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Aluminophosphates Oxynitrides as Base Catalysts: Nature of the Base Sites and Their Catalytic Implications

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By means of IR spectroscopy it has been found that Al–NH–P and P–NH_2 groups are formed during the high temperature NH_3 treatment of amorphous aluminophosphates (ALPONs). The amount of nitrogen incorporated increases with time of exposure to NH_3, while also increasing the ratio of the more basic –NH– with respect to the less basic –NH_2 groups. This is reflected in the catalytic activities of these materials for the Knoevenagel condensation reaction using the activated methylenic groups of different pK_a values as reactants. ALPON materials have stronger basic sites than alkaline exchanged Y zeolites and weaker basic sites than MgO and Hydrotalcites. However, in the case of Knoevenagel condensation reactions the ALPONs present a very adequate basicity, especially when the competing Michael addition can also occur. In such cases the selectivities of the oxynitrides are better that those showed by MgO and hydrotalcites. © 1996 Academic Press, Inc.

1. INTRODUCTION

The Knoevenagel reaction is used in organic synthesis to produce alkenes from molecules containing carbonyl groups. This reaction is catalyzed by bases under mild reaction conditions. The actual tendency in organic synthesis is to use insoluble catalysts which allow handling of the reaction mixture from which the catalyst and products can be separated by filtration. In this way the recycling and handling of the catalyst become much easier, so that the overall process is more efficient (1).

The Knoevenagel reaction can be catalyzed by a large variety of solid bases with strengths of basicity ranging from weak to strong ones. In this sense, alkaline exchanged and over exchanged zeolites (2), sepiolites (3), alkaline earth oxides (4), hydrotalcites (5), resins (6), and alkaline earth carbonates (7) have been used successfully.

The interest of this reaction goes further than its use in a particular synthesis, since it has been proved to be a very adequate test reaction for base catalysts (3, 5). Indeed, by reacting one aldehyde with molecules containing activated methylenic groups with different pK_a values in the presence of a base catalyst, it is possible to find the minimum pK_a value of the reactant for which the catalyst becomes active. Thus, in this way catalysts with different basicities can be conveniently compared (2, 3, 5).

It has been reported in the literature that it is possible to exchange nitrogen by some of the oxygens in amorphous silica (8), crystalline aluminosilicates (zeolites) (9), and aluminophosphates (ALPOS) (10) by treating these materials at high temperatures in the presence of NH_3. More recently Grange *et al.* (11) have shown that this substitution can also occur, to a large degree, in amorphous aluminophosphates, such that the resultant oxynitrides exhibit basic characteristics, such as to catalyze the condensation of benzaldehyde with malononitrile.

In this work, IR spectroscopy has been used to characterize the basic sites of aluminophosphates treated with NH_3 at high temperatures. The influence of the reaction conditions on the total number as well as on the amount of different basic sites has been investigated. We have used the Knoevenagel condensation reaction with reactants with different pK_a values to measure the basicity of the oxynitride amorphous aluminophosphates. Their basic strength has been compared with that of zeolites, alkaline earth oxides, and hydrotalcites.

2. EXPERIMENTAL

2.1. *Materials*

The aluminium phosphate precursor ($ALPO_4$) with a P/Al ratio of 0.9 was prepared following the method proposed by Lindblad *et al.* (12). Nitridation procedure of the aluminophosphate was performed under ammonia flow (85 ml min^{-1}) at 1073 K for different time periods ranging from 3 to 70 h.

The characteristics properties of the resultant oxynitrides (ALPON) are reported in Table 1.

The XCs zeolite was prepared by repeated exchange of Na–X zeolite (13×) 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}.

A MgO sample was prepared following the procedure previously reported (13) and the BET surface area was 278 m^2 g^{-1}.

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TABLE 1

Main Characteristics of the Oxynitride Catalysts

Catalyst	Nitridation time (h)[a]	S_{BET} (m^2/g)	P (wt%)	Al (wt%)	N (wt%)
ALPO-0	0	100	23.6	24.3	0.0
ALPON-1	3	120	23.7	24.4	3.6
ALPON-2	10	107	23.8	24.5	5.0
ALPON-3	24	91	23.8	24.5	6.4
ALPON-4	70	192	23.9	24.6	8.9

[a] Nitridation temperature, 1073 K.

A Mg–Al hydrotalcite was prepared by adding two solutions A and B, each at a rate of addition of 60 ml h^{-1} for 4 h into a mixing tank while stirring. Solution A was prepared by dissolving $Mg(NO_3)_2$ and $Al(NO_3)_3$ in distilled water until the solution was 1.5 *M* with an Al/(Al + Mg) atomic ratio equal to 0.25. Solution B was prepared by dissolving Na_2CO_3 and Na(OH) in water, in such a way that when both solutions A and B were mixed the following ratios were achieved: $CO_3^{2-}/(Al+Mg) = 0.666$ and $OH^-/(Al+Mg) = 2.55$. The final pH after mixing A and B was 13. The resultant gel was heated in an autoclave at 200°C for 18 h. Finally, the product was filtered and washed until the pH of the washing water was 7. After drying at 353 K for 12 h, the hydrotalcite was calcined at 723 K for 18 h. The BET surface area of the resultant catalyst was 214 m^2 g^{-1}.

2.2. Characterization

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

Surface areas of the different ALPON's were obtained on an ASAP 2000 (Micromeritics) using the BET methodology. The samples were pretreated at 673 K prior to the N_2 adsorption.

Infrared measurements were performed on a Nicolet 710 FT spectrophotometer using self supporting wafers of 10 mgr 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 (293, 373, 473, 573, and 673 K), after which the spectra were obtained at room temperature.

2.3. Reaction Procedure

All reactions were carried out under an inert atmosphere (N_2), in a flask that was fitted with a reflux condenser. The flask was immersed in a thermostated silicone oil bath and the reaction mixture was magnetically stirred. A mixture of previously distilled benzaldehyde (10 mmol) and the active methylene compound (10 mmol) was placed in the flask. Once the mixture reached a temperature of 333 K, a specific calculated quantity of the base catalyst was added such that the final wt/wt ratio of base catalyst total sum of reagents was 5%. In case of diethyl malonate the reaction was carried out at 383 K using 10% wt of base catalysts. Samples of the reaction mixture were then periodically withdrawn by a filtering syringe within a time period of 0.1 to 1 h and analyzed by gas chromatography (GC).

Quantitative determinations were based on the calculated response factors for binary and ternary mixtures of the reactants and corresponding reaction products. Each reaction product was identified by ^1H-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).

RESULTS AND DISCUSSION

Characterization of the Oxynitrides by IR Spectroscopy

During the formation of oxynitrides from amorphous aluminophosphates by high temperature NH_3 treatment, one could substitute various types of oxygen atoms, i.e., bridging Al–O–P, Al–OH, and P–OH, with nitrogen atoms to give Al–NH–P, Al–NH_2, and P–NH_2 groups, each one of which exhibiting different base strengths. It is, therefore, important to know the type and the relative amount of basic sites formed when carrying out the synthesis treatments. Furthermore, it is necessary to locate and control their relative population by modifying the preparation conditions.

FT-IR spectroscopy is a suitable technique for monitoring the presence of the different NH_x groups on the surface of these catalysts. Figure 1 shows the IR spectrum of the ALPON-2 sample after treatment in vacuum at 373 K which removes the water of hydration. The following bands were seen: 3670 cm^{-1} (assigned to structural P–OH) (14); 3480, 3370, and 1550 cm^{-1} (stretching and bending modes, respectively, of the group M–NH_2 (M=Al, P)) (15, 16); ~3300 cm^{-1} (probably NH_3 and/or NH_4^+ stretching modes); 1620 cm^{-1}(NH_3, bending modes), and 1450 cm^{-1} (NH_4^+ bending mode) (17). Busca *et al.* (18), however, show the presence of a unique stretching NH band at ~3370 cm^{-1} in a sample of silica treated with NH_3, that was assigned to the Si–NH–Si group. The authors detect also the presence of a low intensity IR band at ~1555 cm^{-1} assigned to the same group.

In organo-phosphorous compounds (19), the group P–NH_2 shows several stretching bands at ~3400 cm^{-1} and a strong bending band at ~1550 cm^{-1}. However, the Al–NH–P groups present, which correspond to secondary amine species, are indicated by a stretching band at ~3370 cm^{-1} and a low intensity bending band at ~1550 cm^{-1}.

From the work reported here and previously published results we can assign bands for the different basic sites which may exist in oxynitride ALPO compounds (Table 2).

It can be seen in Fig. 2 that when treating a sample of ALPON-2 in the IR cell at ~473 K the NH_3 bands

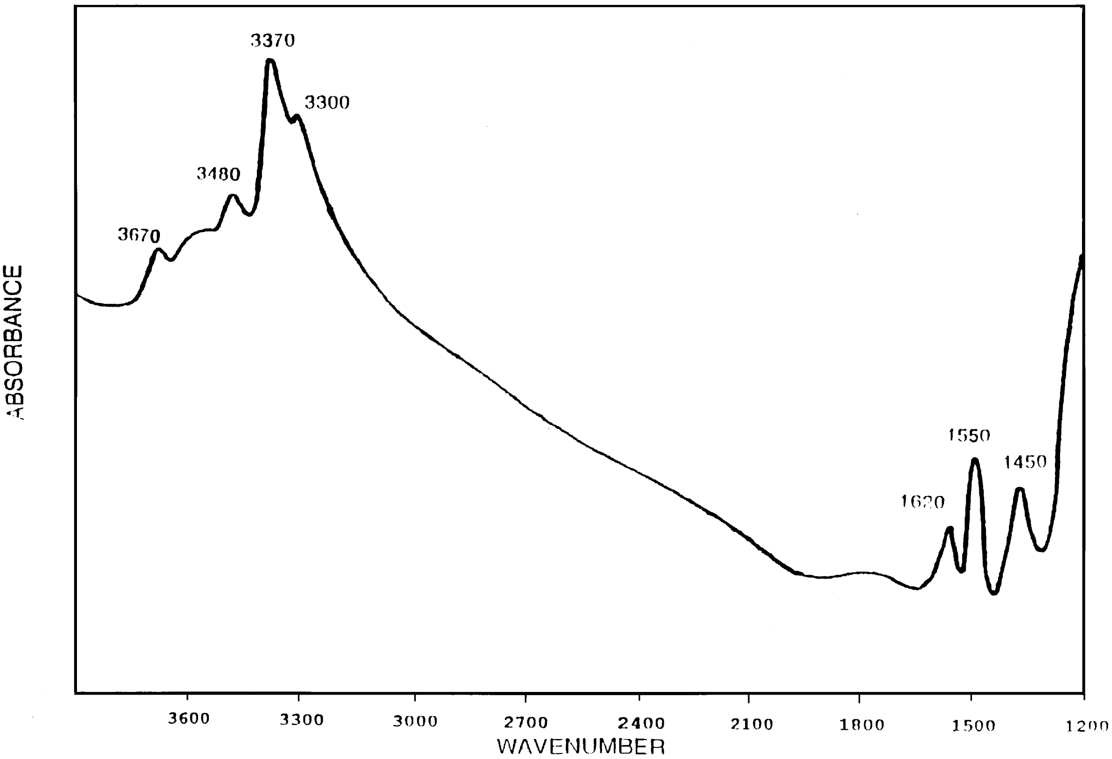
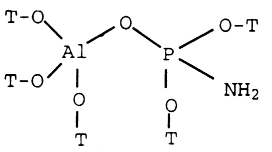


FIG. 1. IR spectrum of ALPON-2 after vacuum treatment at 373 K for 1 h.

(~3300 and 1620 cm^{-1}) as well as NH_4^+ bands (~3300 and 1450 cm^{-1}) have been desorbed while the bands corresponding to $-NH_2$ (3480, 3370, and 1550 cm^{-1}) and/or –NH– groups (3370 cm^{-1}) remain in the spectra. A broad band centered ~3600 cm^{-1}, due to interacting P–OH groups, disappears while the narrow one at 3670 cm^{-1} due to free P–OH groups is restored. At increasing temperatures of desorption a small decrease in the intensities of the IR bands associated to $-NH_2$ and/or to –NH– groups has been observed. No band around 2300 cm^{-1} related to the presence of P–H groups (19) has been detected.

From the above results, it seems that IR spectroscopy is a useful technique for characterizing ALPON materials. The results indicate that during high temperature NH_3 treatment of amorphous aluminophosphates, –NH– and $-NH_2$ groups of the type shown below are formed and could act as base active sites.



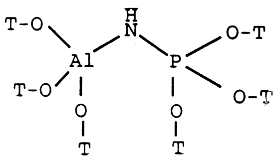


TABLE 2

Assignation of the IR Bands, Given by Aluminium Phosphate Oxynitrides

Wavenumber (cm^{-1})	Assignation
3670	ν_{OH} (POH)
~3480	ν_{NH} ($-NH_2$)
~3370	ν_{NH} ($-NH_2$ and mainly –NH–)
~3300	ν_{NH} (NH_3 and/or NH_4^+)
1620	δ_{NH} (NH_3)
1550	δ_{NH} ($-NH_2$ mainly)
1450	δ_{NH} (NH_4^+)

It should be noted that before using these samples as base catalysts one has to be sure that no NH_3 is adsorbed on the catalyst.

The IR spectra of the different ALPONs obtained at 1073 K for various times of treatment in the presence of NH_3 are qualitatively similar to that presented by the ALPON-2 sample (Fig. 1); but a difference in intensity (Table 3) for each sample is seen.

The duration of the treatment has an important impact on the amount of the different species formed. Long durations of exposure to NH_3 (Table 3) strongly decrease the amount of NH_4^+ and NH_3 remaining on the solid. It is important to note that with increasing reaction time, the 3370 cm^{-1} band associated to $-NH_2$ and –NH– groups clearly increases, while the intensity of the 1550 and 3480 cm^{-1} which corresponds exclusively to $-NH_2$ remains practically unaffected.

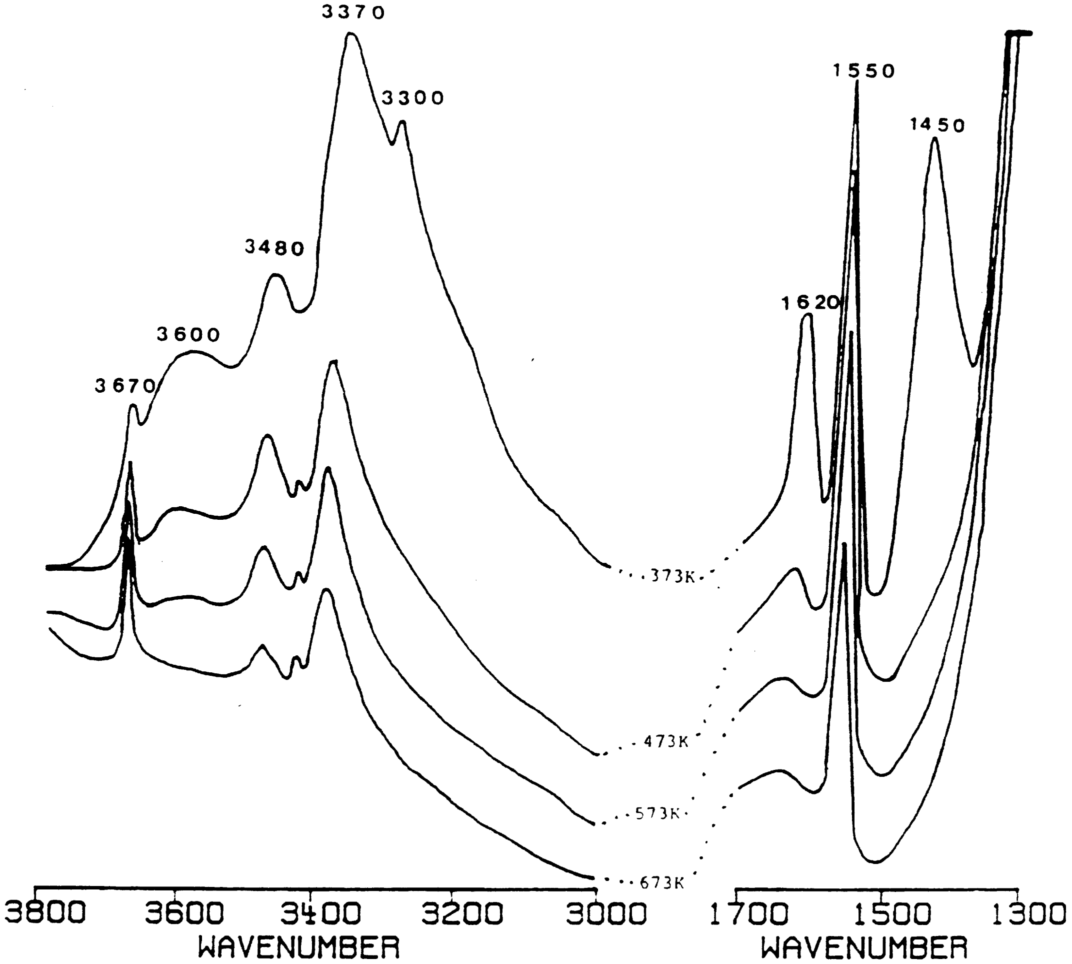


FIG. 2. IR spectra of ALPON-2 treated in vacuum at different temperatures.

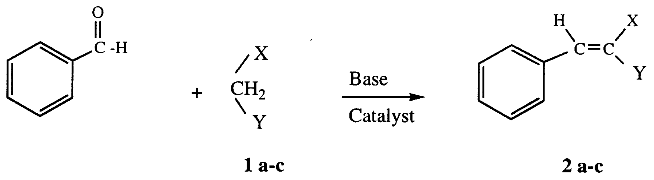
Thus, the general tendency of the I_{3370}/I_{3480} ratio is to increase when increasing the time of exposure to NH_3 at a constant temperature (Table 3). These results clearly indicate that the ratio of sites associated to secondary (–NH–) and to primary (–NH_2) amines increases with reaction time. It must be pointed out that in the case of crystalline ALPOS (10), during the treatment with NH_3 up to 1173 K, no evidence of the presence of secondary amine groups was found, and consequently one has to suppose that only primary amine ALPONS derived from –NH_2 type groups are formed on crystalline ALPO samples.

In the case of amorphous aluminophosphates we cannot rule out the possibility of the formation of tertiary amine groups but from data of Kamiya *et al.* (20) on silicates and Marchand *et al.* (21) on phosphates, these type of groups are expected to be formed at higher temperatures (>1200 K).

TABLE 3

Intensities, in Arbitrary Units, of the Different IR Bands of Oxinitrides of Amorphous ALPO as a Function of Time of Treatment in the Presence of Ammonia at 1073 K

Catalyst	Nitridation *t* (h)	Intensities					$I_{3370/3480}$
		1550 cm^{-1}	3370 cm^{-1}	3480 cm^{-1}	1620 cm^{-1}	1450 cm^{-1}	
ALPON-1	3	0.30	0.36	0.15	0.12	0.30	2.4
ALPON-2	10	0.38	0.90	0.25	0.10	0.19	3.6
ALPON-3	24	0.40	1.00	0.20	0.08	0.18	5.0
ALPON-4	70	0.43	0.80	0.14	0.05	0.18	5.7



1a: X=CN, Y=COOEt
1b: X=Y=CN
1c: X=Y=COOEt

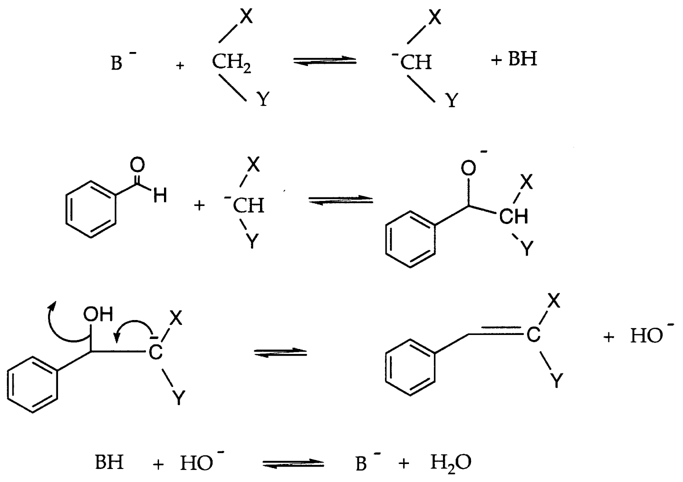
SCHEME I

Catalytic Activity

The Knoevenagel condensation reaction was carried out between benzaldehyde and ethyl cyanoacetate (**1a**), malononitrile (**1b**), and diethyl malonate (**1c**) (Scheme I).

The latter three compounds have active methylenic groups, in which the hydrogen can be more or less easily extracted or polarized by the basic sites of the catalysts depending on their pK_a values. Thus, by comparing the catalytic activity of different base catalysts for carrying out the Knoevenagel condensation reaction with molecules containing active methylenic groups and with pK_as of 9, 11, and 13, such as **1a**, **1b**, and **1c**, respectively, it should be possible to disscuss not only on the total number of basic sites, but also on their relative basic strength.

The initial reaction rates, obtained for conversions lower than 20%, for substrates **1a** and **1b** on ALPON samples with different nitrogen contents are given in Table 4. It is worth noting that the reactivity for malononitrile is much higher than for ethyl cyanoacetate. This result was unexpected since the pK_a value of the former is higher and, therefore, it should be a more demanding reactant from the point of view of basicity. However, when reviewing the literature on this subject, it was found that this indeed is not an unusual observation. The same order of reactivity has been observed previously in homogeneous (22) and heterogeneous catalysis (23). It is clear then that in this case the role of the level of stabilization of the carbanionic intermediate (Scheme II) achieved throughout the different mesomeric forms and/or throughout the particular interactions between the substrate and the catalyst is critical to the final reactivity.



SCHEME II

TABLE 4

Results of the Knoevenagel Condensation Reaction between Benzaldehyde (10 mmol) and Ethyl Cyanoacetate (1a) (10 mmol), and Malononitrile (1b) (10 mmol) on Different Aluminophosphate Oxynitride Catalysts (5%, wt/wt), at 333 K

	r_0 (mol/min)	
Catalyst	Product (**2a**)	Product (**2b**)
ALPO-0	—	—
ALPON-1	0.75	7.70
ALPON-2	—	11.00
ALPON-3	1.40	—
ALPON-4	5.00	33.00

On the other hand, the results from Table 4 also indicate that the activity of the ALPON generally increases with an increasing amount of nitrogen (11), such that the activity per nitrogen atom and unit surface area are much higher for substrate **1b** than for **1a** (Fig. 3). A more detailed analysis of Fig. 3 indicates that in the case of the easier reaction with substrate **1b** a reasonable linear correlation (correlation coefficient, 0.98) is obtained. This indicates that the basic sites produced at different levels of nitrogen content are basic enough and equally active for carrying out the Knoevenagel condensation of benzaldehyde with malononitrile. However, in the case of substrate **1a** it seems that the

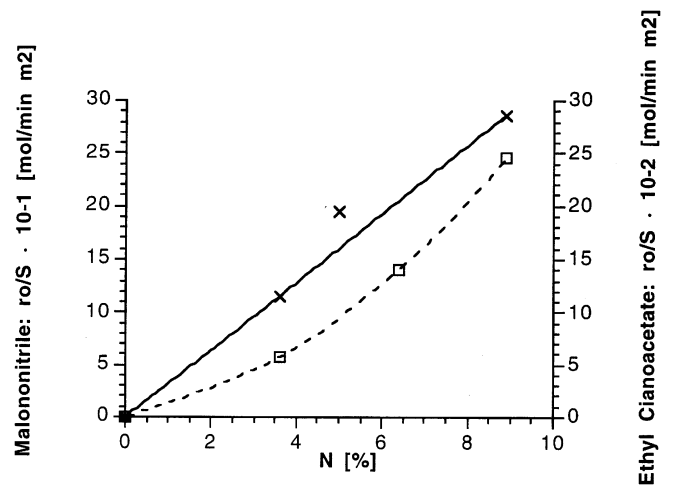


FIG. 3. Effects of N content of the ALPON on the activity for the Knoevenagel condensation reaction between benzaldehyde and malononitrile (×) and ethyl cyanoacetate (□).

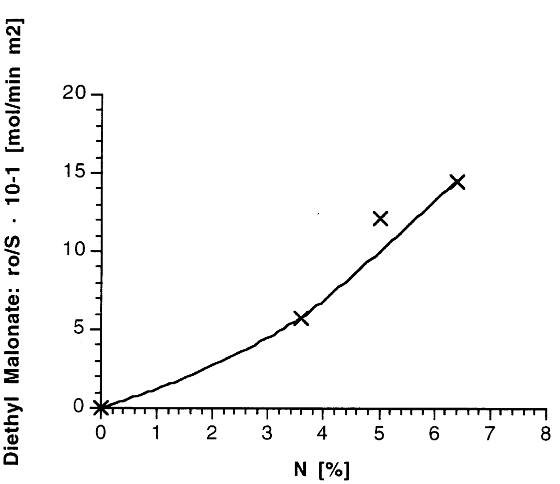


FIG. 4. Effects of the N content of the ALPON on the activity for the Knoevenagel condensation reaction between benzaldehyde and (×) diethyl malonate.

TABLE 5

Results of the Knoevenagel Condensation Reaction between Benzaldehyde (10 mmol) and Ethyl Cyanoacetate (1a) (10 mmol), and Malononitrile (1b) (10 mmol), on Different Base Catalysts (5%, wt/wt), at 333 K

	Product [**2a**]		Product [**2b**]	
Catalyst	Yield[a] (%)	r_0 (mol/min)	Yield[b] (%)	r_0 (mol/min)
ALPON-4	36	5.0	77	33.0
HT	16	0.5	30	3.5
MgO	33	1.1	44	4.0
XCs	7	0.1	78	47.0

[a] Reaction time, 60 min.
[b] Reaction time, 15 min.

intrinsic activity increases with increasing nitrogen content of the catalyst, at least up to the levels studied in this work. If this is so, one may conclude that not all the basic sites introduced when increasing the amount of N are equivalent, but a larger proportion of stronger basic sites are produced at higher amounts of nitrogen content. This effect will be more evident when more demanding reactions have to be carried out.

From the IR study presented above, it was quite clear that the ratio of groups [–NH– + –NH$_2$]/[– NH$_2$], as given by the ratio of intensities of the IR bands at 3370 and 3480 cm^{-1}, increases when increasing the nitrogen content (Table 3). In other words, the proportion of the stronger base sites (–NH–) increases with increasing nitrogen content of the samples. If this is true one would expect that in the case of the more demanding reactant, i.e., diethyl malonate (p$K_a = 13$) the effect of the nitrogen content of the ALPON on activity should be the same as in the case of ethyl cyanoacetate. Results in Fig. 4 show that the initial rate per unit of surface area for the condensation of diethyl malonate increases exponentially with the level of nitrogen content of the catalysts studied here.

With respect to the discussion above, it is clear that it should be possible to control in the ALPON samples not only the total number of basic sites but also their strength by changing the relative amount of –NH– to –NH$_2$ groups formed. This can be done by changing the conditions of preparation as shown in this work.

Basicity of ALPON Compared with Other Solid Base Catalysts

Other high surface area solid base catalysts which have shown high activity and selectivity for catalyzing Knoevenagel condensations (2–5) have been studied. Among them we have chosen to study a catalyst with mild basicity such as a Cs exchanged X zeolite and two catalysts with strong basicities such as MgO and a Mg–Al hydrotalcite. By carrying out the Knoevenagel condensation reaction with the same reactants possessing different pK_a values we will be able to compare the differences in the total number and strength of basic sites; with comparing of these materials with the ALPON base catalysts.

When a reactant with a low pK_a value was used (**1b**), in order to have an idea on the total number of basic sites, the results from Table 5 indicate that the order of activity is XCs > ALPON ≫ MgO > HT. With all the catalysts the only product observed was **2b**. This indicates that the total number of basic sites is larger in the XCs zeolite than in ALPON. However, it should be taken into account that it is possible to increase the content of nitrogen in the ALPON (11) and consequently it should be possible to further increase the total number of active sites on this material.

When using a more demanding reactant **1a** the ALPON exhibits the maximum activity followed by MgO (Table 5).

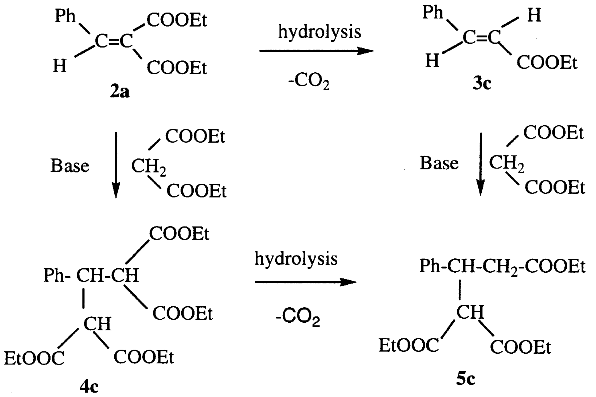
When still a more demanding reactant (**1c**) was used, the hydrotalcite and MgO show a larger catalytic activity than ALPON (Table 6). This is a clear indication that the basic sites on MgO and hydrotalcyte are stronger than on ALPON. This conclusion is also supported by the fact that

TABLE 6

Results of the Knoevenagel Condensation Reaction between Benzaldehyde (10 mmol) and Diethyl Malonate (1c) (10 mmol) on Different Base Catalysts (10%, wt/wt), at 383 K

		Yield (%)			
Catalyst	Total[a] conversion (%)	**2c**	**3c**	**4c**	**5c**
ALPON-4	49	47	2	—	—
HT	58	14	3	26	15
MgO	72	43	2	15	12

[a] Reaction time, 24 h.



SCHEME III

both MgO and HT are able to promote the more demanding Michael addition (**4c**) and the corresponding decarboxylation **5c** (see Scheme III), being the product coming from the Michael addition (**4c**), the most important when hydrotalcite was used as catalyst. However, the lower basicity of ALPON is highly suitable in this case for carrying out selectively the Knoevenagel condensation reaction. Indeed, on this catalyst only the desired product **2c** and its decarboxylated derivative **3c** were formed (Scheme III).

CONCLUSIONS

We have seen, therefore, that the basic groups of the –NH– and $–NH_2$ type are formed during high temperature NH_3 treatment of amorphous aluminophosphates and that they can be clearly identified by IR spectroscopy. When increasing the amount of nitrogen with longer times of treatment the ratio of the "secondary" to the "primary" amine groups is increased, increasing, therefore, the proportion of the stronger –NH– basic groups. This is confirmed by the correlation of activity with the nitrogen content when performing reactions more and more demanding from the point of view of the basicity required.

Finally, for less demanding reactions ALPON is less active than Cs exchanged zeolites, although we believe that this order of reactivity can be reversed if samples with larger contents of nitrogen are used. In any case, ALPONs are more active than either MgO or hydrotalcites for reactions requiring lower basicity. In the case of the proton abstraction in reactants with $pK_a = 13$, we have found that ALPON have basic sites strong enough to carry out the reaction (condensation of diethyl malonate and benzaldehyde), but its activity is lower than that of hydrotalcite or MgO. These results indicate that the alkaline earth oxides have stronger basic sites than ALPONs. Nevertheless, ALPON type materials show an adequate basicity for carrying out Knoevenagel reactions, especially when Michael additions can also take place, such that the selectivity of these oxynitrides is better than that shown by hydrotalcites or MgO catalysts.

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