-S and AlPO$_4$-A-S8) do not catalyze the reaction, and results closely similar to those of the non-catalyzed reaction are obtained. The incorporation of alumina or any other additive worsens the catalysts with the only exception of K cation. Aluminum chloride is the best starting salt and ammonia the best precipitation agent. In particular, AlPO$_4$-A and AlPO$_4$-P5 are excellent catalysts, leading to almost overall conversion in only 1 h with excellent selectivities. The best endo/exo (about 96 : 4) and diastereofacial (about 45% de) selectivities obtained are close to those obtained with other homogeneous and heterogeneous catalysts at the same temperature.

Recently it has been shown that the results of some heterogeneously catalyzed Diels–Alder reactions can be improved by carrying them out in the absence of a solvent [56–58]. In view of these results, the "dry methodology" was incorporated to study the AlPO$_4$-catalyzed reaction of (–)-menthyl acrylate with cyclopentadiene. Conversions are in general increased, which also happens in the non-catalyzed reaction, and can be accounted for by the increase in concentrations of reagents. It is also important to note that conversions decrease, with regard to the non-catalyzed reaction, when solids of a very low surface area are used as catalyst. However, these solids lead to higher percentages of asymmetric induction in spite of the decrease in conversion, as compared to the non-catalyzed reaction. It can be concluded that these solids with low surface area are bad catalysts because their main effect is to dilute the reactant molecules. With the rest of catalysts of high surface area, with the only exception AlPO$_4$-P-Li, conversions near to 100% are obtained, so that differences are mainly shown by changes in selectivities.

In order to increase our knowledge about the potential influence of surface properties of solids on their catalytic behaviour in the Diels–Alder process studied, we built a correlation matrix using all the data in tables 1 and 3. The corresponding values of slopes and intercepts obtained in the regression analysis of those well correlated parameter pairs (significance higher than 90%) are collected in table 4.

Although the correlations are in general significant, the regression coefficients are rather poor ($r \geqslant 0.5$) when surface properties are directly correlated to reaction parameters of the cycloaddition reaction, so that the model so obtained represents only qualitatively the change in reaction results produced by the change in surface properties (entries 3–8 in table 4). However, better results are obtained when the logarithms of the cycloaddition results are correlated to the inverse of the number

Table 4

Results for the single regression models ($y = ax + b$) between the cyclohexene skeletal isomerization (CHSI) and some surface properties of catalysts (table 1) and the catalytic behaviour of these systems in the cycloaddition reaction of cyclopentadiene with (–)-menthyl acrylate in the absence of solvent (table 3)

Entry	y	x	a	b	r	Significance (%)
1	de	yield	0.404	−7.490	0.829	100
2	endo/exo	yield	0.200	−8.429	0.835	100
3	yield	S_{BET}	0.127	65.844	0.753	100
4	endo/exo	S_{BET}	0.021	5.336	0.531	97
5	de	S_{BET}	0.047	19.732	0.574	98
6	yield	acidity-PY	0.109	73.170	0.677	99
7	endo/exo	acidity-PY	0.026	5.560	0.502	90
8	de	acidity-PY	0.058	20.588	0.670	98
9	ln yield	CHSI/S_{BET}	−7.620	90.314	0.508	96
10	ln endo/exo	CHSI/S_{BET}	−1.783	9.731	0.497	95
11	ln de	CHSI/S_{BET}	−3.232	29.035	0.442	92
12	ln yield	BA/S_{BET}	−0.063	4.650	0.604	96
13	ln endo/exo	BA/S_{BET}	−0.223	2.695	0.707	99
14	ln de	BA/S_{BET}	−0.119	3.649	0.691	99
15	ln yield	1/acidity-PY	−20.424	4.674	0.835	100
16	ln endo/exo	1/acidity-PY	−55.943	2.675	0.763	100
17	ln de	1/acidity-PY	−33.826	3.665	0.846	100
18	ln yield	1/S_{BET}	−6.352	4.563	0.756	100
19	ln endo/exo	1/S_{BET}	−14.810	2.326	0.709	100
20	ln de	1/S_{BET}	−10.503	3.462	0.799	100
21	acidity-PY	S_{BET}	0.679	64.162	0.803	100
22	1/acidity-PY	1/S_{BET}	0.393	0.029	0.967	100

of acid sites titrated with pyridine (1/PY) as well as to the number of basic sites or strong acid sites per unit of support BET surface area (BA/S_{BET}, CHSI/S_{BET}, respectively), that is, to the surface density of basic or stronger acid sites [44].

Considering the negative slopes (*a* values in entries 9–20 in table 4) the correlation analyses clearly show the existence of a positive influence of the number of acid sites titrated with pyridine and the surface area of catalysts on the cycloaddition reaction results. By contrast, negative slopes obtained with the density of basic and strong acid sites indicate that they produce a lowering in cycloaddition reaction results by promoting some undesirable reactions. In this respect, negative slopes obtained between CHSI activity and Diels–Alder process may be explained by the action of a diene polymerization reaction. These oligomerization processes constitute a carbocationic process, such as the CHSI reaction (scheme 2) developed only on the stronger acid sites. Besides, a positive influence of the surface area of catalysts becomes also apparent through the corresponding correlations in table 4. However, this could be a consequence of the very narrow relationship obtained in these catalysts between the S_{BET} and the number of acid sites titrated with PY (entries 21 and 22 in table 4).

Thus, these correlations do not allow to reach quantitative conclusions, but they show that AlPO$_4$-solids with high surface area and high number of mild acid sites (those titrated with pyridine) perform the conditions to be a suitable catalyst in the Diels–Alder reaction. Strong acid sites, able to generate cations from cyclohexene, would promote the polymerization of the cyclopentadiene through a cationic mechanism and, in consequence, they disfavour the studied reaction.

The results obtained show that the problem is enough complex to point out the influence of some some other factors associated to the nature of acid sites. Thus, not only the Lewis or Brønsted nature of these sites, but also their "hard" or "soft" character must influence reaction results [59,60]. Some of these effects have been observed when the catalytic role of "clayzic" in Friedel–Crafts alkylations and acylations are compared [61,62].

In conclusion, several synthetic AlPO$_4$ catalysts obtained by using different preparation conditions are effective mild acid heterogeneous catalysts for the cycloaddition reaction of cyclopentadiene and chiral (–)-menthyl acrylate. In particular, the amorphous AlPO$_4$ catalyst obtained by precipitation from $AlCl_3 \cdot 6H_2O$ and H_3PO_4 aqueous solutions by addition of ammonia and calcined at 650°C for 3 h is the best catalyst studied here. Thus, by using these catalysts, the reaction proceeds selectively under mild conditions with an almost total conversion, a high endo/exo ratio, and a reasonable asymmetric induction without the formation of any by-product. Work-up is also reduced to an easy separation of the the catalyst by filtration, followed by removal of the solvent.

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