

Novel mesoporous silicoaluminophosphates as highly active and selective materials in the Beckmann rearrangement of cyclohexanone and cyclododecanone oximes

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Received 25 July 2007; revised 11 September 2007; accepted 11 September 2007

Abstract

Novel mesoporous silicoaluminophosphate molecular sieves with an MCM-41 type structure were synthesized and characterized using various techniques, including XRD, N₂ adsorption, DRIFT, TEM, and ²⁷Al, ²⁹Si, and ³¹P MAS NMR. The surface acidity of the materials was determined by using pyridine and 2,6-dimethylpyridine as probe molecules. The catalytic activity of the mesoporous silicoaluminophosphates in the Beckmann rearrangement of cyclohexanone and cyclododecanone oximes was investigated and compared under gas- and liquid-phase (conventional vs microwave-assisted heating) conditions. The mesoporous silicoaluminophosphate materials are extremely active and selective in both reactions, giving yields comparable to those obtained on aluminosilicates and zeolites in the case of the vapor-phase Beckmann rearrangement of cyclohexanone oxime and the microwave-assisted Beckmann rearrangement of cyclododecanone oxime, respectively. The materials were also highly reusable after reactivation in vapor-phase reactions, with an increase in selectivity to the oxime, although a decrease in the durability (expressed as lifetime at quantitative conversion of the oxime) was also found.

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Keywords: Heterogeneous catalysis; Mesoporous materials; Beckmann rearrangement; ϵ -Caprolactam; ω -Laurolactam

1. Introduction

The scope of molecular sieve catalysis was extended considerably by the discovery of ordered mesoporous materials of the M41S type by Mobil scientists in the early 1990s [1]. Nevertheless, the amorphous pore walls, weak acidity, and low hydrothermal stability of mesoporous aluminosilicates limit their use as catalysts [2,3]. Aluminophosphate (AIPO) and silicoaluminophosphate (SAPO) molecular sieves exhibit great structural and compositional diversity. The most widely studied group of AIPO and SAPO materials are microporous in nature. However, microporous AIPO and SAPO materials cannot be used as catalysts in reactions involving bulky molecules due to pore constraints. Larger pore mesoporous AIPO materials have

been synthesized by several groups [4–7] as well as relatively thermally stable metal-substituted mesoporous AIPO materials containing Ti, Co, Mg, Fe, Zr, and V [8–13]. The incorporation of Si in AIPO molecular sieves generates acidity, generating active materials for acid-catalyzed reactions. Interestingly, only a few studies dealing with the substitution of Si in the framework of mesoporous AIPOs have been reported to date [14–16].

Cyclic ketoximes, in particular cyclohexanone oxime (C-ox), can be rearranged in gas phase (200 to 475 °C) into the corresponding lactam in the presence of a solid acid [17–20]. In contrast, most of the ω -laurolactam (ω -l) preparation methods reported in the patent literature involve liquid-phase Beckmann rearrangements involving mineral acid catalysts [21–25] and anhydrides of organic sulfonic acids [26]; only a very few have been performed using solid acid catalysts [27–30]. Moreover, only a few research highlights have dealt with gas-phase Beckmann rearrangement of cyclododecanone oxime (Cdox)

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[31,32]. Mesoporous MCM-41 molecular sieves have been subjected to extensive study because of its potential use as a catalyst support [33], and they have been shown to be promising catalysts for the rearrangement of ketoximes [20,34,35]. Bifunctional AlPO nanoporous materials also have been used as catalysts in the synthesis of ϵ -caprolactam, allowing the production of hydroxylamine from air and ammonia on the AlPO redox sites, followed by reaction with cyclohexanone to create the oxime, which is then converted to ϵ -caprolactam on the AlPO acid sites [36].

On the other hand, microwave-assisted reactions have received a great deal of attention, because reactions under microwave irradiation are in general not only faster compared with the conventional heating reactions, but also potentially more efficient, cleaner, and safer. Further improvements also have been reported, combining both the advantages of different solid acids and microwaves, which can offer enhanced reaction rates, higher yields, and greater selectivity to the targeted product under milder reaction conditions [37,38].

Here we report the synthesis of mesoporous SAPO materials with high Si loading through the addition of aluminophosphate precursors to preformed mesoporous aluminosilicate MCM-41 phases. We have studied the influence of aluminophosphate content on the mesostructural ordering, textural properties, and surface acidity of the resulting SAPO materials. In addition to this, the Beckmann rearrangement of C-ox and Cdox in a vapor-phase reaction system using the mesoporous SAPO materials were performed. The temperature effect was correlated with oxime transformation, ϵ -caprolactam, and ω -laurolactam selectivity and the catalyst lifetime, to achieve optimal reaction conditions. Finally, in the case of Cdox conversion, results were compared with those obtained in the liquid phase (in conventional heating as well as under microwave irradiation) in toluene and chlorobenzene.

2. Experimental

2.1. Catalysts

A two-step procedure was used to prepare the SAPO materials at $[\text{SiO}_2 + \text{Al}_2\text{O}_3]/\text{AlPO}_4$ molar ratios between 2 and 6. The detailed preparation procedure was reported previously [39]. Al-MCM-41 (Si/Al = 30) mesoporous material and commercial microporous Beta25 zeolite (Si/Al = 12.5, Zeolyst) were also tested for comparative purposes. Samples were designated as SiAlP-*X*, where *X* = 6, 4.5, 3, or 2 is the $[\text{SiO}_2 + \text{Al}_2\text{O}_3]/\text{AlPO}_4$ molar ratio in the synthesis gel.

2.2. Cyclododecanone oxime synthesis

Cyclododecanone oxime was prepared from cyclododecanone by reacting it with hydroxylamine hydrochloride in a mixture of ethanol and pyridine under magnetically stirred reflux in a water bath for 30 min according to a general procedure reported in the literature [40].

Cyclododecanone is the most likely impurity in the final product either arising from incomplete reaction of the starting

materials or from hydrolysis of the product during the isolation steps. The oxime was recrystallized twice in ethanol before its use, to prevent the potential formation of this impurity. The purity was confirmed by GC-MS (see below).

2.3. Characterization

The elemental composition of the calcined samples was obtained by inductively coupled plasma (IRIS Intrepid Instruments, Thermo Electron Corporation). Powder X-ray diffraction patterns were recorded on a Siemens D-5000 diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.518 \text{ \AA}$), over a 2θ range from 1.8 to 10° (low angle), using a step size of 0.02° and a counting time of 1.2 s per step.

Nitrogen physisorption measurements were conducted on a Micromeritics ASAP 2000 instrument at -196°C . Samples were outgassed at 200°C for 24 h under vacuum ($p < 10^{-2} \text{ Pa}$) and analyzed later.

Transmission electron microscopy (TEM) images were recorded on a JEOL 2000-FX microscope operating at an accelerating voltage of 200 kV, with a structural resolution of 0.21 nm. The particles of the samples to be investigated were deposited directly on 3-mm holey carbon-coated copper grids. We achieved this by dipping the grid directly into the powder of the samples (to avoid contact with any solvent), and then blowing off the excess powder.

^{27}Al (pulse: 1 μs ; recycle delay: 0.3 s), ^{29}Si (pulse: 6 μs ; recycle delay: 600 s), and ^{31}P (pulse: 2.6 μs ; recycle delay: 6 s) magic-angle spinning (MAS) NMR spectra were recorded on a Bruker ACP-400 multinuclear spectrometer at 104.26, 79.45, and 161.98 MHz, respectively. Chemical shifts are given in ppm from $\text{Al}(\text{H}_2\text{O})_6^{3+}$, tetramethylsilane, and 85 wt% H_3PO_4 as the external standard references for Al, Si, and P, respectively.

2.4. Surface acidity measurements

Surface acidity was measured in a dynamic mode with a previously reported pulse chromatographic technique involving the gas-phase (300°C) adsorption of pyridine (Py, sum of Brønsted and Lewis acid sites) and 2,6-dimethyl pyridine (DMPy, Brønsted sites) as probe molecules [41].

The procedure used for the TPD of pyridine (Py-TPD) has been reported elsewhere [41]. Py-TPD experiments were performed in the $50\text{--}700^\circ\text{C}$ range after saturation of the sample, followed by purging in N_2 at 100°C for 1 h. Desorption was measured by a flame ionization detector (FID).

2.5. Catalytic reaction procedure

2.5.1. Vapor-phase Beckmann rearrangement of cyclohexanone and cyclododecanone oximes

The reactions were conducted in a vapor-phase continuous stainless-steel down-flow fixed-bed reactor (6 mm i.d.) surrounded by an electric heater. Temperatures ($325\text{--}475^\circ\text{C}$) were measured with an iron-constantan thermocouple placed in the middle of the catalyst bed, and the unit was operated at atmospheric pressure. The substrate (0.3 M C-ox in acetonitrile

or 0.1 M Cdox in toluene) was delivered at a set flow rate (30 or 50 $\mu\text{L min}^{-1}$ for cyclohexanone and cyclododecanone oximes, respectively) using a liquid syringe pump (KD Scientific Md. 100) and was vaporized before being passed through the catalyst bed in the presence of a flow of nitrogen carrier gas (50 mL min^{-1}). The catalyst charges (W) were small (usually ca. 0.05 g), retained by quartz wool at practically the center of the reactor. To prevent any condensation of reactant and products, all connections were heated at 275 °C. Blank runs at 475 °C showed that under the experimental conditions used in this work, thermal effects could be ignored. Moreover, benzene, xylenes, or other products related to the solvent reactivity were not detected under reaction conditions (0.05 g cat. at 475 °C).

The reaction products were sampled online every 25 min and analyzed by GC (HP-5890 II) using a capillary column (HP-101, 25 m \times 0.2 mm \times 0.2 μm). Product characterization was performed by GC–MS (HP 5800 gas chromatograph coupled with a VG AutoSpec high-resolution mass spectrometer) using products condensed in a cold trap. Reaction products of cyclohexanone oxime (C-ox) reaction were ϵ -caprolactam (ϵ -C), cyclohexanone (C), 2-cyclohexen-1-one (EN), 5-hexenenitrile (HN), and aniline (AN). ω -Laurolactam (ω -l), cyclododecanone (Cdone), and dodecanenitrile and 11-dodecenenitrile (CN) were found to be the reaction products of the cyclododecanone oxime (Cdox) reaction.

2.5.2. Liquid-phase Beckmann rearrangement of cyclohexanone and cyclododecanone oximes

2.5.2.1. Conventional heating experiments Liquid-phase experiments were performed following a procedure similar to that reported by Corma et al. [27]. A solution of oxime (100 mg) in chlorobenzene or toluene (20 mL, both from Aldrich) was stirred in the presence of 100 mg of catalyst in a 50 mL two-necked round-bottomed flask fitted with a reflux condenser and a septum for withdrawing samples. The reaction mixture was heated for 24 h at 130 °C (chlorobenzene) and 110 °C (toluene). Aliquots (ca. 0.5 mL) were removed from the reaction mixture, filtered, and then analyzed by GC using a HP-5890 series II gas chromatograph with FID fitted with a capillary column (HP-101, 25 m \times 0.2 mm \times 0.2 μm thickness). Selected samples were also analyzed by GC–MS (HP 5800 gas-chromatographic coupled with a VG AutoSpec high-resolution mass spectrometer) to identify the products.

2.5.2.2. Microwave-assisted experiments Experiments were performed in a Microwave CEM-Discover model with PC control and monitored by filtering a few drops of reaction mixture for analysis, as described above for the conventional heating experiments. A typical experiment was performed as follows: 20 mg oxime, 3 mL solvent (toluene or chlorobenzene), and 20 mg of catalyst were stirred and microwave-irradiated at 275 W for 15 min. A small aliquot from the resulting solution was extracted, filtered, and analyzed.

Table 1
Composition of the synthesis gel mixture and calcined SiAlP- X materials

Sample	Final gel mixture (mol% oxides)			Calcined materials (mol% oxides)		
	SiO ₂	Al ₂ O ₃	P ₂ O ₅	SiO ₂	Al ₂ O ₃	P ₂ O ₅
SiAlP-6	83.8	8.5	7.7	84.5	11.2	4.3
SiAlP-4.5	80.6	10.5	8.9	81.9	12.7	5.4
SiAlP-3	73.8	13.7	12.5	76.9	16.7	6.4
SiAlP-3(150) ^a	73.8	13.7	12.5	80.9	10.4	8.7
SiAlP-2	65.7	17.8	16.5	69.9	21.5	8.7

^a Prepared after hydrothermal treatment at 150 °C.

Table 2
Structural and textural properties of calcined SiAlP- X samples

Sample	d_{100} (Å)	a_0^a (Å)	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore size ^b (Å)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	WT ^c (Å)
Al-MCM-41 ^d	35	42	1047	23(3)	0.91	19
SiAlP-6	36	41	692	22(3)	0.55	19
SiAlP-4.5	36	41	603	21(4)	0.53	20
SiAlP-3	35	41	516	20(5)	0.51	21
SiAlP-3(150)	37	43	401	20(6)	0.39	23
SiAlP-2	32	38	321	18(7)	0.29	21

^a The lattice parameter a_0 is obtained by the formula $a_0 = 2d_{100}/\sqrt{3}$, where d_{100} is basal spacing from XRD patterns.

^b Pore size obtained from BJH analysis of nitrogen adsorption data (values in parentheses are the width at half-height (Å) of PSD curve).

^c WT is wall thickness, calculated as $\text{WT} = a_0 - \text{pore size}$.

^d (Si/Al = 30), included for comparative purposes.

3. Results and discussion

3.1. Properties of mesoporous silicoaluminophosphate material

Table 1 shows the molar composition of the final gel mixtures (expressed as Si, Al, and P oxide mol%) and the composition of the calcined SiAlP. The compositional data reveals that phosphorous was not completely incorporated into the solid in materials synthesized at 100 °C. The incorporation of phosphorous into the calcined solid improved at 150 °C for the SiAlP-3(150) material.

XRD patterns of calcined SiAlP-6 and SiAlP-4.5 materials are typical of MCM-41 mesostructure. As the AlPO_4 content increased, the mesostructural ordering of the samples deteriorated, as indicated by broadening and decrease in intensity of the XRD peaks. We attribute these changes to either partial loss of long-range structural ordering or formation of Al_2O_3 and/or AlPO_4 species within the mesopores [39].

With respect to the nitrogen sorption isotherms, all of the calcined samples exhibited type IV isotherms, typical of mesoporous materials. The textural properties of the samples are summarized in Table 2. The decrease in surface area, pore volume, and pore size as the AlPO_4 content increased can be attributed to the formation of Al_2O_3 and/or AlPO_4 species within the mesopores, which may partially block the pores of the mesostructure. Thus, the incorporation large amounts of aluminophosphate precursor disrupted the quality of the final

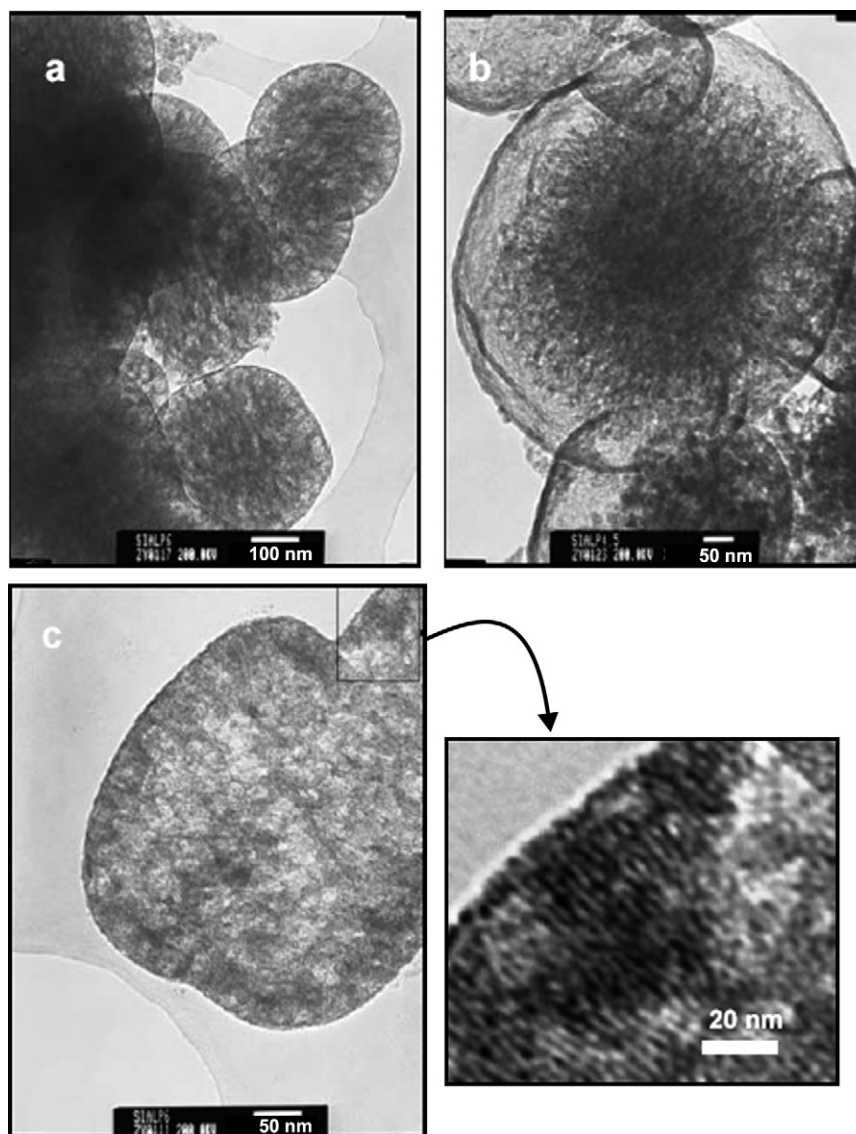


Fig. 1. TEM images of silicoaluminophosphates MCM-41: (a) SiAlP-6 (200 kV, $\times 100k$), (b) SiAlP-4.5 (200 kV, $\times 50k$), and (c) SiAlP-6 (200 kV, $\times 150k$).

SiAlP silicoaluminophosphate mesoporous materials, in good agreement with XRD results [39].

TEM images of calcined SiAlP-*X* samples (Fig. 1) showed a fairly homogeneous distribution of particles with spherical morphology. The spheres are typically 300–700 nm in size and are mainly standalone or loosely aggregated. Higher magnification of the images reveals the presence of well-ordered pore channels (Fig. 1c). Indeed, the TEM images imply the presence of a well-ordered hexagonal array of pores (Fig. 1c). The pore-to-pore distance obtained from the images is ca. 35 Å, in agreement with the d_{100} spacing from the XRD patterns (Table 2). The estimated pore size from the TEM images is ca. 20 Å, which is also very close to the pore size calculated from the porosity data (Table 2).

The local environment of Si, Al, and P atoms in the calcined SiAlP samples was studied by MAS NMR spectroscopy [39]. The peaks in the ^{29}Si MAS NMR spectra were very broad and similar to those of amorphous silica and M41S-type ma-

terials [42]. The ^{27}Al MAS NMR spectra of the hydrated calcined SiAlP samples were similar to those reported previously for mesoporous AIPOs [5,9] and mesoporous SAPOs [8,9,15]. There were two peaks in the ^{27}Al MAS NMR spectra of our SAPO samples, at ca. 37 ppm and -2.5 ppm. Finally, the ^{31}P MAS NMR of the calcined SiAlP samples showed a broad peak centered at ca. -23.5 ppm, which is assigned to tetrahedrally coordinated phosphorus [5,8,9,15,42].

The acidity of the samples (reported as $\mu\text{mol g}^{-1}$ of pyridine or 2,6-dimethylpyridine adsorbed at 300 °C) [41] is given in Table 3. As expected, the total acidity decreased with a decrease in the aluminophosphate content. Nevertheless, the number of Brönsted acid sites (DMPy adsorption) increased for the materials with higher aluminophosphate content. We also observed higher total acidity for the SiAlP samples compared with that of amorphous AIPO mesoporous materials previously reported by Campelo et al. [42]. The total acidity was lower than that of aluminosilicate MCM-41, decreasing at higher AIPO₄

Table 3
Surface acid properties and contributions to the total area for Py-TPD profiles of SiAIP-X materials

Catalyst	Titration at 300 °C		Py-TPD (area%)			
	Py ($\mu\text{mol g}^{-1}$)	DMPy ($\mu\text{mol g}^{-1}$)	$\sim 190^\circ\text{C}$	$\sim 310^\circ\text{C}$	$\sim 480^\circ\text{C}$	$\sim 610^\circ\text{C}$
Al-MCM-41	116	74	29	30	24	17
SiAIP-6	93	45	25	33	33	9
SiAIP-4.5	93	76	31	27	37	6
SiAIP-3	85	69	29	28	37	6
SiAIP-3(150)	43	40	41	37	17	5
SiAIP-2	77	71	22	34	38	5

content (Table 3). However, the surface area also decreased at higher AlPO_4 content, and thus the acid density [(μmol of Py adsorbed/g of catalyst)/(m^2 of surface area/g of catalyst)] was higher for our SiAIP silicoaluminophosphate materials ($0.13\text{--}0.24 \mu\text{mol m}^{-2}$) compared with both Al-MCM-41 ($\text{Si}/\text{Al} = 30$) ($0.11 \mu\text{mol m}^{-2}$) and amorphous mesoporous AIPO materials ($<0.13 \mu\text{mol m}^{-2}$). The higher density of the acid sites was expected to generate highly catalytically active materials.

Py-TPD profiles (Fig. 2) can be deconvoluted in four theoretical curves with four Gaussian peaks centered at ca. 190, 310, 480, and 610 °C. The lowest temperature peak (190 °C) could be attributed to weak acid sites, peaks at 310 and 480 °C could be attributed to moderate to strong acid sites, and the fourth peak centered at ca. 610 °C was due to strong acid sites. Analogous spectra were obtained for all SiAIP-X synthesized at 100 °C, showing a similar acidity distribution (area%; Table 3). Interestingly, the peaks centered at ca. 178 and 282 °C increased in contribution (area%), whereas peaks at ca. 436 and 605 °C decreased for SiAIP-3(150) (Fig. 2; Table 3). Mesoporous silicoaluminophosphates had a lower proportion of strong acid sites (peak centered at ca. 610 °C) compared with the Al-MCM-41 material ($\text{Si}/\text{Al} = 30$), in good agreement with Py and DMPy titration data (Table 3).

3.2. Vapor-phase Beckmann rearrangement

3.2.1. Synthesis of ϵ -caprolactam

The catalytic activity of the MCM-41 silicoaluminophosphates in the gas-phase Beckmann rearrangement of the cyclohexanone oxime was subsequently explored. The effect of the temperature in the cyclohexanone oxime conversion and selec-

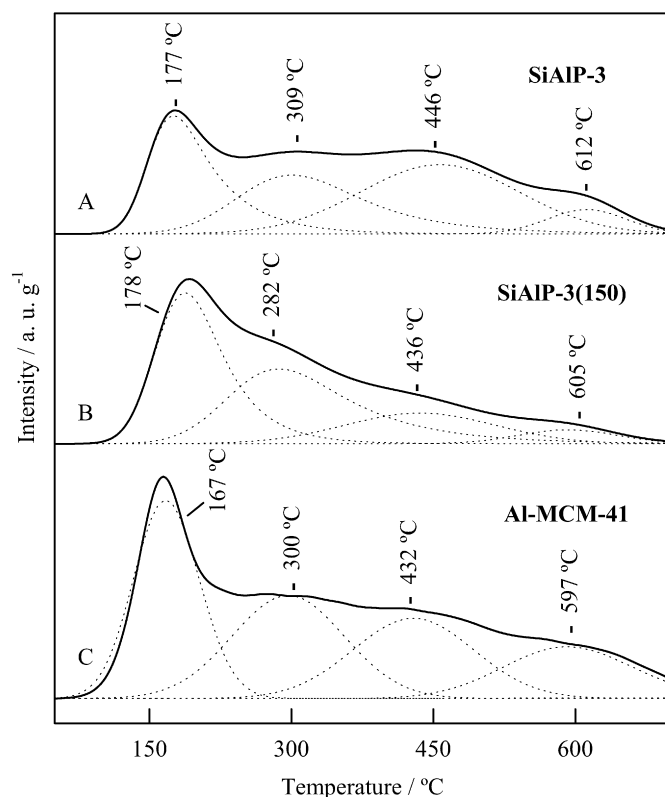


Fig. 2. Py-TPD profiles of (A) SiAIP-3, (B) SiAIP-3(150), and (C) Al-MCM-41 ($\text{Si}/\text{Al} = 30$) materials.

tivity to the different products was investigated at 400–450 °C using acetonitrile as the solvent. Results for SiAIP-4.5 are summarized in Table 4. In general, the initial activities were 100% for all materials. However, product distribution (S_i , mol%) and catalyst durability (defined as D , lifetime at $X_T = 100$ mol%) were strongly influenced by the reaction temperature. Thus, an increase in the temperature from 400 to 475 °C made the materials more active and selective to ϵ -caprolactam, due to the decreased formation of ϵ -caprolactam oligomers that frequently occurs at lower temperatures. Previous studies carried out by our group with aluminoborosilicate MCM-41 [20] demonstrated that a temperature of 425–450 °C was most advantageous for achieving optimum selectivity to ϵ -caprolactam. An increase in selectivity to cyclohexanone (S_C) was found at temperatures above 450 °C. Such behavior is in good agreement with results obtained for the mesoporous silicoaluminophos-

Table 4

Total conversion (X_T , mol%) product distribution (S_i , mol%) and durability (D , lifetime at $X_T = 100$ %), in the Beckmann rearrangement of C-ox at different temperatures using SiAIP-4.5 as catalyst^a

T (°C)	Time of reaction (12 h)							Time of reaction (18 h)							D (h)
	X_T	$S_{\epsilon\text{-C}}$	S_C	S_{EN}	S_{HN}	S_{AN}	S_P	X_T	$S_{\epsilon\text{-C}}$	S_C	S_{EN}	S_{HN}	S_{AN}	S_P	
400	100.0	76.5	4.8	5.9	2.6	6.4	3.8	40.7	67.3	3.6	10.9	12.9	3.3	2.0	12
425	100.0	76.3	5.4	5.5	5.1	5.2	2.5	100.0	78.9	4.8	6.1	3.9	4.5	1.8	24
450	100.0	79.9	7.3	5.4	3.5	3.9	–	100.0	82.0	5.8	5.3	3.1	3.8	–	31
475	100.0	73.0	13.6	6.0	2.8	4.6	–	100.0	80.3	9.6	4.7	1.3	4.1	–	43
475 ^b	100.0	79.8	9.3	4.9	1.7	4.3	–	100.0	84.3	6.5	4.4	1.4	3.4	–	35

^a Reaction conditions: $W/F = 92.8 \text{ gh/mol}$; 0.3 M C-ox in acetonitrile.

^b Catalyst regenerated by heating at 600 °C in air for 1 h.

Table 5
Product distribution (S_i , mol%) and durability (D , catalyst lifetime at 100 mol% conversion level) in the gas-phase Beckmann rearrangement of C-ox (at 450 °C) using various solid acid catalysts^a

Catalyst	Time on stream (12 h)						Time on stream (18 h)						D (h)
	$S_{\varepsilon-C}$	S_C	S_{EN}	S_{HN}	S_{AN}	S_P	$S_{\varepsilon-C}$	S_C	S_{EN}	S_{HN}	S_{AN}	S_P	
Al-MCM-41	63.2	8.1	10.7	8.3	3.5	6.2	66.3	7.1	10.2	6.4	4.0	6.0	27
SiAIP-6	71.8	7.6	7.6	5.3	6.3	1.4	67.0	7.4	11.2	6.6	6.5	1.3	29
SiAIP-4.5	79.9	7.8	5.4	3.9	3.0	–	82.0	5.4	5.4	3.1	4.1	–	31
SiAIP-3	81.0	6.5	5.8	3.1	3.6	–	85.2	5.4	5.4	3.0	1.0	–	30
SiAIP-3(150)	76.1	6.9	5.4	5.2	6.4	–	77.2	4.9	6.8	5.7	5.4	–	21
SiAIP-2	87.1	4.4	2.2	2.1	4.2	–	82.0	3.7	2.5	0.0	11.8	–	26
SiAIP-6 ^b	69.6	12.6	11.4	4.4	2.0	–	71.0	10.1	9.0	4.9	5.0	–	40
SiAIP-4.5 ^b	73.0	13.6	6.0	2.8	4.6	–	80.3	9.6	4.7	1.3	4.1	–	43
SiAIP-3 ^b	75.6	12.8	6.9	2.0	2.7	–	78.9	9.9	6.9	2.0	2.3	–	41

^a Reaction conditions: $W/F = 92.8$ g h/mol; 0.3 M C-ox in acetonitrile; X_T : 100%.

^b Reaction temperature: 475 °C.

phates in which temperatures below 475 °C favored the Beckmann rearrangement of cyclohexanone oxime, whereas the hydrolysis of cyclohexanone oxime to cyclohexanone was the main process at higher temperatures (Tables 4 and 5).

Material regeneration was carried out by calcination in air at 600 °C for 1 h. Regenerated samples exhibited a higher selectivity to ε -caprolactam, even though a decrease in catalyst durability was observed (Table 4). These observations can be correlated to the poisoning of active sites, oligomer adsorption on the catalyst surfaces, and/or formation of physisorbed coke on the materials surface that could not be removed completely after the reactivation in air. In this sense, previous results on aluminoborosilicate MCM-41 demonstrated the presence of carbonaceous species up to ca. 800 °C [20]. However, under those conditions, part of the silanols and hydroxyl bridges present on catalyst surface likely react to form siloxane bridges. If this were the case, then an improvement of the selectivity to the lactam could be expected, as could a serious decrease of the activity to the Beckmann rearrangement.

Table 5 summarizes the catalytic activities in the Beckmann rearrangement (conversion, product distribution, and durability) of the various silicoaluminophosphates samples at 450 °C. The SiAIP- X materials are highly active and selective (100% initial conversion, >70% selectivity to ε -caprolactam) in the reaction. Of note was the increase in the ε -caprolactam selectivity with increasing aluminophosphate precursor content in the materials (Fig. 3). However, these yields are still rather low for a commercial process, which would require selectivity of 95% or more.

Total conversion curves showed higher catalyst durability for SiAIP-4.5 and SiAIP-3 materials (Fig. 3). High selectivity to ε -caprolactam (>90%, SiAIP-2) was found during the reaction. The deactivation of the SiAIP- X catalysts was accompanied by an increased selectivity to various byproducts (S_{by-p}) including cyclohexanone (S_C) and 2-cyclohexen-1-one (S_{EN}) (Table 5). ε -caprolactam oligomers (S_P) were detected only for sample SiAIP-6 and the aluminosilicate MCM-41 ($Si/Al = 30$), which had stronger acid sites (Table 3); therefore, we may conclude that the formation of oligomers is favored in materials

with a higher ratio of strong acid sites. The catalytic activities of SiAIP-6, SiAIP-4.5, and SiAIP-3 at 475 °C indicated the formation of higher quantities of byproducts, particularly cyclohexanone and cyclohexenone, compared with those obtained at 450 °C (Table 5).

3.2.2. Synthesis of ω -lauro lactam

Lacroix et al. [32] studied how temperature affects the yield of ω -lauro lactam and the lifetime of zeolite Beta catalyst and reported that the quantity of byproducts decreased with temperature, accompanied by a concomitant decrease in catalyst lifetime. The maximum yield of ω -l was obtained at 250–375 °C [32]. In the present work, cyclododecanone oxime conversion was performed at 375 °C using the mesoporous SiAIP- X catalysts. The catalytic data are summarized in Table 6.

Quantitative conversion was obtained for all materials, but the selectivity to ω -lauro lactam was lower compared to that of ε -caprolactam. Catalytic deactivation varied, depending on the amount of aluminophosphate in the materials. Thus, selectivity to ω -lauro lactam increased with the quantity of aluminophosphate, reaching values of ~85% for sample SiAIP-2. Interestingly, the ω -l selectivity in SiAIP-3(150) was not above 50%, which could be attributed to the higher quantity of weak acid sites in this material (Table 3).

In terms of deactivation, materials with high aluminophosphate content [i.e., SiAIP-3(150) and SiAIP-2] deactivated more rapidly compared with those with lower aluminophosphate content. The deactivation was accompanied by an increase in selectivity to cyclododecanone (S_{Cdone}) at the expense of ω -l selectivity (Fig. 4). Further studies on the in situ regeneration (600 °C in air for 1 h) and reuse of SiAIP-4.5 demonstrated a significant decrease in catalyst durability, whereas the ω -l selectivity increased at shorter reaction times (Table 6).

In summary, our results indicate that the mesoporous SiAIP- X materials were active and selective in the vapor-phase Beckmann rearrangement of cyclododecanone oxime, giving yields comparable to those obtained on zeolites [32].

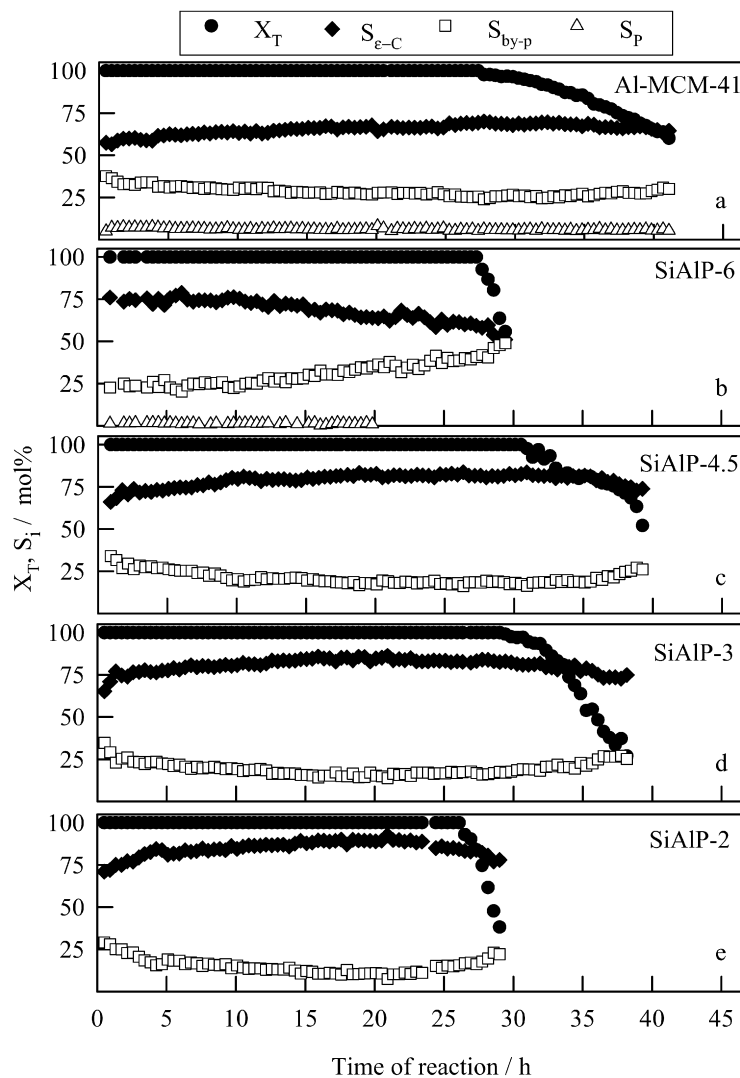


Fig. 3. Variation of C-ox conversion (X_T , mol%) and product selectivity (S_i , mol%) with time of reaction in the gas-phase Beckmann rearrangement of C-ox using various solid acids: (a) Al-MCM-41; (b) SiAIP-6; (c) SiAIP-4.5; (d) SiAIP-3; and (e) SiAIP-2. Reaction conditions: $T = 450^\circ\text{C}$; 0.3 M C-ox in acetonitrile; $W/F = 92.8 \text{ g h mol}^{-1}$.

Table 6

Total conversion (X_T , mol%), product distribution (S_i , mol%) and durability (D , lifetime at $X_T = 100\%$) in the gas-phase Beckmann rearrangement of Cdox at 375°C using various SiAIP catalysts^a

Catalyst	Time on stream (6 h)				Time on stream (18 h)				D (h)
	X_T	$S_{\omega-1}$	S_{Cdone}	S_{CN}	X_T	$S_{\omega-1}$	S_{Cdone}	S_{CN}	
SiAIP-6	100.0	70.1	–	29.9	100.0	73.0	4.4	22.6	23
SiAIP-4.5	100.0	59.8	–	40.1	100.0	70.7	0.0	29.3	28
SiAIP-4.5 ^b	100.0	83.1	–	16.9	84.2	74.2	13.3	12.5	12
SiAIP-3	100.0	56.6	–	43.4	100.0	74.9	0.0	25.1	22
SiAIP-3(150)	100.0	35.6	–	64.4	100.0	49.5	7.4	43.1	18
SiAIP-2	100.0	76.0	–	24.0	95.0	85.0	2.5	12.5	14

^a Reaction condition: $W/F = 169 \text{ g h/mol}$; 0.1 M Cdox in toluene.

^b Catalyst regenerated by heating at 600°C in air for 1 h.

3.3. Liquid-phase Beckmann rearrangement of cyclododecanone oxime

3.3.1. Conventional heating

The liquid-phase Beckmann rearrangement of Cdox on SiAIP- X materials under conventional heating was investi-

gated in chlorobenzene (130°C) and toluene (110°C). The effect of the solvent in the reaction was also studied. The total conversion and product distribution (5 and 24 h reaction times) are given in Table 7. Beta zeolite has been reported as a good catalyst for transforming Cdox into $\omega-1$ under liquid-phase conditions [27]. Our results for Beta25 zeolite were in

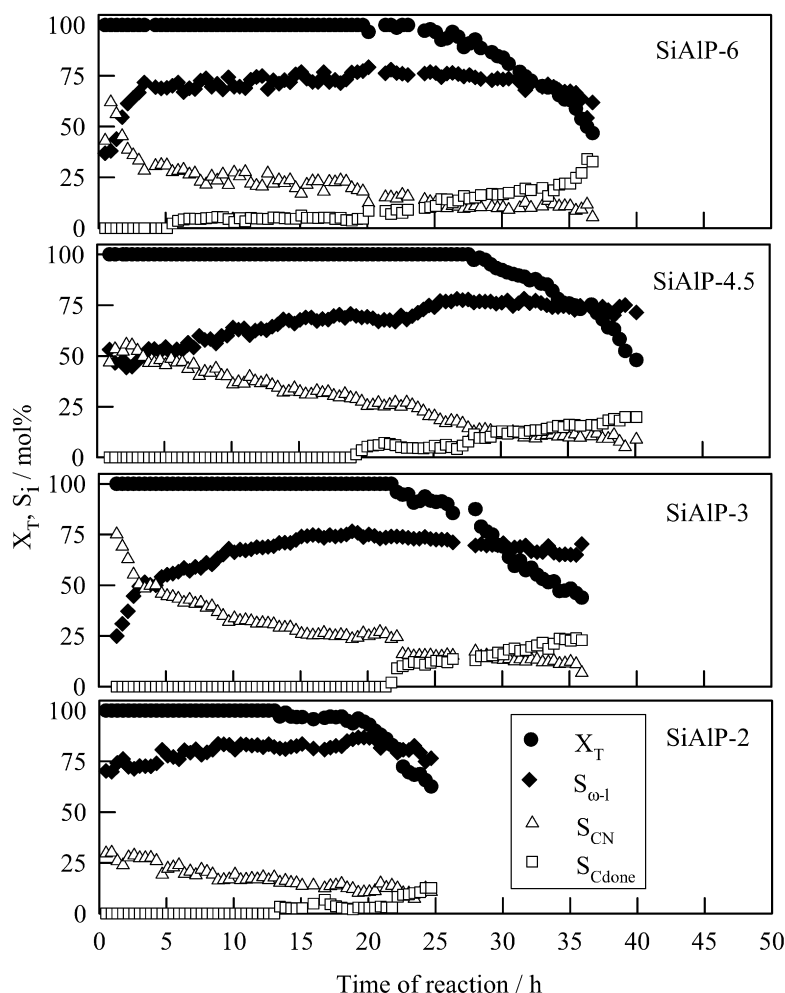


Fig. 4. Variation of Cdox conversion (X_T , mol%) and product selectivity (S_i , mol%) with time of reaction in the gas-phase Beckmann rearrangement of Cdox using SiAIP materials: (a) SiAIP-6, (b) SiAIP-4.5, (c) SiAIP-3, and (d) SiAIP-2. Reaction conditions: $T = 375^\circ\text{C}$; 0.1 M Cdox in toluene; $W/F = 169 \text{ g h mol}^{-1}$.

Table 7

Total conversion (X_T , %) and product distribution (S_i , %) in the liquid-phase Beckmann rearrangement of Cdox using different SiAIP- X materials as catalysts

Catalyst	5 h				24 h			
	X_T	$S_{\omega-1}$	S_{Cdone}	S_{CN}	X_T	$S_{\omega-1}$	S_{Cdone}	S_{CN}
Chlorobenzene at 130°C								
Beta25	78.6	97.0	2.5	0.5	80.2	95.8	3.0	1.2
SiAIP-6	13.9	88.4	–	11.6	15.5	75.5	5.1	19.4
SiAIP-4.5	30.5	92.5	–	7.6	32.9	88.5	1.8	9.7
SiAIP-3	35.4	93.2	–	6.8	41.1	92.0	1.5	6.5
SiAIP-3(150)	18.0	80.6	–	19.4	23.2	71.2	1.3	27.5
SiAIP-2	27.3	90.1	–	9.9	33.3	90.7	–	9.3
Toluene at 110°C								
SiAIP-6	3.6	100.0	–	–	4.9	73.5	–	26.5
SiAIP-4.5	10.5	89.5	–	10.5	13.1	79.4	–	20.6
SiAIP-3	10.6	92.4	–	7.6	14.6	70.9	–	29.1
SiAIP-3(150)	6.8	83.8	–	16.2	8.5	67.0	–	33.0
SiAIP-2	9.1	91.2	–	8.8	13.2	69.7	–	30.3
Chlorobenzene at 110°C								
SiAIP-4.5	10.5	68.3	–	31.7	16.1	63.8	–	36.2
SiAIP-3	12.1	66.1	–	33.9	32.6	56.5	3.8	39.7

good agreement with this fact, because it exhibited the highest activity and selectivity to ω -1 by using chlorobenzene as the solvent at 130°C . High catalytic activities, particularly for materials with higher aluminophosphate content (SiAIP-4.5 and SiAIP-3), were found when using chlorobenzene as solvent at 130°C . However, our SiAIP- X mesoporous materials showed a lower conversion level and selectivity to ω -1 compared with the results for Beta25 under the reaction conditions. Selectivities to ω -lauro lactam were close to 90%. Nevertheless, results obtained at longer reaction times (typically 24 h) pointed out a slight increase in the Cdox conversion while the ω -lauro lactam selectivity dropped. This phenomenon may be attributed to the formation of cyclododecanone (Cdone), dodecanenitrile, and 11-dodecenenitrile (CN) as byproducts in the reaction due to the hydrolysis and the ring opening reaction of Cdox, respectively. This fact is particularly important in materials with lower aluminophosphate content (i.e., SiAIP-6). Catalytic activities of SiAIP- X materials using toluene as a solvent (110°C) were found to be lower than those obtained using chlorobenzene (130°C). Interestingly, the use of chlorobenzene at 110°C gave similar conversions but much lower selectivity to the cyclic lactam.

Table 8
Total conversion (X_T) and product distribution^a (S_i) in the microwave-assisted Beckmann rearrangement of Cdox at 180 °C using various micro-mesoporous materials^b

Catalyst	X_T (mol%)	$S_{\omega-1}$ (mol%)	S_{Cdone} (mol%)
Blank	– ^c	–	–
Beta25	76	>99	–
SiAIP-6	42	98	2
SiAIP-4.5	65	98	2
SiAIP-3	66	>99	–
SiAIP-2	60	>99	–
Beta25 ^d	100	>99	–
SiAIP-4.5 ^d	79	96	4

^a Dodecanenitrile and 11-dodecenenitrile (CN) were not detected.

^b 20 mg Cdox, 3 mL chlorobenzene, 20 mg catalyst, 275 W, 15 min.

^c No reaction.

^d 20 mg Cdox, 3 mL chlorobenzene, 40 mg catalyst, 275 W, 5 min.

3.3.2. Microwave heating

The data obtained from catalytic tests performed under microwave heating, with chlorobenzene as solvent, are summarized in Table 8. In general, the experiments provided very good catalytic activities for SiAIP-*X* materials. This indicates that the activity of the SiAIP-*X* materials is close to that of Beta25 and greater than that of zeolite ZSM-5(30). Dodecanenitrile and 11-dodecenenitrile were not detected in the reaction products, and only traces of cyclododecanone were detected. ω -Laurolactam was obtained in high yields and selectivities (>96%). The activity observed under microwave heating differed from conventional heating where, although relatively high conversion and selectivity values were observed at relatively short reaction times (typically under 5 h), the activities were much lower than those of the zeolites [ZSM-5(30) and Beta25].

The energy efficiency of the reaction was also studied by changing the amount of catalyst used. Quantitative Cdox conversion was found for the Beta25 after 5 min on doubling the quantity of catalyst in the reaction. The SiAIP-4.5 material, in contrast, gave 80% conversion with comparable high selectivity to the lactam when the amount of catalyst used was doubled.

4. Conclusion

We have synthesized and characterized novel silicoaluminophosphate SiAIP-*X* materials and provided strong evidence that the aluminophosphate units were incorporated into the mesoporous aluminosilicate framework. XRD and N₂ sorption studies revealed the partial loss of mesostructural ordering as the aluminophosphate content increased. A high density of acid sites was generated in the materials, resulting in solid acids that are highly active and selective in the gas- and liquid-phase Beckmann rearrangement of various oximes. The SiAIP-*X* catalysts showed significant activity and selectivity to ϵ -caprolactam in the gas-phase Beckmann rearrangement of cyclohexanone oxime. Thermally regenerated and reused SiAIP-*X* catalysts exhibit a higher selectivity to the lactam although with decreased catalyst durability. Catalysis performed

under microwave heating exhibited a significant decrease in selectivity to ϵ -caprolactam.

Quantitative oxime conversion was obtained for all materials in the gas-phase reaction. However, the selectivity to ω -laurolactam was lower than that of ϵ -caprolactam. Liquid-phase results of the Beckmann rearrangement of cyclododecanone oxime on SiAIP-*X* catalysts using conventional heating showed lower conversion and selectivity to ω -laurolactam compared with microporous Beta25 zeolite. Interestingly, under microwave heating, the catalytic activity of the SiAIP-*X* materials was found to be close to that of zeolite Beta25. Overall, ϵ -caprolactam and ω -laurolactam were obtained on SiAIP-*X* catalysts in both the gas and liquid phases.

Acknowledgments

This research was subsidized by grants from the Dirección General de Investigación (projects CTQ2005-04080 and CTQ2007-65754/PPQ), Ministerio de Ciencia y Tecnología, FEDER funds, and the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, project FQM-191).

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