Aldol Condensations on Solid Catalysts: A Cooperative Effect between Weak Acid and Base Sites

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Dedicated to Prof. R. A. Sheldon on the occasion of his 60th birthday.

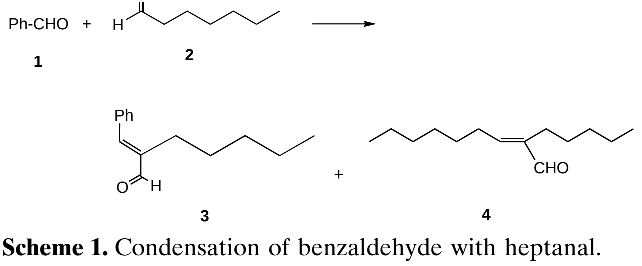
Abstract: An amorphous aluminophosphate (ALPO) catalyst containing weak acid and base centers can carry out the aldol condensation of heptanal with benzaldehyde at much higher rates and selectivities than conventional solid acid (amorphous or crystalline aluminosilicates) or base catalysts (MgO, hydrotalcites, KF/Al_2O_3, nitrurated ALPO). With the weak acid-base catalyst, the reaction occurs through a bifunctional acid-base mechanism that involves the activation of benzaldehyde, by protonation-polarization of the carbonyl group on the acid sites, and the attack of the enolate heptanal intermediate generated on the basic sites. With this type of bifunctional acid-base catalyst, compounds with weak basicities are already able to undergo the reaction with a much higher selectivity than those obtained on stronger acid or base catalysts.

Keywords: aldol condensation; aluminophosphates; bifunctional acid-base catalysts; MgO; solid catalysts for fine chemicals; synthesis of jasminaldehyde

Introduction

Jasminaldehyde, α-*n*-amylcinnamaldehyde (**3**), is a traditional perfumery product with a violet scent which can be obtained by the aldol condensation of heptanal with benzaldehyde (Scheme 1). Its synthesis is traditionally carried out using sodium or potassium hydroxide as basic catalyst, heptanal being added slowly to the reaction mixture at moderate temperatures.[1]

During the synthesis of **3**, different by-products which reduce the yield of amylcinnamic aldehyde can be formed. The most important undesired product comes from the self-condensation of heptanal to form 2-*n*-pentyl-2-*n*-nonenal (**4**) (Scheme 1). The formation of **4** can be inhibited, to some extent, by maintaining a very low concentration of heptanal relative to benzaldehyde in the reaction mixture. This can be achieved by using a high benzaldehyde/heptanal molar ratio or/and by adding slowly the heptanal into the reaction mixture.



Scheme 1. Condensation of benzaldehyde with heptanal.

The tendency in recent years is to develop environmentally friendly solid catalysts for the production of fine chemicals. The use of insoluble catalysts in organic synthesis allows the recycling and handling of the catalyst, so that the overall process is more efficient.[2]

Different solid base catalysts have been reported for the synthesis of jasminaldehyde. Among them, the most interesting are anionic exchange resins,[3] potassium carbonate in the presence of a solid-liquid phase transfer catalyst,[4] and solid-liquid phase transfer catalyst in dry media under microwave irradiation.[5] It is known that the condensation of heptanal and benzaldehyde can also be carried out in the presence of solid acid catalysts. Indeed, in a previous work[6] we have tested the activity and selectivity of different acid molecular sieve catalysts, and found that mesoporous (MCM-41) material gave better results than microporous aluminosilicates. These results were attributed to the confinement effects of the reactants and products inside the voids of the microporous materials, which lead to the preferential formation of the self-condensation product as well as to a fast deactivation of the catalyst.

Here, we show that it is possible to carry out very effectively this reaction with solid catalysts containing both weak acid and weak basic sites [aluminum phosphate (ALPO)]. It will be shown that, when the number of acid sites of the aluminum phosphate is systematically reduced while increasing the number and strength of the basic ones (nitrurated aluminum phosphate, ALPON),[7,8] both activity and selectivity decrease. It will be shown that the bifunctional system is able to perform the synthesis of jasminaldehyde at much higher rates than either acid (silicates) or basic (MgO, KF/Al_2O_3, ALPON) catalysts. The results show the possibility for designing bifunctional acid-base catalysts which can replace the use of stronger solid bases, avoiding the associated problems of stability towards water and CO_2.

Results and Discussion

In a previous work, it was found[6] that AlPO (amorphous aluminophosphate) was more active and selective than other more acidic solids, such as zeolites and mesoporous aluminosilicates, for producing jasminaldehyde from the condensation of benzaldehyde and heptanal. Since these results were difficult to explain from the point of view of an acid mechanism, the following hypothesis was introduced: the superior behavior of amorphous aluminum phosphate over other more acid catalysts could be due to a combined acid-base catalyzed condensation where the weak acid sites of ALPO are interacting with the carbonyl group of benzaldehyde producing a polarization of this group, and as a consequence increasing the positive charge on the corresponding carbon atom. This should favor the attack of the enolate heptanal intermediate formed on the relatively weak Lewis basic sites associated to bridged oxygens. This hypothesis would be consistent with the observation that in homogeneous base-catalyzed condensations of alkanals with benzaldehyde, the selectivity to α-alkylcinnamaldehydes can be increased by the presence of a small amount of an acid.[9]

In order to verify or reject this hypothesis we have worked here from another starting point. Indeed, the condensation of benzaldehyde with heptanal can also be catalyzed by bases since the commercial process uses NaOH or KOH as catalyst. The mechanism of the reaction catalyzed by basic sites would involve the formation of the anion of heptanal followed by its attack to the carbonyl group of benzaldehyde.

Thus a series of basic catalysts with increasing basicities, i.e., NaCsX zeolite $<$ MgO $<$ $KF\text{-}Al_2O_3$ was tested here and in all cases (*E*)-amylcinnamaldehyde (**3**) and (*E*)-2-*n*-pentyl-2-*n*-nonenal (**4**) were produced. Moreover, with the most basic catalysts (KF-alumina and MgO) a by-product (**5**) was detected in the reaction mixture, the structure of which was assigned by mass spectroscopy to a compound coming from the Michael addition of heptanal to **4**. In Table 1 the initial rates for the disappearance of heptanal as well as the selectivity, and yields of **3** after 8 h reaction time are summarized. As can be observed there, the order of activity of the catalysts is $KF\text{-}Al_2O_3$ $>$ MgO $>$ NaCsX which follows the order of the basicity of the solids. It appears then that on these catalysts the basic sites are responsible for the reaction to occur, following the mechanism described above. However, these catalysts do not exhibit high selectivities to jasminaldehyde (**3**), the selectivity to this compound being especially low in the case of MgO. With this catalyst the self-condensation of heptanal (**4**) is highly favored, while the Michael addition reaction (**5**) also takes place albeit to a much lower extent (Figure 1 and Table 1).

When comparing the selectivity results obtained with MgO and NaCsX zeolite one can think, in a first approximation, that the higher selectivity of MgO to **4** and **5** should be due to the stronger basicity of MgO which is able to carry out the more difficult heptanal self-condensation and Michael addition.[7] In our opinion, while this is a realistic assumption and basic strength certainly has an important influence on the selectivities

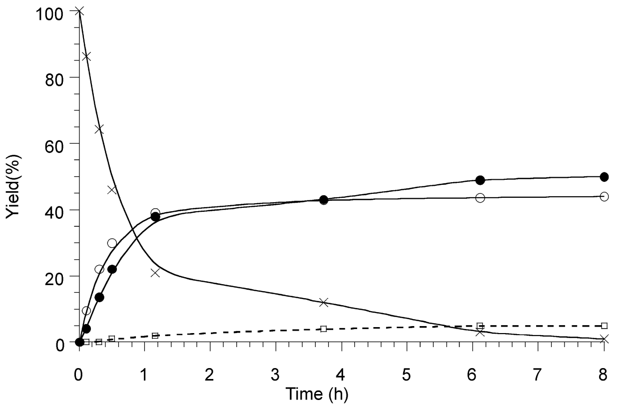


Figure 1. Conversion versus time plot for reaction of benzaldehyde (50 mmol) and heptanal (10 mmol) in the presence of MgO (10 wt %) at 398 K: **2** (×), **3** (●),**4** (o), **5** (□).

Table 1. Results of the condensation of benzaldehyde with heptanal in the presence of different solid base catalysts.

Catalysts	r_o 10^3 [mol min^{-1} g^{-1}]	Selectivity[a] to **3**	Yield [%][b]		
			3	**4**	**5**
NaCsX[c]	0.1	60	27	5	–
MgO[d]	3.3	52	50	43	5
KF/Al_2O_3	3.9	66	50	25	3
ALPO	3.2	85	83[e]	13	–

[a] Selectivity at 90% of conversion of heptanal.
[b] 8 h reaction time, using 10 wt % of catalyst at 398 K.
[c] The maximum conversion achieved was 45% and 13% of heptanoic acid was detected.
[d] MgO was activated before reaction by heating the solid at 723 K under nitrogen atmosphere during 9 h.
[e] 3 h reaction time.

obtained, this cannot be the only variable and some other factors should also play an important role for controlling the selectivity of these catalysts. Indeed, while KF/Al_2O_3 has stronger basicity than MgO, it gives nevertheless a higher selectivity to α-*n*-amylcinnamaldehyde (**3**) and lower selectivities to products **4** and **5** than MgO. It appears to us that adsorption effects may also play an important role on selectivities by favoring the relative adsorption of heptanal in the case of MgO. In any case, it can be seen that the selectivity to **3** obtained with any of these basic catalysts is much lower than with ALPO (Table 1). Thus, we have to conclude that neither purely acidic or basic catalysts are more active and selective than ALPO.

At this point, we thought of starting from ALPO and by a high temperature treatment in the presence of NH_3, to react hydroxy groups bonded to phosphorus (P-OH) with NH_3. This reaction should convert the acid P-OH into basic P-NH_2 groups as indicated in Equation 1, leading to an amorphous aluminophosphate oxynitride (ALPON).

$$-POH + NH_3 \rightleftharpoons -PNH_2 + H_2O \qquad (1)$$

Indeed, by IR spectroscopy we can see (Figure 2) that the intensity of the hydroxy band at 3670 cm^{-1} which is associated to P-OH groups decreases upon NH_3 treatment while the intensity of an IR band at 1559 cm^{-1} associated to the presence of P-NH_2 groups increases (Table 2). This observation clearly indicates that we are progressively reducing the number of weak Brönsted acid sites (P-OH), while increasing the number of the basic sites (P-NH_2). The acidity and basicity of these samples were studied by means of two test reactions, i.e., acetalization of benzaldehyde with trimethyl orthoformate (TMOF) and Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate, which are exclusively catalyzed by acid and base sites, respectively. Furthermore, these two reactions can already take place on weak acid and base sites.

The results for the acid-catalyzed acetalization showed that, as was predicted from the IR results, the

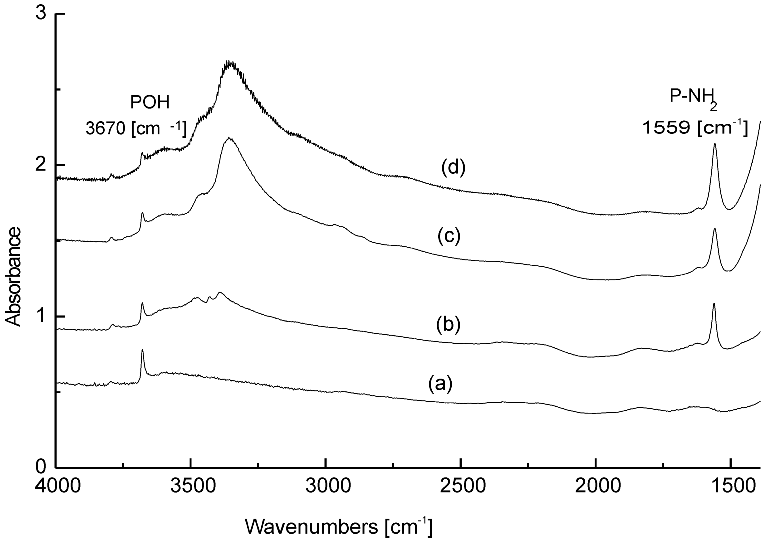


Figure 2. IR spectra of ALPON samples with different nitrogen contents after vacuum treatment at 473 K for 2 h. (a) ALPO; (b) ALPON-1; (c) ALPON-2; (d) ALPON-4.

Table 2. Intensity of the IR bands assigned to $-POH$ and $-NH_2$ groups as function of N content of the sample and initial rates obtained in the test reactions.

Catalysts	N (wt %)	$-NH_2$	$-POH$	Acetalization[a] r_o [mmol min^{-1} g^{-1}] 10^4	Knoevenagel[b] r_o [mmol min^{-1} g^{-1}] 10^4
ALPO	–	–	0.29	18.00	2.00
ALPON-1	1.3	0.11	0.18	2.75	2.50
ALPON-2	6	0.28	0.06	2.20	5.61
ALPON-3	9.4	0.60	0.04	1.70	11.00
ALPON-4	13.7	0.50	0.01	0.82	10.10

Reaction conditions:

[a] Benzaldehyde (10 mmol), TMOF (25 mmol), catalyst (360 mg) at reflux temperature of tetrachloromethane (15 mL).

[b] Benzaldehyde (10 mmol), ethyl cyanoacetate (10 mmol), 5 wt % of catalyst at 333 K.

acidity of the samples decreases when increasing the N content of the catalyst, and consequently when decreasing the number of P-OH groups. Meanwhile, the activity for the base-catalyzed reaction (Knoevenagel condensation) increases when increasing the nitrogen content and consequently when increasing the number of basic sites (–NH_2). It should be remarked that ALPO also shows activity as base catalyst through weak basic sites (bridged oxygens).

In other words, the characterization and catalytic results of these samples indicate that by the NH_3 treatment we are converting a bifunctional catalyst such as ALPO, containing both weak acid and basic sites, into a more and more basic catalyst.

The nitrurated ALPO samples were tested for the production of jasminaldehyde and the results are given in Table 3. It can be seen there that a reduction of the acid sites of ALPO by NH_3 treatment causes first a decrease of activity, followed by an increase of activity for samples with nitrogen content $\geq$ 9.4 wt %. Nevertheless, it is evident that the selectivity to the desired product (**3**) decreases, while the *n*-heptanal self-condensation increases when decreasing the number of acid POH groups, and at the same time as the number of purely basic sites is increased. These results strongly support the hypothesis that catalysts with weak acid and base sites are better than catalysts containing only acid or base sites irrespective of whether they are weak or strong.

It would also be interesting to proceed now from the amorphous aluminum phosphate to silicon aluminum phosphates (SAPO) with different Si:Al:P ratios. In this case, by increasing the silicon content we should increase the acidity of the material while decreasing its basicity, the amorphous silica alumina (SAM) being the most acid material. Indeed, the results obtained with the acid (acetalization) and base (Knoevenagel condensation) test reactions showed that the order of catalyst acidity was: SAM > SAPO > ALPO, whereas the order of basicity was: ALPO > SAPO > SAM.

Table 3. Results obtained in the condensation of benzaldehyde with heptanal in the presence of aluminophosphates with different percentages of nitrogen content.

Catalysts	N [%]	r_o (10^3) [mol min^{-1} g^{-1}]	Selectivity to **3**[a]	Yield[b] [%]		
				3	**4**	**5**
ALPO	0	3.2	85	85	13	–
ALPON-1	1.3	2.8	83	75	15	1
ALPON-2	6.0	2.7	78	76	13	8
ALPON-3	9.4	3.9	74	74	17	8
ALPON-4	13.7	3.0	70	70	23	6

[a] Selectivity at 90% of heptanal conversion.

[b] At 8 h reaction time, using 10 wt % of catalyst at 398 K.

Table 4. Condensation of benzaldehyde with heptanal on different catalyst.[a]

Catalysts	Yield of **3** [%]	Yield of **4** [%]	Others [%][b]	Selectivity to **3** [%]
ALPO	83	13	–	86
SAPO	70	18	6	74
SAM	52	32	10	55

[a] Reaction conditions: 3 h reaction time, molar ratio benzaldehyde/heptanal = 5, 10 wt % of catalysts at 398 K.

[b] Phenylheptene and heptanoic acid were detected.

Thus, when the above samples were used for producing jasminaldehyde (Table 4), we can see that SAPO are active since they are acid catalysts but, nevertheless, neither their activity nor their selectivity is higher than that of the amorphous aluminum phosphate in which weak acid and base sites coexist.

From all the above, we have to conclude that jasminaldehyde can be formed *via* three different mechanisms.

Catalysis by Acid Sites

In this mechanism the carbonyl group of the benzaldehyde should be preferentially protonated and the enolic form of the heptanal attacks the activated benzaldehyde.

When benzaldehyde is adsorbed on ALPO and SAM samples, we can detect by IR spectroscopy (Figure 3) the presence of a band $\sim$1690 cm^{-1} corresponding to the carbonyl group of the free aldehyde (adsorbed in excess) while a second band appearing at 1654 cm^{-1} in ALPO and 1634 cm^{-1} in SAM must be assigned to the carbonyl groups interacting with acid centers. The observed shift towards low wavenumbers indicates that SAM possess stronger acid sites than ALPO.

Heptanal can also be protonated by Brönsted acid sites, however taking into account that the protonated species formed are less stable than in the case of benzaldehyde, and that benzaldehyde is used in excess with respect to heptanal (benzaldehyde/heptanal molar ratio = 5), we have to expect that the surface population of activated benzaldehyde was larger than that of heptanal. This leads to a lower selectivity to the self-condensation of heptanal when using acid than when using base catalysts (see Tables 5 and 1).

Catalysis by Basic Sites

In this case proton extraction from the α-carbon of the heptanal by the basic sites occurs generating a carbanion species which will attack the carbonyl group of the benzaldehyde.

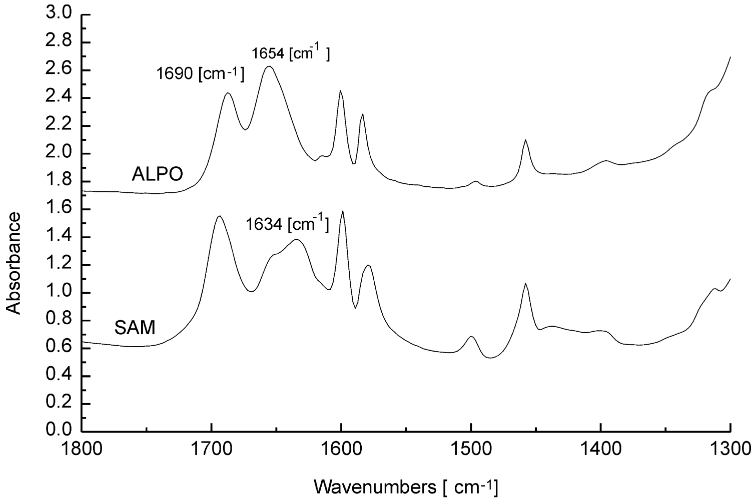


Figure 3. IR spectra of benzaldehyde adsorbed on ALPO and SAM.

Table 5. Results obtained in the condensation of benzaldehyde and heptanal (molar ratio 5:1) with different acid catalysts (10 wt %) at 398 K.

Catalysts	Reaction Time [h]	Conversion of **2** [%]	Poison in the Catalyst [%][a]	Selectivity to **3**	Yields [%]		
					3	**4**	Others[b]
H-Beta	6	93[b]	5.1	21	20	40	28
HY-100	16	53	7.4	52	28	15	3
AlMCM-41	10	99	–	56	56	35	8
ALPO	3	96	1.5	86	83	13	–

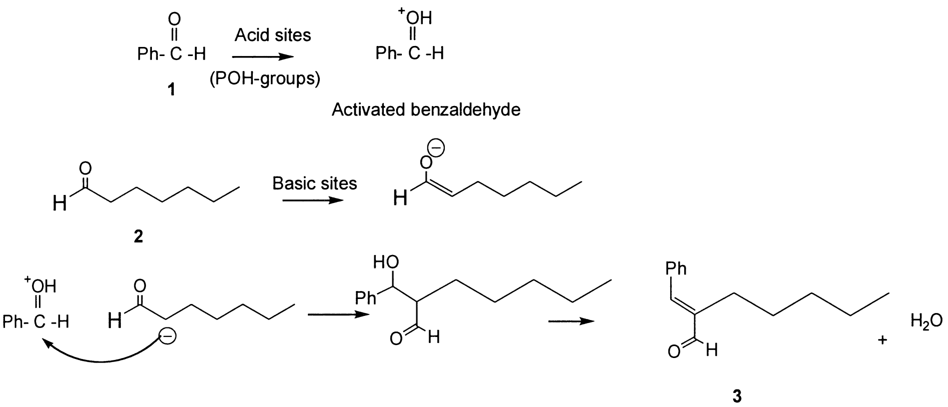
[a] Determined by TG analysis and based on mole of heptanal retained.

[b] Phenylheptene and heptanoic acid were also detected.

Catalysis by Cooperative Acid and Base Sites

A third mechanism which involves acid and base sites is consistent with the results obtained in this work, and is operative in the case of amorphous ALPO (Scheme 2).

In this mechanism a weak Brönsted acid site (P-OH) will interact with the carbonyl group polarizing the carbon-oxygen bond and increasing the density of positive charge on the carbon supporting the carbonyl group. This makes this carbon more susceptible to be attacked by the carbanion of the heptanal formed by interaction of this molecule with the basic oxygen sites of the ALPO. This bifunctional mechanism is effective from a conversion point of view showing that it should



Scheme 2. Acid-base catalyzed condensation mechanism of benzaldehyde with heptanal.

be possible, in some cases, to replace stronger bases by other catalysts which have lower basicities and acid sites strong enough to activate one of the reactants. When this mechanism works, it gives good selectivities to the cross-condensation, specially in those cases in where the molecule to be attacked by the carbanion can be preferentially activated by the acid sites of the catalyst, as it occurs in the case of jasminaldehyde.

Conclusions

It has been shown that the use of purely acid or purely basic catalysts for the condensation of benzaldehyde and heptanal leads to lower selectivities to jasminaldehyde than solid catalysts bearing an acid-base bifunctional character, such as the exhibited by the amorphous aluminum phosphate (ALPO).

The role of the weak acid sites is the activation of benzaldehyde by interaction with the carbonyl group favoring then the attack of the enolate heptanal intermediate generated on the relatively weak basic sites of ALPO. Indeed, it has been shown that by a high temperature treatment of the ALPO in the presence of NH_3 acid sites are systematically reduced while increasing the number and strength of the basic ones. This change in the nature and distribution of active sites of the catalyst causes a decrease in the selectivity to jasminaldehyde. In an analogous way, introduction of Si in the aluminum phosphate produces silico-aluminophosphates in which the acid-base character is shifted towards higher acidities causing again a decrease in the selectivity to jasminaldehyde.

Experimental Section

Materials

The amorphous aluminum phosphate (ALPO) with a P/Al ratio of 1.0 and surface area of 211 $m^2\,g^{-1}$ was prepared following the method proposed by Lindblad et al.[10] To reduce the acid sites while increasing the basicity, nitridation of the aluminophosphate was performed under an ammonia flow at the conditions indicated in Table 6.

The following materials have been used as basic catalysts. The XNaCs zeolite was prepared by repeated exchange of NaX zeolite (13X) at room temperature using an aqueous solution of CsCl (0.5 M). The BET surface area of the resultant catalyst was 650 $m^2\,g^{-1}$. An MgO sample was prepared following the procedure previously reported[11] and its BET surface area was 246 $m^2\,g^{-1}$.

The KF/Al_2O_3 sample with 40 wt % of KF was purchased from Aldrich.

Beta zeolite (Si/Al = 13) was supplied by PQ corporation in the acidic form.

The HY-100 zeolite (where the number indicates the percentage of Na^+ to NH_4^+ exchange) was prepared by stirring a commercial NaY sample (SK-40, Union Carbide, Si/Al = 2.5) with different aqueous solutions of ammonium acetate followed by calcination at 823 K.[12] Al-MCM-41 (Si/Al = 15) with a pore diameter of 3.5 nm, was prepared following the procedure given in ref.[13]

Amorphous SAPO sample with an SiO_2 content of 10% was prepared starting from an aqueous solution of H_3PO_4, $AlCl_3$ and tetraethyl orthosilicate (TEOS) acidified with nitric acid at pH < 0. A hydrogel with of typical composition: 1.0 P_2O_5: 1.0 Al_2O_3: 0.6 SiO_2, was then formed by adding concentrated ammonia solution until a pH of 6. After 1 h the solvent was filtered off and the hydrogel washed with distilled water. The solid was dried at 393 K for 16 h and calcined at 773 K. The BET surface was 210 $m^2\,g^{-1}$.

Amorphous silica alumina (SAM) with a Si/Al ratio of 50, with a very narrow pore distribution at ~1.5 nm, and with a surface area of 719 $m^2\,g^{-1}$ was prepared according to the procedure reported by Bellusi et al.[14]

Elemental analyses of the pure as-synthesized ALPON's were carried out by using a CHNS analyzer (Fisons EA 1108).

Infrared measurements were performed with a Nicolet 710 FT spectrophotometer using self-supporting wafers of 10 mg cm^{-2} and a Pyrex vacuum IR cell. Prior to the collection of spectra the samples were heated in the cell for 2 h at increasing temperatures, after which the spectra were obtained at room temperature. IR spectra of the adsorbed benzaldehyde were obtained by the following procedure: catalyst samples were prepared as thin self-supported wafers and they were heated for 16 h at 673 K under vacuum (10^{-5} torr) to remove any adsorbed water. Benzaldehyde was then admitted at room temperature and, after saturation, the aldehyde excess was removed from the samples at 10^{-5} torr, and the IR-spectra were recorded at room temperature.

N_2 and Ar adsorption/desorption isotherms were performed at 77 and 87.3 K, respectively, in an ASAP 2010 apparatus from Micromeritics, after pre-treating the samples under vacuum at 673 K overnight and the specific surface area were obtained using the BET methodology.

Table 6. Main characteristics of the oxynitride samples.

Catalysts	N [wt %]	Nitridation Time [h]	NH_3 flow rate [ml min^{-1}]	Nitridation Temperature [K]	S_{BET} [$m^2\,g^{-1}$]
ALPO	–	–	–	–	210
ALPON-1	1.3	24	150	773	210
ALPON-2	6.0	16	50	1073	205
ALPON-3	9.4	16	150	1073	207
ALPON-4	13.7	16	150	1123	141

Reaction Procedure: Condensation of Benzaldehyde and Heptanal

All reactions were carried out under nitrogen atmosphere, in a flask that was fitted with a reflux condenser. The flask was immersed in a thermostatted silicone oil bath and the reaction mixture was magnetically stirred. A mixture of previously distilled benzaldehyde (50 mmol) and heptanal (10 mmol) was placed in the flask. Once the mixture reached a temperature of 398 K, a specific calculated quantity of the catalyst was added such that the final wt/wt ratio of catalyst versus the total sum of reagents was 10%. Zeolites (HY and HBeta) and AlMCM-41 catalysts were activated before reaction at 323 K under vacuum (1 torr) for 3 h. Samples of the reaction mixture were periodically withdrawn with a filtering syringe and analyzed by gas chromatography (GC) (Hewlett-Packard 5990A spectrometer provided with a 25-m capillary column of cross-linked 5% phenylmethylsilicone).

Quantitative determinations were based on the measured response factors of the reactants and reaction products. Reaction products were identified by ^{1}H NMR spectroscopy (Varian VXR – 400 S, 400 MHz) and GC-mass spectrometry (Hewlett-Packard 5988A mass spectrometer connected with a 25-m capillary column of phenylmethylsilicone).

Yield for jasminaldehyde (**3**) was defined as the mmole formed of this product divided by the initial mmole of the limiting reactant (heptanal). Yield for 2-pentyl-2-nonenal (**4**) was defined as the mmole formed of this product multiplied by two (according the 2:1 stoichiometry for formation of **4**) and then divided by the initial mmole of heptanal. Selectivity to jasminaldehyde (**3**) was defined as the mmole of this compound divided by the total mmole of heptanal converted.

Spectroscopic Data of the Reaction Products

(*E*)-α-Amylcinnamaldehyde (**3**): ^{1}H-NMR: $\delta = 9.54$ (s, 1H, -C$\underline{\text{H}}$O), 7.20 (s, 1H, Ph-C$\underline{\text{H}}$=CCHO-), 2.52 (tt, 2H, -C$\underline{\text{H}}_2$-C=CH-Ph), 1.50 [m, 2H, -CH$_2$-C$\underline{\text{H}}_2$-(CH$_2$)$_2$-CH$_3$], 1.34 [m, 4H, -CH$_2$-(C$\underline{\text{H}}_2$)$_2$-CH$_3$], 0.89 (m, 3H, -C$\underline{\text{H}}_3$); MS: $m/z = 202$ (M$^+$, 12), 145 (9), 129 (48), 115 (100), 105 (28), 91 (14).

(*E*)-2-Pentyl-2-nonenaldehyde (**4**): ^{1}H-NMR: $d = 9.36$ (s, 1H, -C$\underline{\text{H}}$O), 6.44 (t, 1H, -CH$_2$-C$\underline{\text{H}}$=CCHO-), 2.34 (m, 2H, -C$\underline{\text{H}}_2$-CCHO=CH-), 2.21 (m, 2H, -C$\underline{\text{H}}_2$-CH=CCHO-); MS: $m/z = 210$ (M$^+$, 98), 153 (30), 139 (34), 125 (41), 41 (100).

3-Hexyl-2,5-dipentylpentanedial (**5**): MS: $m/z = 324$ (M$^+$, 5), 295 (43), 266 (10), 252 (100), 177 (10), 41 (35).

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