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Solid catalysts for the production of fine chemicals: the use of ALPON and hydrotalcite base catalysts for the synthesis of arylsulfones

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α-phenylsulfonylcinnamononitrile and derivatives as well as α-phenylsulfonylchalcone have been obtained by condensation of phenylsulfonylacetonitrile and phenylsulfonylacetophenone with benzaldehyde and 4-substituted benzaldehydes, using solid base catalysts with different basic strengths. Cs-exchanged X zeolite showed low activity for the above reactions, while high-surface-area MgO and MgO–Al_2O_3 mixed oxides derived from hydrotalcite were active and selective catalysts. An optimum basicity was observed with MgO–Al_2O_3 with the atomic ratio Al/(Al + Mg) between 0 and 0.20, showing the increase in basicity when introducing Al in the MgO structure. Nitridation of a high-surface-area aluminophosphate gives active and selective catalysts for the above reactions. The activity per unit surface area for the less demanding reaction between sulfonylacetonitrile and benzaldehyde is directly proportional to the level of nitridation. However, formation of α-phenylsulfonylchalcone, which is a more demanding reaction, does not increase linearly but goes through a maximum with the nitrogen content of the solid, showing the heterogeneity of active sites on ALPONs and the decrease in the activity coefficient of the basic sites when the density of N atoms increases.

Keywords: catalysis on solid bases, fine chemical production on solid bases, Knoevenagel condensations on solid bases, hydrotalcites as base catalysts, ALPON as base catalysts

1. Introduction

The application of sulfones as intermediates in organic synthesis has increased considerably in the last years [1]. This interest comes from the fact that arylsulfonyl groups can stabilise adjacent carbanions [2] and may easily be removed by hydrolysis, reduction or elimination [3] and, when appropriate, may be eliminated to introduce carbon–carbon double bonds into organic molecules [4]. Thus they are useful temporary activating groups for alkylation [5], acylation [6] and addition [7] reactions.

The method of choice for the synthesis of unsaturated arylsulfones is the Knoevenagel condensation of arylsulfonylalkanes with aldehydes. The deprotonation of phenylsulfonylalkanes generally involves strong bases such as butyllithium [8], lithium diisopropylamide (LDA) [9] or sodium hydride [5(g),(h)]. However, the deprotonation energy strongly depends on the presence of adjacent electron-withdrawing groups such as ester [2], nitrile or ketone [10].

The development of clean and economical processes for the production of fine chemicals is becoming an area of growing interest and the replacement of liquid by solid base catalysts has the advantages of decreasing corrosion and environmental problems, while allowing the separation and recovery of the catalyst. Besides the classic low-surface-area alkaline earth oxide solids and the strong alkaline metal catalysts, researchers have looked into high-surface-area basic compounds, which can combine base catalysis and, in some cases, shape selectivity. Among those, zeolites [11], sepiolites [12], organic resins [13], mixed magnesium–aluminium oxides derived from hydrotalcites [14], and more recently, aluminophosphates oxynitrides (ALPON) [15–19] can be prepared in a wide range of basic strengths, and consequently, the most appropriate catalyst can be selected to catalyse selectively the desired reaction.

In the present work, the Knoevenagel condensation of arylsulfones with benzaldehydes has been carried out on a series of environmentally friendly base catalysts of different base strengths. The influence of chemical composition of the catalysts and the nature of the reactants has been studied.

2. Experimental

2.1. Materials

ALPONs were prepared starting from an aluminium phosphate precursor ($ALPO_4$) with a P/Al ratio of 0.9, which was obtained following the method proposed by Kearby [20]. The nitridation procedure was performed following previous publications [16,17] by flowing a stream of pure ammonia (150 $\mathrm{ml\,min^{-1}}$) over the aluminophosphate precursor calcined at 773 K. Time and temperature of nitridation were varied in order to incorporate different amounts of nitrogen. At the end of the nitridation procedure, samples were treated with a dry stream of nitrogen (99.99%).

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Table 1
Main characteristics in synthesis of the oxynitride catalysts.

Catalyst	N (wt%)	Nitridation time[a] (h)	Nitridation temperature[a] (K)	Surface[b] (m^2/g)	Atomic ratio Al : P : N
ALPON-1	1.1	24	773	199	1 : 0.95 : 0.09
ALPON-2	5.1	16	973	210	1 : 0.95 : 0.42
ALPON-3	8.3	16	1073	220	1 : 0.95 : 0.70
ALPON-4	13.9	16	1123	190	1 : 0.95 : 1.17

[a] Ammonia flow: 150 $ml\,min^{-1}$.
[b] Determined by N_2 physisorption and following the BET procedure.

Table 2
Synthesis composition of hydrotalcites.

Sample	Gel composition	Al/(Al + Mg)
HT-1	$2.4Mg(NO_3)_2 : 0.6Al(NO_3)_3 : 2Na_2CO_3 : 6.6NaOH$	0.20
HT-2	$2.25Mg(NO_3)_2 : 0.75Al(NO_3)_3 : 2Na_2CO_3 : 6.75NaOH$	0.25
HT-3	$2.1Mg(NO_3)_2 : 0.9Al(NO_3)_3 : 2Na_2CO_3 : 6.9NaOH$	0.30
HT-4	$2Mg(NO_3)_2 : 1Al(NO_3)_3 : 2Na_2CO_3 : 5NaOH$	0.33

Table 3
Compositions, surface areas and crystallite sizes of the calcined basic catalysts.

Catalyst	Surface[a] (m^2/g)	Al/(Al + Mg)	Crystallite size[b] (μm)
CsX	650	–	–
MgO	200	0	–
HT-1	211	0.20	0.4
HT-2	251	0.25	<0.5
HT-3	262	0.30	0.4
HT-4	246	0.33	0.4

[a] Determined by N_2 physisorption and following the BET procedure.
[b] Determined by SEM.

The nitridation conditions and the main characteristics of the resultant ALPONs are reported in table 1.

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

The CsX zeolite was prepared by repeated exchange of NaX zeolite (13X) with an aqueous solution of CsCl (0.5 M) at room temperature.

The preparation of the magnesium oxide was based on a modification of the method described by Putanov et al. [21], and was directed to obtain a high surface magnesium oxide. Magnesium oxalate was prepared at 313 K by adding a solution of oxalic acid (2 M) to a magnesium acetate solution (2.5 M). The magnesium oxalate was filtrated, washed and dried overnight at 353 K, and calcined at 973 K for 3 h.

Al–Mg hydrotalcites were prepared from gels produced by mixing two solutions: solution A, containing $Mg(NO_3)_2$ and $Al(NO_3)_3$ 1.5 M in Al + Mg, with Al/(Al + Mg) atomic ratios equal to 0.20, 0.25, 0.30, and 0.33 (table 2), and solution B prepared by dissolving Na_2CO_3 and NaOH to achieve a Na_2CO_3 concentration equal to 1 M. The solutions were mixed at 60 $ml\,h^{-1}$ addition rate for 4 h with vigorous stirring. The concentration of NaOH was adjusted to obtain pH = 13. The gels were aged at 473 K for 18 h, and then filtered and washed to pH = 7. After drying the solids at 353 K for 12 h, the hydrotalcites were calcined at 723 K in air in order to obtain Mg–Al mixed oxides (HT) [14]. Composition, surface areas and particle sizes of the calcined basic catalysts are presented in table 3.

2.2. Reaction procedure

All reactions were carried out under inert atmosphere (N_2), in a flask equipped with a reflux condenser. The flask was immersed in a thermostated silicone oil bath and a mixture of previously distilled benzaldehyde (4.7 mmol) and the phenylsulfone (4.4 mmol) was introduced. Once the magnetically stirred mixture reached a temperature of 373 K, the desired quantity of the base catalyst (5 wt% on reactants) was added. Samples of the reaction mixture were periodically withdrawn by means of a filtering syringe 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 GC-MS (Hewlett–Packard 5988A with a 25 m capillary column of phenylmethylsilicone), and by ^{1}H-NMR spectroscopy. The ^{1}H-NMR analyses of the products were carried out with a Varian VXR-400S, 400 MHz spectrometer in deuterated trichloromethane with TMS as the internal standard. Chemical shifts are reported in δ (ppm) and are referenced to TMS.

2.3. Spectroscopic-spectrometry data of the reaction products

α-(phenylsulfonyl)cinnamonitrile (**3a**): ^{1}H-NMR: 8.20–7.30 (m, 10H, Ar$\underline{H}$ and 1H, C$\underline{H}$=C); MS: 271 (M^{2+}, 3), 269 (M^+, 34), 141 (37), 102 (14), 77 (99).

α-phenylsulfonyl(4-nitrocinnamonitrile) (**3b**): ^{1}H-NMR: 8.50–7.60 (m, 9H, Ar$\underline{H}$ and 1H_1 C$\underline{H}$=C); MS: 316 (M^{2+}, 3), 314 (M^+, 29), 173 (15), 207 (15), 141 (30), 77 (100).

α-phenylsulfonyl(4-methylcinnamonitrile) (**3c**): ^{1}H-NMR: 8.20–7.20 (m, 9H, Ar<u>H</u> and 1H, C<u>H</u>=C), 2.4 (s, 3H, CH_3); MS: 285 (M^{2+}, 20), 283 (M^+, 100), 142 (29), 115 (27), 77 (100).

α-phenylsulfonyl(4-methoxycinnamonitrile) (**3d**): ^{1}H-NMR: 8.20–6.95 (m, 9H, Ar<u>H</u> and 1H, C<u>H</u>=C), 4.85 (s, 3H, OC<u>H</u>$_3$); MS: 301 (M^{2+}, 9), 299 (M^+, 100), 157 (55), 114 (10), 77 (22).

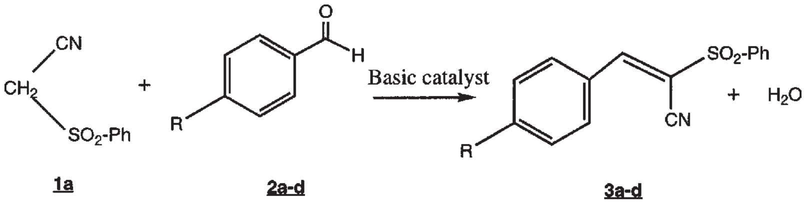
α-phenylsulfonylchalcone (**4**): ^{1}H-NMR: 8.20–6.95 (m, 16H, Ar<u>H</u>+C<u>H</u>=C); MS: 384 (M^+, 2), 284 (27), 207 (28), 191, (26), 105 (100), 77 (81).

3. Results and discusion

The preparation of α-phenylsulfonylcinnamonitrile (**3a**) (scheme 1) was carried out by condensation of phenylsulfonylacetonitrile (**1a**) and benzaldehyde (**2a**) on a series of base catalysts which were found to be active and selective in the Knoevenagel condensation [11,12,14]. We have chosen here a Cs-exchanged X-zeolite with mild basicity, and two catalysts with strong basicities: MgO, and a mixed aluminium–magnesium oxide derived from hydrotalcite. Finally, the reaction was also performed on a series of aluminophosphate oxinitride catalysts and their catalytic behaviour was related to the total number and strength of the basic sites, and compared with that of the CsX, MgO and MgO–Al_2O_3 catalysts. In all cases the reaction proceeded cleanly and **3a** was the only product observed during the condensation experiments.

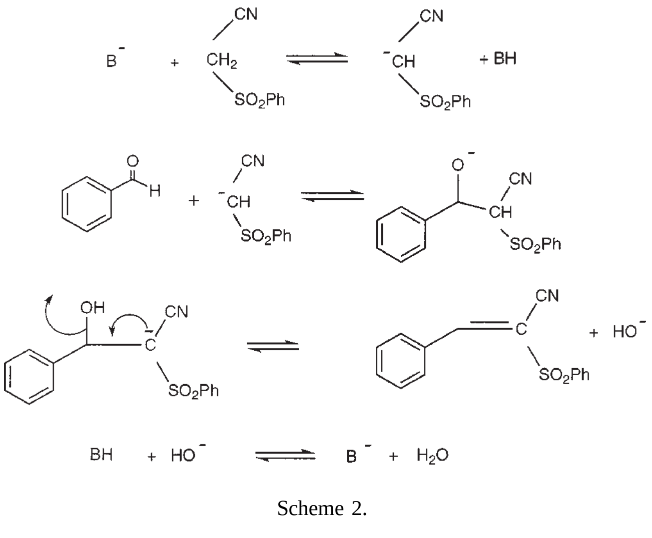
The accepted mechanism for this type of reaction involves, as a first step, the abstraction of a proton of the methylene group by the base catalyst with formation of the corresponding carbanion. The carbanion formed attacks the carbonyl group of the aldehyde, giving the corresponding intermediate alcohol. In a final step, water is removed, the olefin is formed and the active site of the catalyst is restored (scheme 2).

The results (figure 1) indicate that zeolite CsX, MgO, Mg-hydrotalcite and ALPON are active catalysts for the condensation of phenylsulfonylacetonitrile with benzaldehyde. The order of reactivity is ALPON-2 $>$ MgO $>$ HT-2 $>$ CsX. When the surface area is taken into consideration (table 4), it can be seen that the activity of the zeolite is much lower than that of any of the other catalysts. These results can be explained taking into account that besides the possible geometric constraints present in the zeolite, its basicity, measured as the capacity for abstracting acidic hydrogens in activated methylenic compounds with $pK_a = 9$–10.7 [11,12], is in the limit to abstract the acidic protons of the phenylsulfonylacetonitrile. In fact, the higher activity shown by MgO and HT, which are strong enough to abstract the proton from the methyl group in a



	a	b	c	d
R =	-H	$-NO_2$	$-CH_3$	$-OCH_3$

Scheme 1.



Scheme 2.

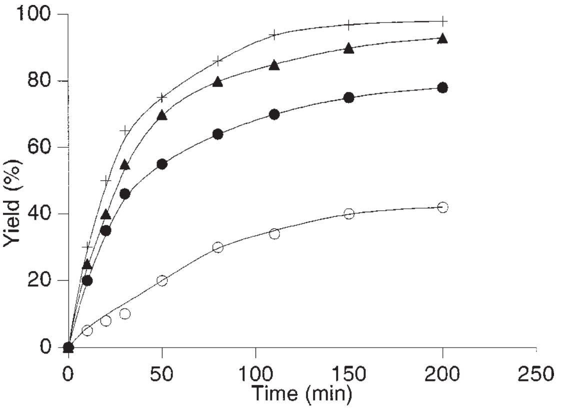


Figure 1. Yields of **3a** versus time in the Knoevenagel condensation between phenylsulfonylacetonitrile (**1a**) with benzaldehyde (**2a**) in presence of different basic catalysts: (+) ALPON-2, (▲) MgO, (●) HT-2, (○) X-Cs.

Table 4
Experimental results of the reaction of benzaldehyde (**2a**) with phenylsulfonylacetonitrile (**1a**) on different catalysts at 373 K.

Catalyst	$V_0 \times 10^5$ ($\mathrm{mol\,h^{-1}\,m^{-2}}$)	Yield[a] **3a** (%)
CsX	2.3	35
MgO	47.2	86
HT-2	35.0	71
ALPON-2	53.8	95

[a] Reaction time: 2 h.

molecule such as acetophenone (p$K_a = 15.8$) [22,23], will be in good agreement with this hypothesis. Furthermore, the high activity shown by the aluminophosphate oxinitride agrees with our previous results [19] on the Knoevenagel condensation of methylenic active compounds with different pK_a's, where we found that these materials, depending on the levels of nitrogen content, have basic sites strong enough to carry out the condensation of diethyl malonate (p$K_a = 13$) and benzaldehyde.

3.1. Influence of catalyst chemical composition

For a specific base-catalyzed reaction, the number and strength of the active sites are of paramount importance in order to control the activity and selectivity of the catalyst. From the results presented above, we can conclude that magnesium oxides and ALPON are adequate catalysts to carry out this process, and in both cases it should be possible to modify the number and strength of the active sites by changing the chemical composition.

In the case of the magnesium oxides, it has been indicated [24] that the incorporation of aluminium into MgO forming Al_2O_3–MgO oxides after calcination of hydrotalcites, produces a decrease in the total number of basic sites, but the proportion of the stronger ones increases. Thus, for any base-catalyzed reaction, a maximum in activity should occur for an optimum Mg/Al ratio, and this optimum will depend on the base strength needed to activate the particular reactant. Thus the higher the basicity needed, the lower the Mg/Al ratio for which the maximum in activity will be found.

In order to find the optimum for the reaction studied here, different catalyst samples with Al/(Al + Mg) ratios ranging from 0 (MgO) to 0.33 were prepared. For the present reaction, in which the methylenic group is strongly activated by the cyano and sulfone groups, it should be relatively easy for the catalysts to generate the carbanion by extracting the proton. Therefore, basic sites with weak to medium strength should already be able to perform the reaction, and consequently, the maximum in activity should be shifted to relatively low aluminium containing samples. In fact, when the results of activity per unit surface area are plotted (figure 2), it can be seen that the maximum in activity appears between the pure MgO sample and the magnesium hydrotalcite with the lowest aluminium content. Furthermore, when the aluminium content increases, the catalytic activity for the Knoevenagel condensation strongly decreases. These results indicate that in magnesium–aluminium hydrotalcites with Al/(Al + Mg) = 0.20 an optimum between the total number and the strength distribution of basic sites exists for this reaction.

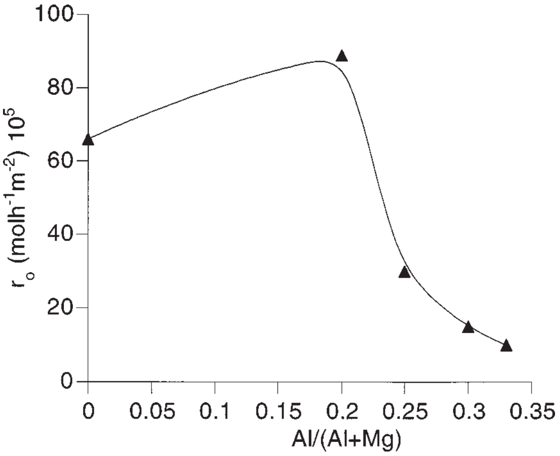


Figure 2. Influence of the Al/(Al + Mg) ratio of the starting hydrotalcite on the initial rate per unit surface area (r_0) for the condensation reaction between **1a** and **2a**.

Table 5
Experimental results of the reaction of benzaldehyde (**2a**) with phenylsulfonylacetonitrile (**1a**) on ALPON with different nitrogen content.

Catalyst	$V_0 \times 10^2$ ($\mathrm{mol\,h^{-1}\,g^{-1}}$)	Yield[a] **3a** (%)
ALPON-1	0.5	5
ALPON-2	11.3	80
ALPON-3	22.7	85
ALPON-4	36.7	95

[a] Reaction time: 1 h.

On the other hand, in the case of aluminophosphate oxynitrides it has been shown that by changing the nitridation conditions it is possible to modify the level of nitrogen content. The amount of nitrogen not only has an influence on the total number of active sites but also on the their strength [18,19]. Up to now the nature of the aluminophosphate oxynitride basic sites is not yet exactly known, but IR spectroscopic studies [19] have shown that basic sites such as –NH–, $-NH_2$ and even strongly adsorbed NH_3 are created by nitridation, and their proportion changes with the amount of nitrogen content, as well as with the treatment conditions.

In order to optimize the catalytic acitivity of the ALPON catalysts for the Knoevenagel reaction between benzaldehyde (**2a**) and phenylsulfonylacetonitrile (**1a**) we have prepared samples with different nitrogen contents, within a range between 0 and 13.9 wt% N, and the initial reaction rates as well as the yields of α-phenylsulfonylcinnamonitrile (**3a**) obtained on these catalysts are summarised in table 5. The results from this table indicate that the activity of the

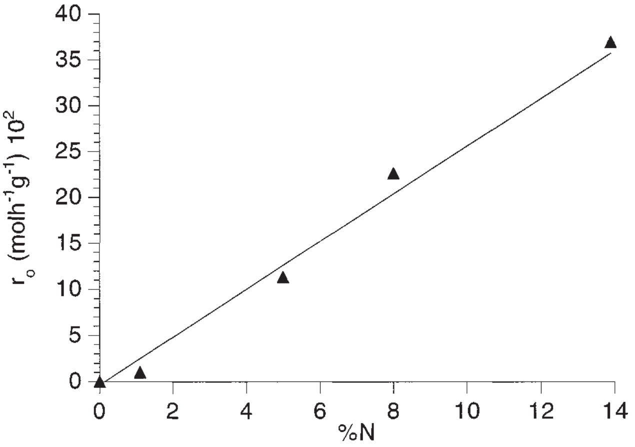


Figure 3. Effects of the N content of the ALPON on the activity for the Knoevenagel condensation reaction between phenylsulfonylacetonitrile (**1a**) and benzaldehyde (**2a**).

ALPONs increases when increasing the amount of nitrogen. On the other hand, when the initial rates are plotted versus the nitrogen content, a linear correlation is obtained (figure 3) indicating that all basic sites produced at different levels of nitrogen content were equally active for carrying out this condensation. These results agree with previous work, where a similar behaviour was observed for reactants which are not highly demanding from the point of view of basicity, i.e., Knoevenagel condensation between benzaldehyde and malononitrile [16–18] or ethyl cyanoacetate [19].

3.2. Influence of the nature of reactants

In order to study the effect of the presence of electron acceptor or donor groups in the aromatic ring of benzaldehyde, the Knoevenagel condensation was carried out between phenylsulfonylacetonitrile (**1a**) and substituted benzaldehyde derivatives (**2b–d**) using ALPON-4 as catalyst. Results from table 6 show that the presence of electron donor groups in the aromatic ring decreases the reaction rate proportionally to the value of the Hammet constant. Meanwhile, the presence of electron acceptor groups increases the reaction rate, demonstrating the participation of the aldehyde in the controlling step of the reaction.

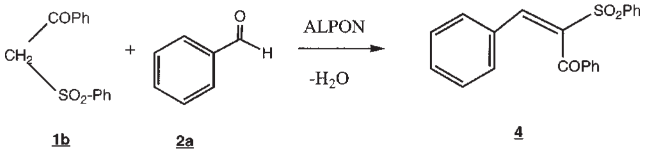
From the results shown in this work we can conclude that the new aluminophosphate oxynitride catalysts present an efficient catalytic activity to perform the Knoevenagel condensation between benzaldehyde and phenylsulfonylacetonitrile (**1a**) and the activity is directly proportional to the N content of the ALPON.

At this point we decided to study the capacity of ALPON for abstracting protons from a more demanding arylsulfone, i.e., phenylsulfonylacetophenone (**1b**) (scheme 3). The reaction between this reactant and benzaldehyde was carried out in the presence of ALPONs, with different level of nitrogen content, at 383 K and using 10 wt% of catalyst. In table 7 are summarised the yields for α-phenylsulfonylchalcone (**4**) obtained for each catalyst, the selectivity to the Knoevenagel condensation product being 100% in all cases.

Table 6
Experimental results of the reaction of benzaldehyde derivates with phenylsulfonylacetonitrile (**1a**) over ALPON-4.

Product	$V_0 \times 10^2$ (mol h^{-1} g^{-1})	Yield[a] (%)
3a	36.7	95
3b	70.0	98
3c	19.7	88
3d	15.0	80

[a] Reaction time: 1 h.



Scheme 3.

Table 7
Experimental results of the reaction of benzaldehyde (**2a**) with phenylsulfonylacetophenone (**1b**) on ALPON with different nitrogen content at 387 K.

Catalyst	$V_0 \times 10^3$ (mol h^{-1} g^{-1})	Yield[a] **4** (%)
ALPON-1	1.60	7.5
ALPON-2	4.45	20
ALPON-3	4.80	20
ALPON-4	3.45	12.5

[a] Reaction time: 1 h.

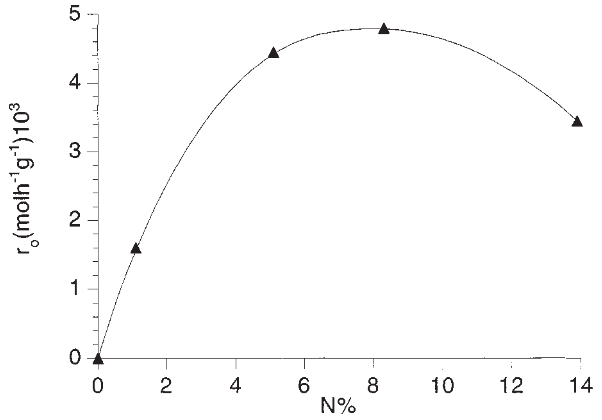


Figure 4. Effects on the N content of the ALPON on the activity for the Knoevenagel condensation reaction between phenylsulfonylacetophenone (**1b**) and benzaldehyde (**2a**).

When the initial rates versus the nitrogen content are plotted (figure 4) it is seen that the activity goes through a maximum (at 87 wt% N) and then decreases. When these results are compared with those given in figure 3 for a less demanding reaction, we conclude that the strongest basic sites formed in ALPON materials are obtained when lower amounts of nitrogen are incorporated (up to ∼5–6 wt% N), i.e., when the basic sites formed are isolated. When higher amounts of nitrogen are introduced, all the sites are still basic enough to catalyze an easy reaction such as the condensation of phenylsulfonylacetonitrile with benzaldehyde, but they are not basic enough to catalyze the more demanding condensation of phenylsulfonylacetophenone and benzaldehyde. This is a clear indication that the overall basicity of the solid decreases when higher amounts of N have been introduced. This may be a consequence of the proximity of the basic sites which will result in a decrease in the activity coefficient of each individual basic site.

4. Conclusion

We have found that high-surface-area MgO and MgO–Al_2O_3 oxides as well as ALPON type materials are active and selective catalysts for the condensation of arylsulfones with benzaldehyde and substituted benzaldehyde. The ALPONs were the most active catalysts, and a linear correlation between the amount of nitrogen incorporated and the catalyst activity has been found for reactants which are not highly demanding from the point of view of basicity. However, for a more demanding reactant, the activity increases with the amount of the nitrogen incorporated up to a certain level of nitrogen content from which the activity decreases, showing not only the heterogeneity of active sites on ALPONs and the relative changes in the population of surface nitrogen species with the level of nitridation, but also a decrease in the overall basicity of the sites probably due to the presence of N atoms in next nearest neighbour positions.

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