

# Liquid phase aldol condensation of cyclopentanone with valeraldehyde catalysed by oxynitrides possessing tuneable acid–base properties

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## Abstract

The aldol condensation reaction between valeraldehyde and cyclopentanone was carried out in a batch reactor, at atmospheric pressure and 130 °C over “AlPON” and “ZrPON” catalysts. Those catalysts were obtained by heating  $\text{AlPO}_4$  and  $\text{Zr}_{0.9}\text{PO}_{4.3}$  phosphates in a flow of gaseous ammonia at 750 and 700 °C, respectively. The nitridation treatment allows to substitute framework oxygen atoms by nitrogen atoms, consequently reducing the number of solid acid sites and increasing the number of basic sites. Nitridation has a positive effect on valeraldehyde conversion which increases from 33 to 57% after 2 h of reaction for the “AlPO” system and from 80 to 94% after 2 h for the “ZrPO” system. The influence of the acid–base properties of catalysts for this particular reaction is discussed by measuring the activity and selectivity of basic (MgO), and amphoteric ( $\text{Al}_2\text{O}_3$ ) catalysts. The zirconophosphate precursor “ZrPO” and its nitrated samples are the most active for the reaction.

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**Keywords:** Oxynitrides; Acid–base catalysis; Aldol condensation reaction

## 1. Introduction

Aldol condensation reactions are used in the synthesis of numerous large-volume chemicals such as mesityl oxide, diacetone alcohol, isophorone, and 2-ethylhexenal, which are frequently hydrogenated to yield valuable solvents and plasticizers. In addition, the aldol condensations are also used for the synthesis of fine chemicals such as fragrances, pharmaceuticals, and flavours (jasminaldehyde, pseudoionone, etc.) [1].

The present work deals with the aldol condensation of cyclopentanone (**1**) (Scheme 1) with valeraldehyde (**2**) to produce 2-pentylidene-cyclopentanone (**3**) which is a precursor of perfume ingredients. Compound (**3**) is used in the synthesis of methyl dihydrojasmonate (2% incorporated in “Eau Sauvage” (Dior, 1966)) [2] and 2-pentylcyclopentanone (used in

low-cost fragrances for use in laundry powders and household cleaners) [3].

The homogeneous aldol condensation reaction of valeraldehyde with cyclopentanone has already been studied by several authors, using either catalytic amounts of KOH [4–7], or neutral solubilized catalysts. For instance, the solvent-free condensation of cyclopentanone with valeraldehyde catalysed by zirconocene complexes  $\text{cp}_2\text{ZrH}_2$  or  $\text{cp}_2\text{Zr}(\text{O}-i\text{-Pr})_2$  in an autoclave at 130 °C under argon for 8 h gave (**3**) with a yield of 47% [8]. The same reaction run with  $\text{Ti}(\text{O}-t\text{-Bu})_4$  as catalyst in toluene refluxed for 2 h gave (**3**) with a yield of 74% [9].

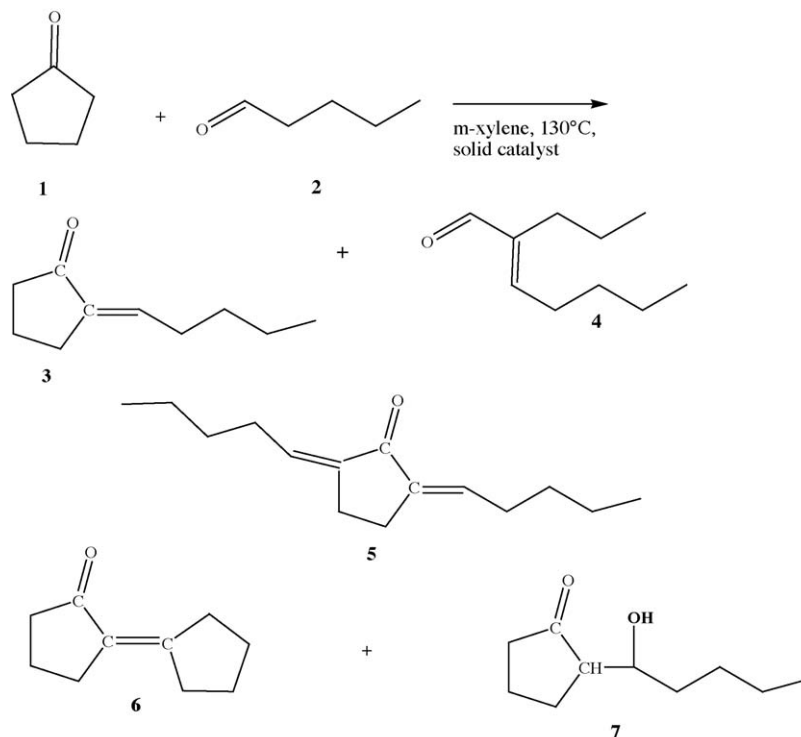
2-Pentylidene-cyclopentanone (**3**) was also synthesized in a two-step procedure by the successive transformation of cyclopentanone into an ene-amine, which thereafter was condensed with valeraldehyde. Refluxing cyclopentanone with morpholine in the presence of *p*-toluenesulfonic acid gave 1-morpholino-1-cyclopentene, which was refluxed with valeraldehyde; when heated in water the condensation product gave compound (**3**) [10].

Nowadays, because of growing environmental concerns, the substitution of homogeneous catalysts by heterogeneous cata-

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Scheme 1. Aldol condensation reaction between cyclopentanone and valeraldehyde.

lysts in industrial production processes is however highly desirable.

The replacement of liquid bases by solid heterogeneous base catalysts enables the easy separation and recycling of the catalyst from the reaction mixture. In this way the generation of noxious substances and wastes (which consist primarily of inorganic salts formed in the reaction or in subsequent neutralization steps) is avoided. Moreover, it is frequently possible to prepare solid base catalysts with a different nature of active sites (Brønsted, Lewis, chiral), with a wide range of basic strengths, or even acid–base bi-functional catalysts.

The substitution of oxygen by nitrogen in “AlPON”, “ZrPON” and “AlGaPON” oxynitrides during nitridation of metallophosphates leads to compounds with specific catalytic properties [11,12]. As their acidity decreases while their basicity increases with their nitrogen content, they are particularly interesting in the field of acid–base catalysis. Previous IR, microcalorimetry and chemisorption studies have highlighted the evolution of the number, nature and strength of the acid and basic sites with the nitrogen content, leading to the full mastering of the acid–base properties of phosphates through nitridation. We are now at the stage of exploring the possibility to use those new families of catalysts for the production of fine chemicals through aldol condensation reactions. For those reactions, the balance between acid and basic sites has a significant impact on selectivities.

The amorphous, mesoporous and high surface area solid AlPO (aluminium phosphate) and its oxynitride derivatives (AlPON) give – for the cross-condensation of benzaldehyde with heptanal to  $\alpha$ -amylcinnamaldehyde (jasminaldehyde) – much higher rates and selectivities than conventional solid acid

amorphous or crystalline aluminosilicates, or base catalysts ( $\text{MgO}, \text{Al}_2\text{O}_3$ ) [13]. AlGaPO (aluminium-gallium phosphate) and ZrPO (zirconium phosphate) and their oxynitride derivatives (AlGaPON and ZrPON) give for this condensation still higher rates and selectivities for the cross aldolization product [14]. At our knowledge, the catalysis of the liquid phase condensation of cyclopentanone with valeraldehyde by high surface area oxides or by ion exchangers has not been reported in the literature so far. In the present work, the catalysis of this condensation by AlPO and ZrPO, and by their oxynitrides has been studied, in comparison with the catalysis by solid acid (amorphous  $\text{SiO}_2\text{--Al}_2\text{O}_3$ ), amphoteric (amorphous  $\text{Al}_2\text{O}_3$ ) or base catalysts (crystalline MgO).

## 2. Experimental

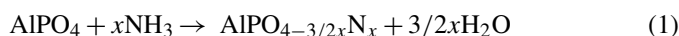
### 2.1. Materials

The first step of the AlPON and ZrPON synthesis involves the preparation of reactive phosphate precursors. The sol–gel process developed by Kearby was used for the synthesis of  $\text{AlPO}_4$  [15] and zirconophosphate precursor  $\text{Zr}_{0.9}\text{PO}_{4.3}$  was obtained according to the citrate method [16]. Those soft chemistry routes allow obtaining highly divided oxides with specific surface areas of 297 and 226  $\text{m}^2/\text{g}$  for  $\text{AlPO}_4$  and  $\text{Zr}_{0.9}\text{PO}_{4.3}$ , respectively. The high specific surface area of the oxide is one of the most important criteria for further activation to high surface area oxynitrides. The second step of the preparation of the oxynitrides is the activation of the precursors under ammonia flow. During the nitridation process, nitrogen atoms progressively replace the oxygen atoms of the framework. Nitridation

Table 1  
Chemical compositions and nitridation parameters of the oxynitrides “ZrPON” and “AlPON” catalyst

Catalysts	Composition	Nitridation		N content (Grekov) (wt.%)	$S_{\text{BET}}$ (m <sup>2</sup> /g)
		Time (h)	$T$ (°C)		
AlPO	AlPO <sub>4</sub>	–	–	–	297
AlPON–9% N	AlPO <sub>2.92</sub> N <sub>0.71</sub>	48	750	9.0	255
AlPON–14% N	AlPO <sub>2.23</sub> N <sub>1.10</sub>	111	750	14.0	235
ZrPO	Zr <sub>0.9</sub> PO <sub>4.3</sub>	–	–	–	226
ZrPON–8% N	Zr <sub>0.9</sub> PO <sub>2.79</sub> N <sub>1.01</sub>	13	700	8.2	139

of the AlPO<sub>4</sub> precursor occurs via the following equation:



The nitridation conditions (time and temperature) determine the final nitrogen content of the samples.

The total nitrogen content of the AlPON and ZrPON samples was determined by titration with a sulphuric acid solution of the ammonia liberated in alkaline digestion at 400 °C with melted KOH according to Grekov's method [15]. The specific surface area was measured by the single-point BET method in a Micromeritics Flowsorb II 2300 apparatus, after 20 min degasification at 250 °C. The nitridation conditions and the main characteristics of the studied oxynitrides are presented in Table 1. All samples are X-ray amorphous white powders. The composition of the nitrided samples presented in Table 1 was established from their total nitrogen content. It has been shown that the Al/P and Zr/P ratios were maintained during nitridation temperatures lower than 800 °C, and that the weight loss recorded during nitridation corresponds to the replacement of three oxygen atoms by two nitrogen atoms.

The main physico-chemical properties of the reference oxide catalysts are presented in Table 2, as well as data relative to their synthesis procedure.

## 2.2. Catalytic tests

Cyclopentanone (1.691 g, 20.13 mmol, Aldrich 99%), valeraldehyde (0.356 g, 4.14 mmol, Aldrich 97%), *n*-decane (0.292 g, 2.05 mmol, Aldrich 99%, internal analysis standard) and *m*-xylene (30 ml, Aldrich 99%) were introduced into a 50-ml Teflon autoclave containing a magnetic bar for stirring. The powdered catalyst (0.21 g, 10% of the total weight of cyclopentanone plus valeraldehyde, particle size fraction of 100–200 μm) was added. All the reagents and solvents were used without purification. In

Table 2  
Characteristics of the reference oxide catalysts

Catalyst	$S_{\text{BET}}$ (m <sup>2</sup> /g)	Structure	Synthesis procedure
SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> (6.38 wt.% Al)	370	Amorphous	Co-gel
Al <sub>2</sub> O <sub>3</sub>	361	Amorphous	Sol-gel [24]
MgO	108	Periclase	Sol-gel [25]

order to remove H<sub>2</sub>O and CO<sub>2</sub>, known to poison basic sites after exposure to ambient air, the MgO catalyst was heated at 550 °C for 12 h under helium flow, prior to the reaction. The other catalysts were simply dried overnight at 120 °C in air prior to the tests. Care was taken to avoid rehydration before introduction of the catalysts in the Teflon autoclave.

After addition of the catalyst, a static atmosphere of nitrogen was established, the autoclave was closed and heated in an oil bath, and the magnetic stirring was started. The reaction time was 2 or 5 h after the reaction temperature (130 °C) was reached. For quantitative comparison between the catalysts, we took care to ensure that the kinetics was not controlled by external or internal diffusion. We checked that increasing the stirring rates or decreasing the catalyst particles diameter had no significant influence on the conversion of valeraldehyde or on the yields obtained under our standard reaction conditions.

After reaction, the autoclave was cooled in an ice bath. A liquid sample was withdrawn with a filtering syringe and analyzed by a Perkin-Elmer AutoSystem Gas Chromatograph equipped with an automatic sampler/injector, an FID detector and a capillary column (CP Sil 8 CB, 25 m). Identification of reaction products was performed on a Magnum gas chromatograph—mass spectrometer (GC–MS) from Finnigan (EI ± ionisation at 70 eV), equipped with a Chrompack CP Sil 8 CB column. All the isomers (*Z,E*) of cross- and self-condensation reactions were separated. Quantitative determinations were based on the measured response factors of the reactants and reaction products. The identities of the products of reaction were ascertained by comparison of their GC retention times and of their MS spectra with those of authentic analysis standards. The reactants cyclopentanone (**1**) and valeraldehyde (**2**), the analysis standard decane, and the reaction products 2-pentylidene-cyclopentanone (**3**), 2-propyl-2-heptenal (**4**), and 2-cyclopentylidene-cyclopentanone (**6**) were obtained from Aldrich, Fluka and Avocado. The products 2,5-dipentylidene-cyclopentanone (**5**) and 2-(1-hydroxypentyl)-cyclopentanone (**7**) were identified by GC–MS.

## 3. Results and discussion

### 3.1. Reaction products

The products detected after the reaction of cyclopentanone (**1**) with valeraldehyde (**2**) were the following (Scheme 1; Table 3)—the desired product of cross-condensation: 2-pentylidene-cyclopentanone (**3**); the product of self-condensation of valeraldehyde: 2-propyl-2-heptenal (**4**); the product of overcondensation of cyclopentanone (**1**) with valeraldehyde (**2**): 2,5-dipentylidene-cyclopentanone (**5**); the product of self-condensation of cyclopentanone (**1**): 2-cyclopentylidene-cyclopentanone (**6**); the aldol: 2-(1-hydroxypentyl)-cyclopentanone (**7**). The latter was only observed in exploratory assays performed at 90 °C, but was not detected in the assays described here which were carried at 130 °C. The sum of the products (**3**), (**4**), (**5**) and (**6**) corresponded to 95–100 % of the transformed cyclopentanone (**1**) and

Table 3

Results of the catalysed aldol condensation of cyclopentanone (**1**) with valeraldehyde (**2**) after 2 or 5 h of reaction in *m*-xylene at 130 °C: product distribution in mol%

Catalyst	Valeraldehyde conversion		(Product distribution) <sub>pi</sub> <sup>b</sup> (mol%)			
	%	(mmol/h m <sup>2</sup> ) <sup>a</sup>	(3)	(4)	(5)	(6)
After 2 h of reaction						
Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	31	0.0083	91	5	4	0
Al <sub>2</sub> O <sub>3</sub>	71	0.0194	84	9	7	0
MgO	40	0.0366	86	7	7	0
AlPO	33	0.0110	86	10	4	0
AIPON-9% N	50	0.0194	79	12	5	4
AIPON-14% N	57	0.0239	68	9	18	5
ZrPO	80	0.0349	62	8	6	25
ZrPON-8% N	94	0.0667	72	14	4	10
After 5 h of reaction						
Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	72	0.0077	89	4	3	4
Al <sub>2</sub> O <sub>3</sub>	99	0.0108	83	7	1	9
MgO	88	0.0321	89	5	6	0
AlPO	83	0.0110	85	8	3	5
AIPON-9% N	87	0.0134	78	7	9	6
AIPON-14% N	95	0.0159	77	7	11	5
ZrPO	97	0.0169	41	6	6	47
ZrPON-8% N	97	0.0275	70	8	4	18

<sup>a</sup> Valeraldehyde conversion (in mmol/m<sup>2</sup> h) = (mmol of valeraldehyde initially present – mmol of valeraldehyde remaining after 2 or 5 h)/(reaction time (h) × *n* (square meters of catalyst in the reactor)).

<sup>b</sup> (3): 2-pentylidene-cyclopentanone; (4): 2-propyl-2-heptenal; (5): 2,5-dipentylidene-cyclopentanone; (6): 2-cyclopentylidene-cyclopentanone.

valeraldehyde (**2**). When the reaction was run without catalyst at 130 °C, the conversion of valeraldehyde (**2**) was lower than 2%. The conversions of valeraldehyde and the distribution of the products were reproducible within 1–2%.

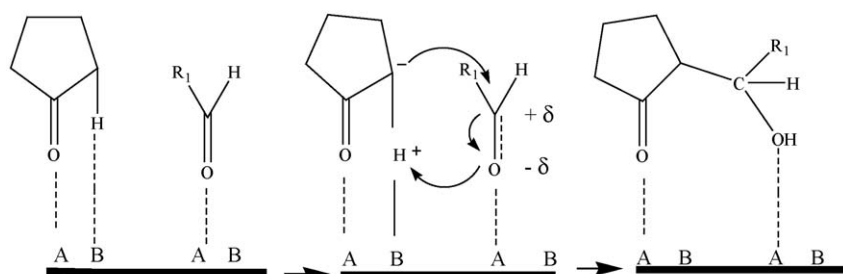
### 3.2. Reaction mechanisms over reference oxides

In first experiments, we studied valeraldehyde and cyclopentanone conversions as well as the product distribution over reference oxides with well known and contrasted acid–base properties. The amount of heptanal converted (in % and mmol/m<sup>2</sup> h), as well as the product distribution (mol%) in the reactor after 2 and 5 h of test over those oxides are presented in Table 3.

After 2 h of reaction, the conversions of valeraldehyde (the reactant in default; 4.14 mmol initially) are already higher than 30% and significant differences are observed between the reference catalysts.

With the increase of the reaction time up to 5 h, the conversion of valeraldehyde still increases and reaches almost 100% for alumina. The amount of valeraldehyde converted per hour decreases when going from 2 to 5 h, because of the progressive impoverishment of the solution in free valeraldehyde. Some differences are observed between product distribution obtained after 2 and 5 h of reaction, the most obvious one being the appearance of **6** among reaction products. One of the factor that has to be taken into account when discussing changes in product distribution with increasing the reaction time, is that the initial cyclopentanone/valeraldehyde ratio of 5/1 is modified during the reaction. Other factors could be poisoning of the catalyst by reactants or reaction products as well as secondary reactions, but our work strategy does not allow us to discuss it presently.

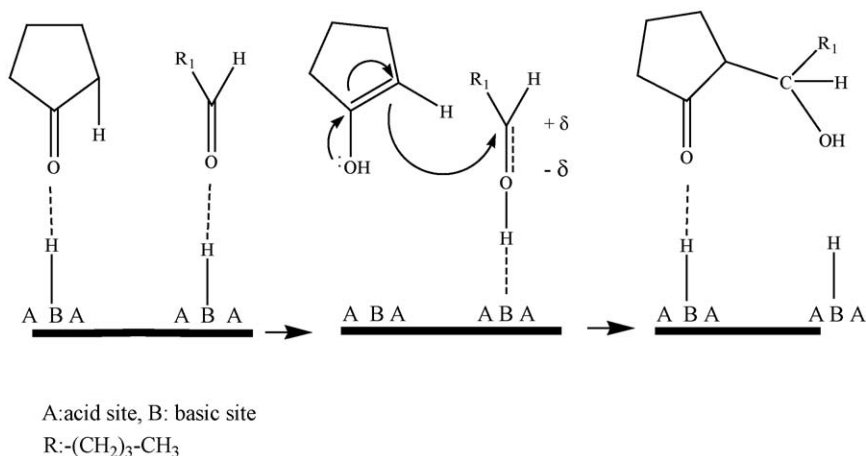
What we intend to do is to discuss correlations between the acid–base properties of the catalysts and the conversions/selectivities observed under similar reaction conditions.



A: acid site, B: basic site

R: -(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>

Scheme 2. Heterogeneously base-catalysed cross-condensation (adapted from Ref. [1]).



Scheme 3. Heterogeneously acid-catalysed cross-condensation (adapted from Ref. [1]).

Usually, the aldol condensation reactions are catalysed by bases. Scheme 2 gives a detailed mechanism of the cross-aldol condensation reaction between valeraldehyde (electron acceptor) and cyclopentanone (electron donor) catalysed by a base. The first step is the proton extraction from the alpha-carbon of cyclopentanone by a basic site, generating a carbanion species which will attack the carbonyl group of valeraldehyde.

For the correlation of the product distribution with the acid–base properties of the catalysts, it must be taken into account that valeraldehyde also can be activated on a basic site, through proton extraction from its alpha-carbon. In our study, MgO was used as strong solid base reference, and was found to convert 40 and 88% of the valeraldehyde after 2 and 5 h of reaction, respectively (Table 3).

However, the reaction can also be catalysed by acids, as presented in Scheme 3. Aluminium trichloride, boron trifluoride or sulphuric acid catalyse the reaction in homogeneous phase. In this case, the first step is the activation of valeraldehyde by the acid to form a carbocation. Silica–alumina is known to be a strong acid. Under our operating conditions, it catalyses the conversion of 31 and 72% of the valeraldehyde after 2 and 5 h of reaction, respectively (Table 3). The reaction should also be feasible over bi-functional acid–base catalysts, possessing acid–base site pairs of intermediate strength able to interact simultaneously with the acid and basic functional groups in valeraldehyde and cyclopentanone. In this original mechanism, the carbonyl group of valeraldehyde would be protonated by an acid site, while cyclopentanone would be activated on an adjacent basic site. To demonstrate the feasibility of this mechanism under our operating conditions, we used an amphoteric solid, namely  $\text{Al}_2\text{O}_3$ . It is the most active of our reference oxides, as it catalyses the conversion of 71 and 99% of valeraldehyde after 2 and 5 h, respectively (Table 3). However, when these results are normalized with respect to the respective surface areas, the following order of conversion of valeraldehyde is observed:

- MgO ( $1.76\%/m^2$ ) >  $\text{Al}_2\text{O}_3$  ( $0.94\%/m^2$ ) >  $\text{SiO}_2\text{-Al}_2\text{O}_3$  ( $0.40\%/m^2$ ) after 2 h.

- MgO ( $3.88\%/m^2$ ) >  $\text{Al}_2\text{O}_3$  ( $1.31\%/m^2$ ) >  $\text{SiO}_2\text{-Al}_2\text{O}_3$  ( $0.93\%/m^2$ ) after 5 h.

All three reference oxides give the desired 2-pentylidene-cyclopentanone (3) as major product with high selectivity. The strongly basic and strongly acid character of MgO and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalysts, respectively, as well as the bi-functional acid–base character of  $\text{Al}_2\text{O}_3$  have been demonstrated previously through butan-1-ol and butan-2-ol dehydrogenation/dehydration tests [17].

### 3.3. Influence of nitridation on the catalytic activity

As shown in Table 3, progressive nitridation increases the catalytic activity (measured by the conversion of valeraldehyde (2)) of AIPO (from 33 to 57% after 2 h of reaction, and from 83 to 95% after 5 h) and of ZrPO (from 80 to 94% after 2 h).

Intermediate conversions are observed at lower nitrogen content in the “AIPO” system. The positive impact of nitridation on the conversion of valeraldehyde is even clearer when the decrease in surface area induced by nitridation is taken into account in the normalisation of the results (Fig. 1).

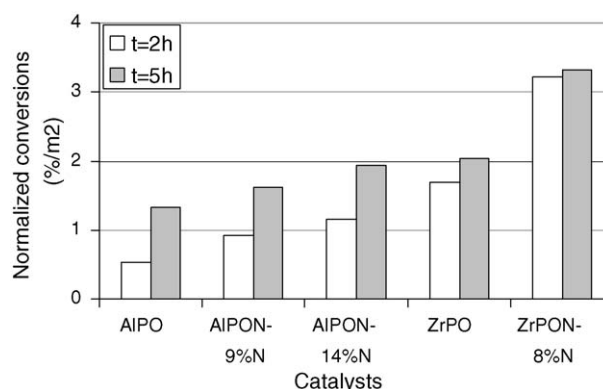


Fig. 1. Normalized valeraldehyde conversions over AIPO(N) and ZrPO(N) after 2 and 5 h of reaction in *m*-xylene at 130 °C.



The ZrPO and ZrPON catalysts are particularly active for this reaction. ZrPON is even more active than MgO, with normalized valeraldehyde conversion of 3.22%/m<sup>2</sup>, as compared to 1.76%/m<sup>2</sup> for MgO, after 2 h. For the mixed aldol condensation between benzaldehyde and heptanal to form jasminaldehyde, the ZrPO(N) family already revealed particularly active [14].

### 3.4. Influence of nitridation on product distribution

#### 3.4.1. Relative activation of valeraldehyde and cyclopentanone

The product of the self-condensation of cyclopentanone, 2-cyclopentylidene-cyclopentanone (**6**) was not observed among the reaction products formed over the reference oxides after 2 h of reaction. It appears as minor reaction product after 5 h of reaction over silica–alumina (4%) and alumina (8%) (Table 3). It is also formed over the AlPO(N) catalysts, but always represents less than 6% of the total reaction products. This reflects the lower reactivity of cyclic ketones towards aldolization as compared to aldehydes.

However, the ZrPO precursor generates a high percentage of 2-cyclopentylidene-cyclopentanone (**6**): 25 and 47% after 2 and 5 h of reaction, respectively. Its nitridation reduces its ability to catalyse the self-condensation of cyclopentanone.

The basic properties of the ZrPO and ZrPON samples were investigated by adsorption calorimetry of SO<sub>2</sub> [18]. The heats of adsorption of SO<sub>2</sub> at zero coverage can be used as an indication of the strength of the basic sites; the total number of sites that adsorb SO<sub>2</sub> can be used as an indication of the amount of the basic sites.

Under the chosen experimental conditions, the results are the following:

- *Heat of adsorption:* ZrPO (130 kJ/mol) < ZrPON (160 kJ/mol).
- *Total amount of SO<sub>2</sub> adsorbed:* ZrPO (0.41 μmol/m<sup>2</sup>) < ZrPON (0.49 μmol/m<sup>2</sup>).

Other literature data indicate that the heat of adsorption of SO<sub>2</sub> on MgO is equal to 215 kJ/mol [19].

As the strength of the basic sites on the ZrPO is lower than on MgO, and as nitridation increases the number and the strength of basic sites, the particularly high activity of the ZrPO precursor for the self-condensation of cyclopentanone cannot be attributed to its basic properties solely.

The hypothesis that some of the Zr–OH and P–OH Brønsted acid groups present on its surface could play a role on the reaction should be investigated. Indeed, according to [20], it is known that aldol reactions between two ketones can be accomplished much more readily under acid than base catalysis. The acid promotes the formation of the enol form and the latter undergoes attack on by the protonated form of a second molecule of carbonyl compound. However, if this hypothesis is valid, one should explain the poor reactivity of the acid silica–alumina for the same reaction.

Table 4

Results of the catalysed aldol condensation of cyclopentanone (**1**) with valeraldehyde (**2**) after 2 or 5 h of reaction in *m*-xylene at 130 °C: distribution of the products containing 1 or 2 equiv. valeraldehyde (in equiv. valeraldehyde, %)

Catalyst	Cross-condensation products <sup>a</sup> (equiv. valeraldehyde, %)		Self-condensation product <sup>b</sup> (equiv. valeraldehyde, %)
	(3)	(5)	(4)
After 2 h of reaction			
Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub>	83	7	9
Al <sub>2</sub> O <sub>3</sub>	72	12	16
MgO	75	12	12
AlPO	75	7	18
AIPON–9% N	70	9	22
AIPON–14% N	56	30	14
ZrPO	69	14	17
ZrPON–8% N	67	7	27
After 5 h of reaction			
Al <sub>2</sub> O <sub>3</sub>	83	2	15
MgO	80	11	9
Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub>	87	6	7
AlPO	80	5	14
AIPON–9% N	71	17	12
AIPON–14% N	68	20	12
ZrPO	63	18	20
ZrPON–8% N	74	9	17

The distribution of the products containing 1 or 2 equiv. valeraldehyde ( $D_{\text{product } P_i}$ ) is calculated from Table 3 as follows:  $D_{\text{product } P_i} (\%) = \frac{(\text{product distrib.})_{P_i} (\text{mol}\%)}{\sum_{i=3,4,5} \{(\text{equiv. valerald.})_{P_i} \times (\text{product distrib.})_{P_i} (\text{mol}\%)\}} \times 100$ . Example: for

“AIPON–9% N”: for product (**3**):  $D_3 (\%) = \frac{79}{1 \times 79 + 2 \times 12 + 2 \times 5} \times 100 = 70$ .

<sup>a</sup> (**3**): 2-pentylidene-cyclopentanone; (**5**): 2,5-dipentylidene-cyclopentanone.

<sup>b</sup> (**4**): 2-propyl-2-heptenal.

#### 3.4.2. Cross-condensation versus self-condensation

The distribution of the products containing 1 or 2 equiv. valeraldehyde is presented in Table 4.

As far as the reference oxides are concerned, the smallest percentages of self-condensation products, namely 2-propyl-2-heptenal (**4**), are obtained for MgO (12 and 9% after 2 and 5 h, respectively) and for SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (9 and 7% after 2 and 5 h, respectively). Both catalysts lack the presence of acid–base site pairs of intermediate strength, MgO being a strong base, and SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> being a strong acid. The amphoteric Al<sub>2</sub>O<sub>3</sub> is more selective for (**4**) (16 and 15% after 2 and 5 h, respectively). Hence, in the case of the cross-condensation of cyclopentanone with valeraldehyde, the bifunctional reaction pathway decreases the percentage of cross-condensation products as compared to self-condensation of valeraldehyde. This is at the opposite of what Hasni et al. [21] observed for the catalysed aldol condensation of benzaldehyde with heptanal, yielding the cross-condensation product  $\alpha$ -amylcinnamaldehyde (jasminaldehyde), and the product of self-condensation of heptanal, 2-pentyl-2-nonenal (Table 5). They observed that amphoteric Al<sub>2</sub>O<sub>3</sub> was the most selective for the product of cross-condensation, jasminaldehyde. They concluded that the presence of weakly basic sites on the surface favoured the cross-condensation of benzaldehyde with heptanal.

Table 5  
Results of the aldol condensation between benzaldehyde and heptanal over MgO, Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (125 °C, in *m*-xylene) [14,25]

	MgO	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>
Heptanal conversion (%/m <sup>2</sup> ) after 2 h; selectivity (%) at 20% conversion of heptanal	1.1	0.4	0.5
Jasminaldehyde	43	60	54
2-Pentyl-2-nonenal	57	40	39
1-Phenylhept-1-ene	–	–	7

The selectivity in the desired jasminaldehyde results from the competitive reaction of the activated  $\alpha$ -methylene of heptanal with the carbonyl of benzaldehyde or with the carbonyl of heptanal. With the condensation of cyclopentanone with valeraldehyde, however, the selectivity in the cross-condensation product 2-pentylidene-cyclopentanone (**3**) results from the competitive reaction of the carbonyl of valeraldehyde with an  $\alpha$ -methylene of cyclopentanone or with the  $\alpha$ -methylene of valeraldehyde (Scheme 4). The mechanisms of the competition between the cross and the self-condensations being different for benzaldehyde with heptanal and for cyclopentanone with valeraldehyde, it is understandable that the presence of weak basic sites on the surface could have different effects on the selectivities of each of these reaction systems.

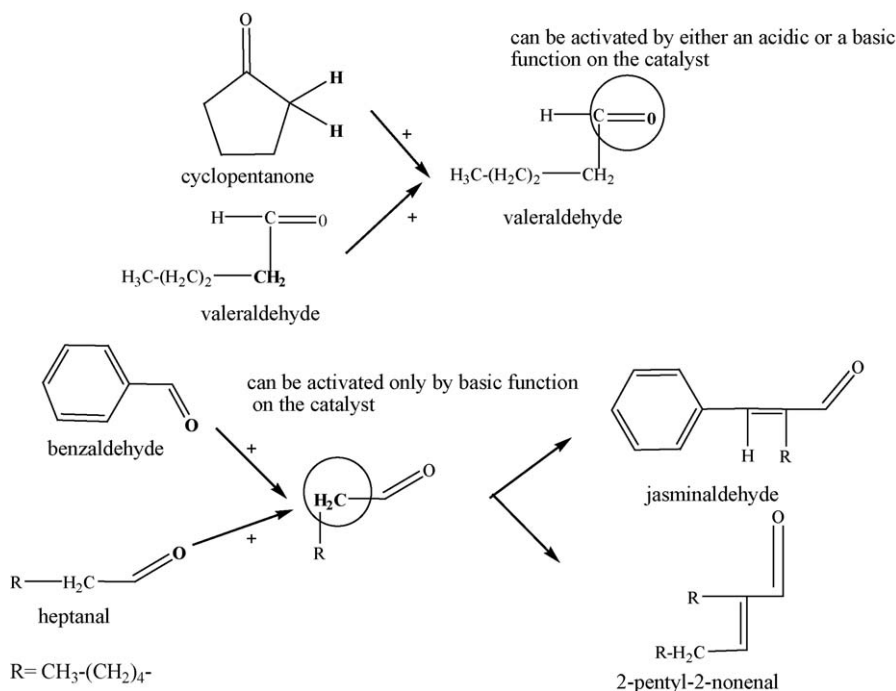
When considering the effect of nitridation on the activity and selectivity of amorphous phosphates, Hasni et al. [14] observed that the nitridation increased both the activity and the selectivity in jasminaldehyde. In the present study, the effect of nitridation on the conversion of valeraldehyde is very clear, while the impact of nitridation on the relative importance of

self- and cross-condensation products is less straightforward. Besides, significant differences between the impact of nitridation on the product distribution are observed over AIPON and ZrPON. For the AIPON system, nitridation favours the product of overcondensation of cyclopentanone (**1**) with valeraldehyde (**2**), 2,5-dipentylidene-cyclopentanone (**5**), while nitridation of ZrPO reduced its formation. It is not surprising to observe major differences between the activity and selectivity of AlPO and ZrPO as well as of AIPON and ZrPON oxynitrides having similar nitrogen contents. Indeed, the acid–base properties of those systems are somewhat different.

The AIPO precursor is more acidic and less basic than the ZrPO precursor. It has been empirically demonstrated previously [12] by studying the interactions of those two phosphates with acid (SO<sub>2</sub>) and basic (NH<sub>3</sub>) probes through microcalorimetry and chemisorption experiments, respectively. These differences could be explained in terms of Allred–Rochaw electronegativities (Al(III): 1.47; Zr(IV): 1.22) [22], and sizes (ionic radius (nm): Al<sup>3+</sup>: 0.053; Zr<sup>4+</sup>: 0.073, for tetracoordinated species [23]).

The importance of nitrogen incorporation in the phosphate network on the density of acid and base sites is also affected by the substitution of Al<sup>3+</sup> by Zr<sup>4+</sup> ions. For AIPON, the number of acid sites is strongly reduced as nitrogen is introduced in the phosphate network. However, for nitrogen contents higher than 10 wt.%, the decrease is less pronounced. For ZrPON, the density of acid sites hardly changes with nitrogen enrichment.

For the ZrPON and AIPON series the number of basic sites increases with nitrogen enrichment in the 0–20 wt.% N range. However, whatever the nitrogen content, ZrPON possess more basic sites than AIPON.



Scheme 4. Competition between the cross- and the self-condensations for benzaldehyde with heptanal and for cyclopentanone with valeraldehyde.

#### 4. Conclusion

The condensation of cyclopentanone with valeraldehyde is a complex aldol condensation, because cyclopentanone has two methylenes in  $\alpha$  position with respect to the carbonyl, and valeraldehyde has one alpha methylene. Moreover, the carbonyls of both valeraldehyde and cyclopentanone are able to react. This potential complexity for the aldol condensation in the liquid phase permits to show the orientation capability of the solid catalysts and of their nitridation, onto the selectivities and the distributions of the products.

The most active catalysts for this reaction are the zirconophosphate ZrPO and its nitrided form. They are even more active than MgO, yet known to be a strong base, and do not require any pre-treatment at high temperature prior to the test, as always necessary with strong basic oxides like CaO or MgO to remove adsorbed H<sub>2</sub>O and CO<sub>2</sub> poisoning the basic sites. Up to now, the high selectivity in 2-cyclopentylidene-cyclopentanone (**6**) over zirconium containing catalysts remains unexplained. Nitridation of the aluminophosphate AlPO and zirconophosphate ZrPO has a positive effect on activity, which is very clearly evidenced when the decrease in surface area induced by nitridation is taken into account in the normalisation of the results. Contrarily to what was observed for the aldol condensation between benzaldehyde and heptanal to form jasminaldehyde, the creation of weak basic sites on the surface, through nitridation, does not favour the cross-condensation of cyclopentanone with one or two molecules of valeraldehyde over the self-condensation of valeraldehyde.

On the contrary, the lowest percentages of 2-propyl-2-heptenal (**4**) were obtained over MgO and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> that both lack acid–base site pairs of intermediate strength. This difference is understandable, as the mechanisms of the competition between the cross- and the self-condensation are different for benzaldehyde with heptanal and for cyclopentanone with valeraldehyde.

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