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Acid–Base Bifunctional Catalysts for the Preparation of Fine Chemicals: Synthesis of Jasminaldehyde

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Jasminaldehyde was prepared by condensation between benzaldehyde and heptanal. Large-pore acid zeolites (HY and Beta), mesoporous aluminosilicate (Al MCM-41), and amorphous aluminophospates (ALPO) were used as catalysts. The results indicated that zeolites showed lower activity and selectivity than mesoporous aluminosilicate (Al MCM-41). These results were attributed to the confinement effects of the reactants and products inside of the voids of the microporous materials, which lead to the preferential formation of the heptanal self-condensation product, as well as to a fast deactivation of the catalyst. However, the amorphous aluminophosphate (ALPO) which possesses weaker acid sites than zeolites and MCM-41, but combines acidic and basic sites, showed the maximum activity and selectivity to jasminaldehyde. This finding was explained on the basis of the acid–base bifunctional character of the ALPO catalyst. The role of the weak acid sites is to activate benzaldehyde by protonation of the carbonyl group, favoring then the attack of the enolate heptanal intermediate generated on the relatively weak basic sites of ALPO.

Key Words: **synthesis of jasminaldehyde; aldol condensation; zeolites; MCM-41 acid catalysts; solid acid–base catalysts for fine chemicals; ALPO; acid–base bifunctional catalyst.**

INTRODUCTION

Jasminaldehyde, α-*n*-amylcinnamaldehyde (**3**) with a violet scent, is considered a fine chemical of commercial interest and may be obtained by the condensation of heptanal with benzaldehyde (Scheme 1). This aldol condensation is carried out in the presence of alkali as catalyst (sodium or potassium hydroxide), heptanal being added slowly to the reaction mixture at moderate temperatures (1).

A limitation of aldol condensation reactions in general, and more specifically in the synthesis of jasminaldehide, is the formation of by-products which reduce the yield of amylcinnamic aldehyde (**3**) to $\cong 70\%$. The most abundant undesired product comes from the self-condensation of heptanal to form 2-*n*-pentyl-2-*n*-nonenal (**4**) (Scheme 1). Therefore, the general methodology for producing jasminaldehyde with high selectivity requires a low concentration of heptanal relative to benzaldehyde in the reaction mixture. This can be achieved using a high benzaldehyde/heptanal molar ratio and/or by adding slowly the heptanal into the reaction mixture.

Different solid base catalysts have been reported for the synthesis of jasminaldehyde. Among them, the most interesting are anionic exchange resins (2), potassium carbonate in the presence of a solid–liquid phase-transfer catalyst (3), and solid–liquid phase-transfer catalyst in dry media under microwave irradiation (4). It is known that the condensation of heptanal and benzaldehyde can also be carried out in the presence of solid acid catalysts. However, due to the lower selectivity generally found, processes involving the use of heterogeneous acid catalysts in the production of jasminaldehyde are scarce (5). In a previous work we observed that using aluminosilicate molecular sieves as acid catalysts, the selectivity to jasminaldehyde was strongly dependent on the topology of the catalysts and on the acid strength of the active sites (6). Therefore, we thought that by controlling these parameters in a heterogeneous acid catalyst it should be possible to improve the selectivity to jasminaldehyde. The aim of this work is to study the synthesis of jasminaldehyde by the acid-catalyzed condensation of benzaldehyde and heptanal in order to find the optimum heterogeneous acid catalyst. With this target, we selected different solid catalysts covering a wide range of acid strengths, including amorphous and crystalline solid acids. It will be shown that it is possible to obtain very good solid catalysts for the synthesis of jasminaldehyde when a bifunctional acid–base bifunctional system is prepared.

EXPERIMENTAL

Materials

Amorphous aluminum phosphate (ALPO) with a P/Al ratio of 1 was prepared following the method proposed by Lindblad *et al.* (7). Na-exchanged ALPO (Na-ALPO) was prepared by adding to a 1 M aqueous solution of sodium acetate (100 ml), 1 g of ALPO precursor. The mixture was

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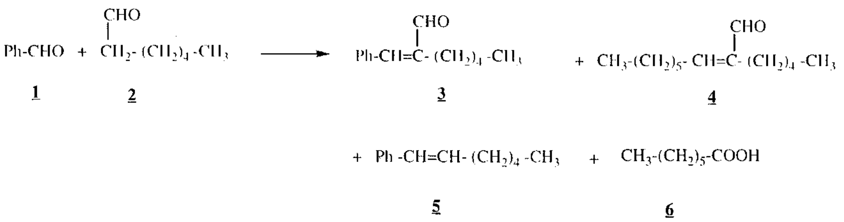


SCHEME 1

heated at 333 K for 8 h. The solid was then filtered and the exchange was repeated three times. Finally the solid was filtered, thoroughly washed with water, and dried at 333 K for 12 h.

An Al MCM-41 sample with a Si/Al ratio of 15 and a pore diameter of 3.5 nm, as well as an MCM-41 Al-free sample, were prepared following the procedures given in Refs. (8) and (9), respectively.

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 (10).

The Beta sample with a Si/Al ratio of 13 was supplied in the acid form by PQ Corp.

Reaction Procedure

Condensation of benzaldehyde with heptanal. All reactions were carried out under a nitrogen atmosphere, 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 (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%. All catalysts except ALPO and Na-ALPO were activated before reaction, at 323 K under vacuum (1 Torr) for 3 h. Samples of the reaction mixture were periodically withdrawn by a filtering syringe and analysed 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. 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).

Diffuse reflectance UV–vis spectra were recorded using a Cary 5G spectrophotometer adapted with a Praying Mantis accessory for solid samples. $BaSO_4$ was used as the standard for baseline correction.

The IR spectra were obtained with an FT-IR Nicolet 710 instrument using sealed cells provided with CaF_2 windows. Wafers (10 mg) of solid catalysts were pressed (1 Tm cm^{-2}) and outgassed under vacuum (10^{-2} Pa) for 1 h at increasing temperatures.

Thermogravimetric analyses and differential scanning calorimetry of the catalysts after the aldol condensation reaction were obtained in a Netszch microbalance under an air stream using kaolin as the inert standard.

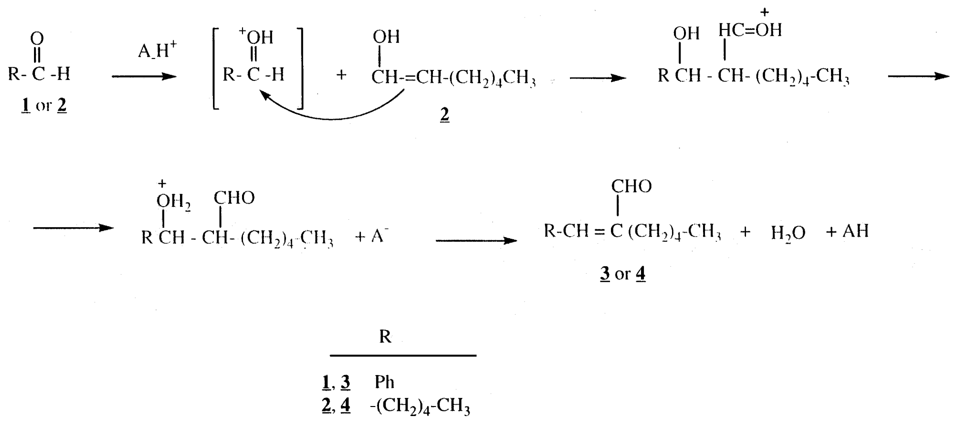
Acetalization of benzaldehyde with trimethyl orthoformate (TMOF). This was selected as a test reaction for determining the presence of weak acid sites on the bifunctional catalysts.

A 200-mg portion of ALPO or Na-exchanged ALPO catalyst was added to a solution of benzaldehyde (5 mmol) and TMOF (25 mmol) in tetrachloromethane (15 ml). The resulting suspension was magnetically stirred at reflux temperature. Samples of the reaction mixture were periodically withdrawn by a filtering syringe within a time period of 0.1 to 5 h and analyzed by GC.

Knoevenagel condensation between benzaldehyde and malononitrile. This experiment was carried out as a test reaction to show the presence or absence of basic sites on the catalysts. Thus, a mixture of benzaldehyde (10 mmol) and malononitrile (10 mmol) under an inert atmosphere was magnetically stirred and heated at 333 K, and 85 mg of the catalyst (ALPO or Na-exchanged ALPO) was added. Samples of the reaction mixture were periodically withdrawn by a filtering syringe within a time period of 0.1 to 5 h and analyzed by GC.

RESULTS AND DISCUSSION

The condensation reaction between benzaldehyde (**1**) and heptanal (**2**) was carried out with H-Beta zeolite that was taken as a prototype of strong acid catalysts. A molar ratio of benzaldehyde/heptanal of 5 was chosen in order to minimize heptanal self-condensation. Although the actual concentration of reagents inside the pores may be different from the reagent ratio in solution, this large excess still ensures that benzaldehyde is likely the predominant reagent



SCHEME 2

at the catalytic sites. A reactant/catalysts ratio of 10 and 398 K were chosen as the other reaction parameters. After 8 h of reaction time, the composition of the final mixture was 20% of (*E*)-*α*-*n*-amylcinnamaldehyde (jasminaldehyde) (**3**), 40% of the self-condensation product, (*E*)-2-*n*-pentyl-2-*n*-nonenal (**4**), 23% of the *trans*-1-phenylheptene (**5**), and 5% of heptanoic acid (**6**) (Scheme 1). The formation of **3** and **4** can be explained through a competitive acid-catalyzed aldolic condensation which involves the electrophilic attack of a protonated carbonyl group, from benzaldehyde or heptanal, to the enolic form of heptanal (Scheme 2). Product **5** could be formed by oxidation of jasminaldehyde followed by a fast decarboxylation or by direct deformylation following an acid-catalyzed tandem Aldol–Grob sequence (11).

In Fig. 1 are presented the yields of the different products versus time. As can be seen there, the rate of the competitive self-condensation (**4**) is significantly larger than the rate of formation of jasminaldehyde. This fact should indicate that even with a benzaldehyde/heptanal ratio of 5 heptanal is diffusing faster than benzaldehyde and that the self-condensation is favored by the smaller size of the transition state which better fits in the pores of the zeolite.

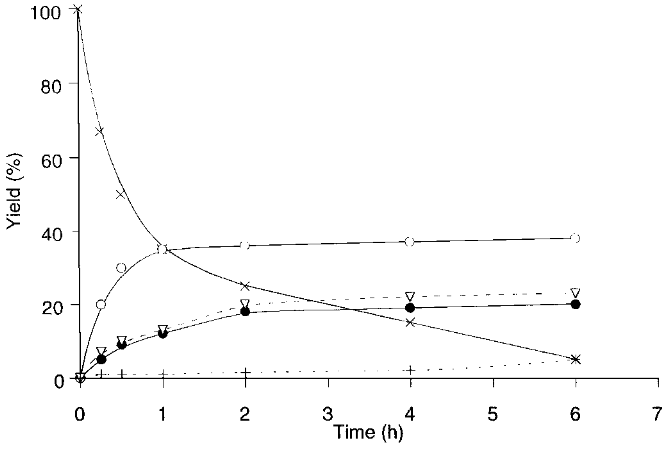


FIG. 1. Yields of the different products **2** (×), **3** (●), **4** (○), **5** (▽), and **6** (+) versus reaction time in the condensation of benzaldehyde and heptanal using HBeta zeolite (10 wt%), a reactant molar ratio PhCHO : heptanal = 5 : 1 at 398 K.

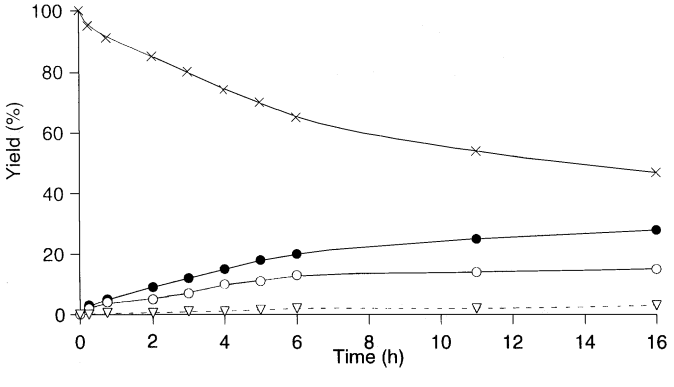


FIG. 2. Yields of the different products **2** (×), **3** (●), **4** (○), and **5** (▽) versus reaction time in the condensation of benzaldehyde and heptanal using HY-100 zeolite (10 wt%), a reactant molar ratio PhCHO : heptanal = 5 : 1 at 398 K.

In order to improve the selectivity to jasminaldehyde, we have used as acid catalysts a 12-membered-ring tridirectional Y zeolite, in which the diffusion of reactants and product should be easier, and which has larger internal void spaces (internal cavities) than H-Beta zeolite. The reaction was carried out under the same reaction conditions and Fig. 2 shows the yields of the different products obtained versus time. As can be seen there, the zeolite pore topology clearly affects the rate as well as the final distribution of the different products with the Y zeolite. In this case, we observe that jasminaldehyde (**3**) and 2-*n*-pentyl-2-nonenal (**4**) are formed with similar reaction rates, the selectivity to jasminaldehyde being higher than that obtained with Beta zeolite. Only 2% of product **5** was detected in the final reaction mixture. However, despite the higher selectivity to jasminaldehyde, the final conversion of heptanal was low, achieving after 16 h of reaction time 57% of the maximum attainable conversion, and this conversion remained constant with time. The behavior of the reaction with time indicates that a fast deactivation of the catalyst is occurring during the process. In a series of previous articles we have shown that one of the major causes of zeolite deactivation during liquid-phase organic reactions is the formation of persistent carbocationic species (12).

Deactivation derives from two different effects: (i) formal replacement of catalytically active protons by fairly stable unactive carbocations, and (ii) blocking of the pores by these strongly adsorbed, bulky reaction intermediates (12b). In some cases we have proved that these poisons have a definite structure that can be unequivocally characterized by spectroscopic techniques (13).

Particularly intriguing has been the case of styrene and its derivatives, wherein earlier reports claiming the generation of adsorbed radical cations have been shown later by us to correspond in reality to diphenyl allylic carbocations (14). In the present case we noticed that one of the reaction products corresponds to an α-alkyl-substituted styrene. We speculate that this product could also lead to diphenyl allyl carbenium poisons analogous to those previously reported by us. Thus, we undertook a spectroscopic study of the deactivated catalyst used in the reaction after being submitted to exhaustive solid–liquid extraction. The purpose is to demonstrate whether deactivation of the catalyst in the present aldolic condensation also occurs by formation of persistent diphenyl allyl carbocations.

Figure 3 shows the diffuse reflectance UV–vis spectrum of deactivated HY-100 and H-Beta catalysts showing a characteristic absorption band centered at 520 nm with a shoulder at the short-wavelength side of the peak. These bands have close similarity with the reported diffuse reflectance UV–vis spectrum of the parent 1,3-diphenyl allyl cation embedded within ZSM-5 (13a). Furthermore, according to the Woodward rules of additivity on the influence of substituents on λ_{max} of conjugated $C{=}C$ double bonds (15), it is calculated that λ_{max} of the parent 1,3-diphenyl allyl cation should redshift 30 nm by double alkyl substitution on the allylic moiety, thus giving a value of 530 nm, as is in fact observed for deactivated HY and H-Beta catalysts.

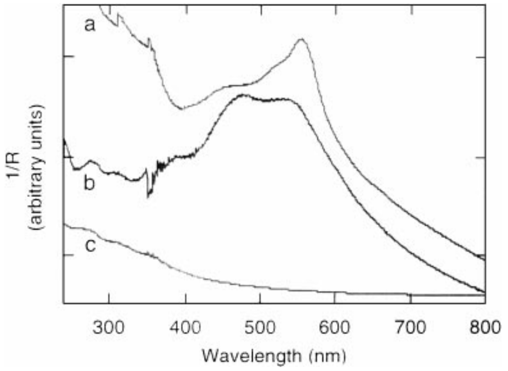


FIG. 3. Diffuse reflectance UV–vis spectra (plotted as the inverse of the reflectance, *R*) of HY (a), H-Beta (b), and ALPO (c) used as catalysts for the jasminaldehyde formation after exhaustive solid–liquid extraction.

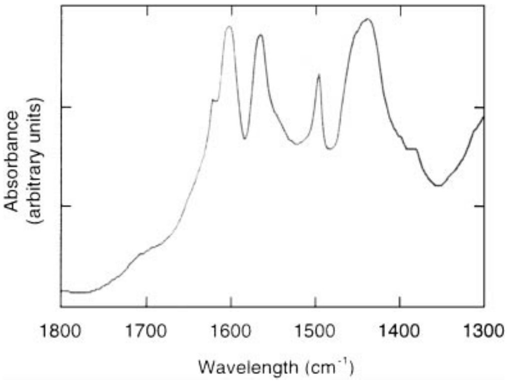
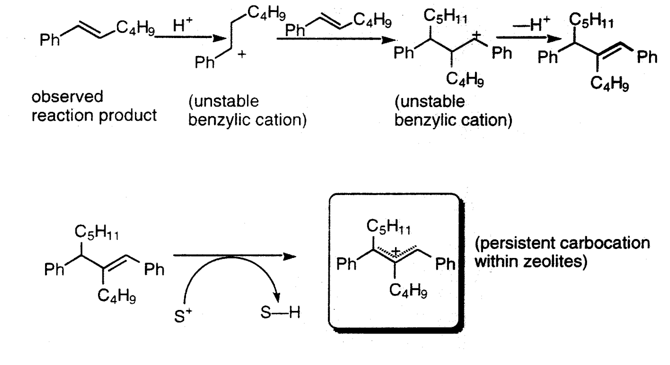


FIG. 4. Aromatic region of FT-IR spectrum of self-supported H-Beta wafers after exhaustive solid–liquid extraction. The spectrum was recorded at room temperature after outgassing at 473 K for 1 h. Note the absence of any $C{=}O$ vibration band at about 1690 cm^{-1} and the presence of a strong absorption at 1615 cm^{-1} characteristic of allylic cations.

The IR spectrum of self-supported wafers of deactivated HY catalyst is shown in Fig. 4. It has been proposed that diphenyl allyl cation has a characteristic vibration band at ca. 1550 cm^{-1}, probably due to the the stretching vibration of a C−C bond with a single and a half bond order. As it can be seen in Fig. 4, this specific band is present accompanied by other bands at 1605 and 1595 cm^{-1} attributable to the skeletal vibration of phenyl rings.

Thus, on the basis of the diffuse reflectance UV–vis and IR spectra as well as the known behavior of related styrenes, we propose that deactivation of HY catalyst is due, in this case, to the formation of 2-butyl-1,3-diphenyl-2-octen-1-yl cation. The same species is observed also using H-Beta as catalyst. A likely reaction mechanism to account for the generation of this carbocation is shown in Scheme 3.

From the results presented above we can conclude that the use of microporous acid materials as catalysts for the



S$^+$ indicates any carbocation less stable than final allylic species-

SCHEME 3

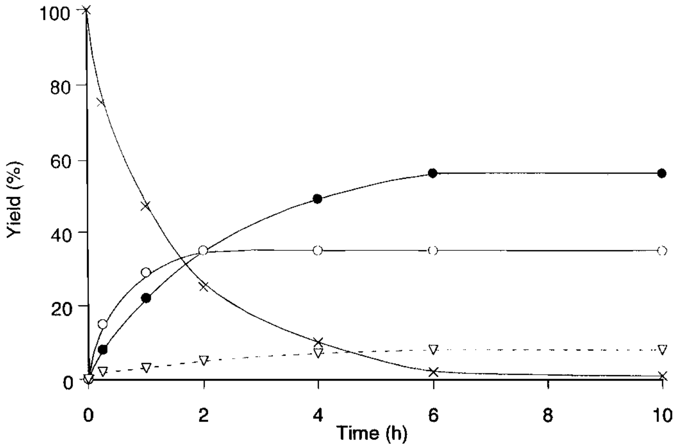


FIG. 5. Yields of the different products **2** (×), **3** (●), **4** (○), and **5** (▽) versus reaction time in the condensation of benzaldehyde and heptanal using Al MCM-41 catalyst (10 wt%), a reactant molar ratio PhCHO : heptanal = 5 : 1 at 398 K.

TABLE 1

Relevant Physicochemical Parameters of the Catalysts Used in This Work

Catalysts	Surface area ($m^2\,g^{-1}$)	Pore volume[a] ($cm^3\,g^{-1}$)	Average pore[b] diameter (nm)	Si/Al
Beta	606	0.175	0.76 × 0.64 0.55 × 0.55	13
HY-100	709	0.323	0.74	2.5
Al MCM-41	900	0.500	3.5	15
ALPO (Al/P = 1)	211	0.328	7.2	—

[a] Measured by N_2.
[b] Measured by Ar.

condensation of benzaldehyde and heptanal leads to low selectivities to jasminaldehyde and fast deactivation of the catalyst due to consecutive reactions occurring within the pores, which end with the formation of persistent 2-butyl-1,3-diphenyl-2-octen-1-yl cation. Because of that, we thought that mesoporous aluminosilicates materials could be better acid catalysts for this condensation than the most constrained microporous molecular sieves. Indeed, the presence of large regular mesopores can allow the diffusion of reactants and conversely the fast diffusion of the products out, minimizing unwanted consecutive reactions and catalyst decay. The condensation between benzaldehyde and heptanal was then carried out using as catalyst Al MCM-41 with a Si/Al ratio of 15 and pore diameter of 3.5 nm. The evolution of the different reaction products with time is presented in Fig. 5. In contrast with the results obtained with the microporous catalysts, two facts are now observed: first, it is possible to achieve a total conversion of heptanal in relatively short reaction times (6 h), indicating that in this case the catalyst decay is practically negligible. Second, at heptanal conversions higher than 75%, the formation of jasminaldehyde is favored as could be expected from our previous hypothesis on the catalytic behavior of the microporous materials for that reaction.

Furthermore, the better results obtained with Al MCM-41 despite the weaker acitity of the sites present in this material (16) allow us to conclude that, under our reaction conditions, the presence of strong acid sites is not necessary to perform the aldolic condensation. Moreover, it is not unreasonable to think that the absence of confinement effects along with the weakness of the acid sites in Al MCM-41 decreases the fast conversion of jasminaldehyde to compound **5** that was largely obtained when using zeolites as catalysts.

In order to check these hypotheses, we selected as catalysts two solids with weaker acid sites than the Al MCM-41 sample studied: an Al-free MCM-41 sample and an amorphous aluminum phosphate (ALPO). The physicochemical parameters of the catalysts used are summarized in Table 1. With the first one the acid character should be attributed exclusively to silanol groups, whereas amorphous aluminium phosphate, built of tetrahedral units of AlO_4 and PO_4, is structurally similar to silica and its surface contains both Al and P hydroxyl groups (17). When the reaction was tested with both catalysts we observed that while the all-silica MCM-41 did not catalyze the condensation at all, with the ALPO material optimum results were obtained. Indeed, amorphous ALPO behaves as an active and selective catalyst for this reaction, achieving practically a total conversion after 3 h of reaction time with a selectivity to jasminaldehyde of 85% (Fig. 6). In Table 2 the results obtained in the condensation between **1** and **2** on the different catalysts used in this work are summarized. Moreover, in contrast to HY, H-Beta, and Al MCM-41, product **5** was not detected in the reaction mixture and the spectroscopic

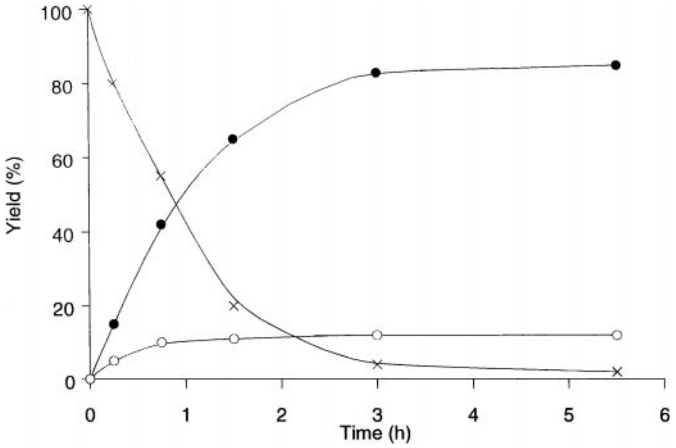


FIG. 6. Yields of the different products **2** (×), **3** (●), and **4** (○) versus reaction time in the condensation of benzaldehyde and heptanal using ALPO catalyst (10 wt%), a reactant molar ratio PhCHO : heptanal = 5 : 1 at 398 K.

TABLE 2

Results Obtained in the Condensation of Benzaldehyde and Heptanal with Different Catalysts

Catalysts	Reaction time (h)	Conversion (%)	Poison in the catalyst (%)[a]	Selectivity to **3**	Yields (%)		
					3	**4**	**5**
H-Beta	6	93[b]	5.1	21	20	40	23
HY-100	16	53	7.4	52	28	15	3
Al MCM-41	10	99	—	56	56	35	8
ALPO	3	96	1.5	86	83	13	—
Na-ALPO	22	71	—	67	48	23	—

[a] Determined by TG analysis and based on moles of heptanal retained.
[b] 5% of heptanoic acid was also detected.

characterization of the ALPO catalyst after the reaction indicated that the 1,3-diphenyl allylic cation was absent (see Fig. 3). We propose that the lower acidity of the latter solid and its lack of microporosity can explain the absence of any persistent carbocationic poison. In this case even if such positive species were formed, they would be able to react with nucleophiles, giving a neutral compound that would desorb from the acid site. Thus, ALPO would be less prone than zeolites to undergo deactivation.

It has been reported in the literature that ALPO is a bifunctional catalyst whose surface acid–base sites are able to participate in catalytic processes (18). The presence of acid and basic sites has been convincingly demonstrated by tritation with weak bases or acids using Hammet indicators (19), or spectrophotometric methods (20), as well as by IR spectroscopy of absorbed probe molecules, and by means of test reactions (18, 21).

Concerning the nature of the acidic and basic sites, molecular orbital calculations on acidic active sites on ALPO catalysts (22, 23) showed that P–OH groups represent the most stable Brønsted acid sites, while phosphorous atoms function as Lewis acid sites on ALPO surfaces. In addition, the proton abstraction energies for Al–OH groups indicate that these centers cannot be considered as strong Brønsted sites but, however, might enhance the Brønsted acidity of P–OH groups through H-bonding. On the other hand, exposed oxygens of P–OH groups are found to act as Lewis basic sites since they have higher electronic density than bridged oxygens (22).

On the basis of the demonstrated acid–base bifunctionality of the ALPO catalysts, we have tried to explain the excellent catalytic activity and selectivity of ALPO for the synthesis of jasminaldehyde.

In a previous work (24) it has been demonstrated that the reactivity of benzaldehyde for Knoevenagel condensation reactions could be enhanced by introducing substituting groups in the aromatic ring that increase the density of positive charge on the carbon of the carbonyl group, facilitating the attack of the carbanion formed on a basic site. The reaction rate is thereby increased since the controlling step of the reaction has been shown to be the bimolecular condensation step, i.e., the attack of the carbanion to the carbonyl group. Following this idea, it is obvious that the weaker the basic site of the catalyst the less negatively charged will be the carbanionic species, and consequently a higher density of positive charge will be necessary on the carbon of the carbonyl group in the benzaldehyde derivative in order for the condensation reaction to proceed efficiently.

Using this model as an analogy, we can assume that in an acid–base bifunctional catalyst, such as ALPO, the role of the weak acid sites is to interact with the carbonyl group of the benzaldehyde producing a polarization of this group and increasing the positive charge on the corresponding carbon atom. If this occurs then the attack of the carbanion formed on the relatively weak basic sites of ALPO should be favored and this would explain the good reactivity of ALPO for the reaction studied. Furthermore, it has been reported that in the homogeneous base-catalyzed condensation of alkanals with benzaldehyde the selectivity to α-alkylcinnamaldehydes can be increased by the presence of a small amount of an acid (25).

In order to support such a model we have adsorbed benzaldehyde on pure silica MCM-41 and ALPO in a vacuum IR cell and it can be seen in Fig. 7 that, while in MCM-41 benzaldehyde is physically adsorbed (see the carbonyl group at $\sim$1700 cm^{-1}), on ALPO we observe the majority presence of a chemically interacting carbonyl group at 1655 cm^{-1} (interaction shift of $\sim$50 cm^{-1}). This is an indication that a certain polarization of the carbonyl group has occurred in accordance with the proposed reaction model. Finally, the presence of those weak acid sites in ALPO has also been shown by using a reaction test for weak acid sites such as the acetalization of benzaldehyde with trimethyl

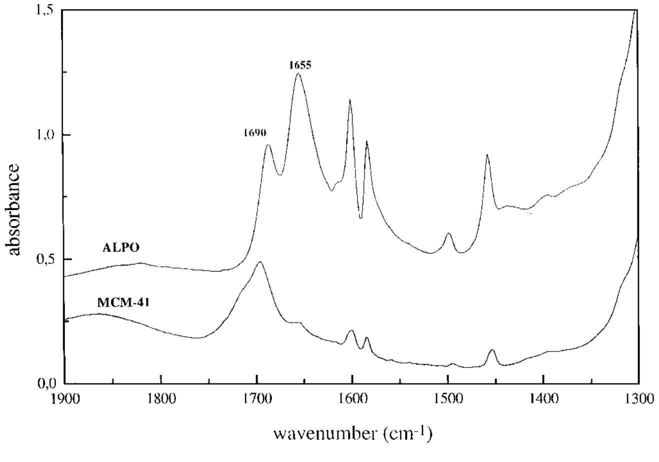
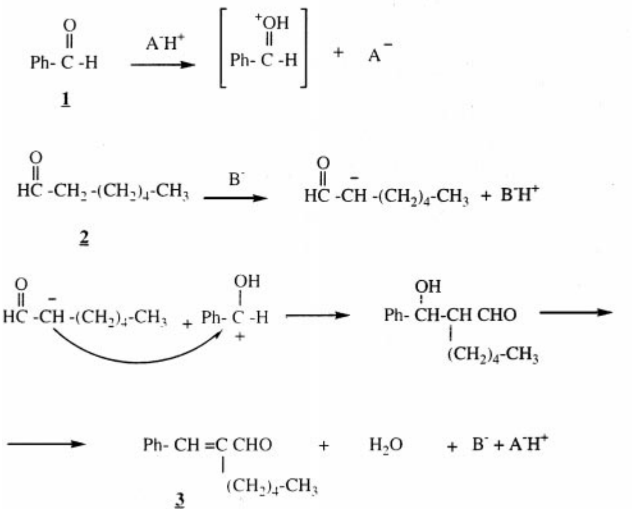


FIG. 7. IR spectra of benzaldehyde adsorbed on ALPO and Al-free MCM-41.



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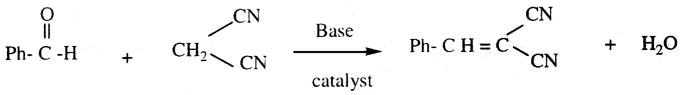

SCHEME 5

orthoformate. Indeed, the results showed that ALPO catalyst is able to catalyze the formation of acetals achieving the benzaldehyde dimethyl acetal (formed with an initial rate of 1.8×10^{-4} mol min^{-1} g^{-1}), in good agreement with the results reported by Bautista *et al.* (26).

In another experiment that can give information on the potential role of the acid sites in the condensation reaction, we prepared an ALPO sample in which the acidity was neutralized by treating the ALPO with a 1 M solution of sodium acetate followed by washing and drying. After this treatment, we showed by IR that the stretching bands of OH groups associated with Al and P (3793 and 3678 cm^{-1} respectively), and which were present in the original ALPO, have disappeared (see Fig. 8). Meanwhile, the catalytic activity for the acetalization of benzaldehyde with TMOF was dropped to zero, confirming that with the above treatment we have neutralized the acid sites present in ALPO. Nevertheless, by neutralizing the acid sites by Na$^+$ exchange one also increases the basicity of the solid. We have seen that this occurs in our case by using a test reaction that can only be catalyzed by basic sites, i.e., the Knoevenagel condensation between benzaldehyde and malononitrile (Scheme 5). The results presented in Fig. 9 show that both the ALPO and the Na-exchanged ALPO have basic sites active for this reaction, but the activity of Na-ALPO is higher as a consequence of its higher basicity.

At this point, we know that ALPO has acid and base sites, while Na-exchanged ALPO has only basic sites that are stronger than those of ALPO. Thus, if only the basic sites of ALPO were responsible for the catalytic behavior of this material in the synthesis of jasminaldehyde, we could expect Na-ALPO to be an even more active catalyst than ALPO for this reaction. However, the results presented in Fig. 10 clearly indicate that Na-ALPO gives a lower activity and a worse selectivity to jasminaldehyde than ALPO. Thus, we can conclude that a bifunctional acid–base mechanism such as the one presented in Scheme 4 would be consistent with the results obtained for the synthesis of jasminaldehyde on ALPO.

Influence of the Reaction Conditions

As was said before, the general methodology to obtain jasminaldehyde with high selectivity requires that the concentration of heptanal be kept low in order to decrease the reaction rate of the self-condensation. This can be achieved by adding slowly the heptanal into the reaction mixture

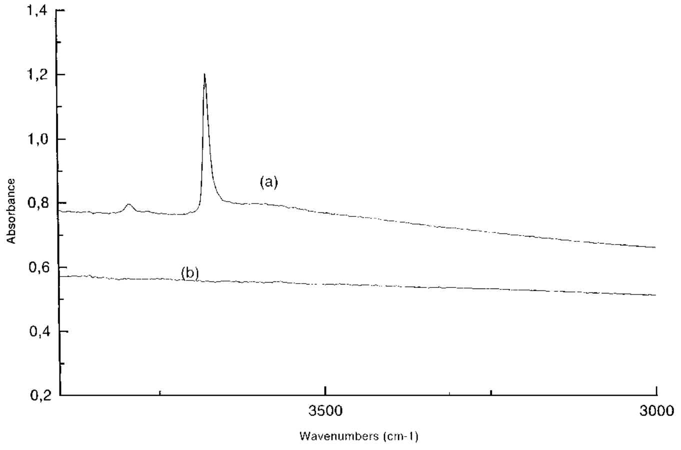

FIG. 8. IR spectra in the hydroxyl range of ALPO (a) and Na-exchanged ALPO (b).

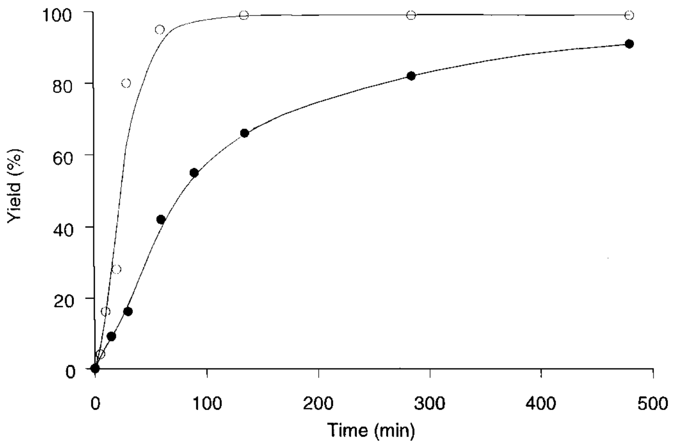

FIG. 9. Knoevenagel condensation between benzaldehyde (10 mmol) and malononitrile (10 mmol) at 333 K on ALPO (●) and Na-ALPO (○).

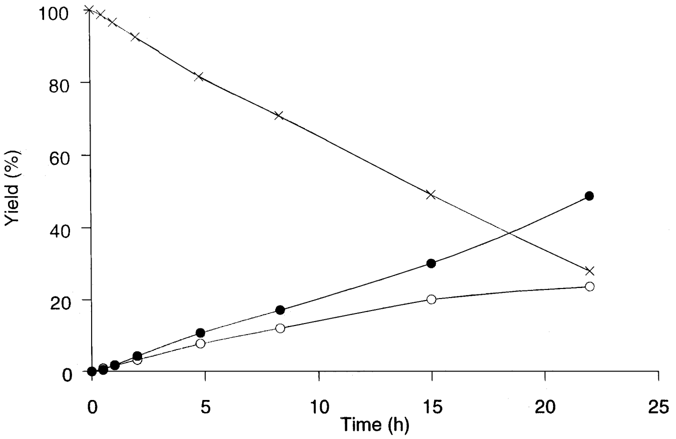

FIG. 10. Yields of the different products **2** (×), **3** (●), and **4** (○) versus reaction time in the condensation of benzaldehyde and heptanal using Na-ALPO catalyst (10 wt%), a reactant molar ratio PhCHO : heptanal = 5 : 1 at 398 K.

which involves long reaction times or by directly using a high benzaldehyde to heptanal molar ratio, which requires larger reactors.

In order to study the influence of the molar ratio of the reagents on the selectivity to jasminaldehyde and then to optimize this parameter, we have carried out the condensation reaction using molar ratios of benzaldehyde to heptanal of 3, 5, 7, and 9 in the presence of ALPO as catalyst (10 wt%) at 398 K. Interestingly, on decreasing the ratio of benzaldehyde to heptanal from 5 to 3, the initial heptanal disappearance rate undergoes a 3-fold increase. This result could be explained on the basis that when the concentration of heptanal is increased, this reagent competes with benzaldehyde for adsorption on the acid sites, in such a way that it would be possible that the protonation and consequently the activation of heptanal carbonyl group would take place to a considerable extent. If this is so, it should be expected that the self-condensation would be favored and the selectivity to jasminaldehyde would decrease. Indeed, when the yield of jasminaldehyde versus conversion using different molar ratio of reagents is plotted (Fig. 11) it can be seen the decrease in jasminaldehyde selectivity for a benzaldehyde/heptanal ratio of 3.

On the other hand, when the molar ratio of reagents is increased above 5 appreciable changes in the heptanal disappearance reaction rate were not observed, indicating that beyond this molar ratio the majority of acid sites are already preferentially interacting with benzaldehyde, and therefore, no changes in selectivity to jasminaldehyde are observed for benzaldehyde/heptanal molar ratios higher than 5 (Fig. 11).

Temperature is another important parameter which not only affects the reaction rate but also can affect the selectivity for a given reaction. In order to study the influence of the temperature, the condensation reaction was carried

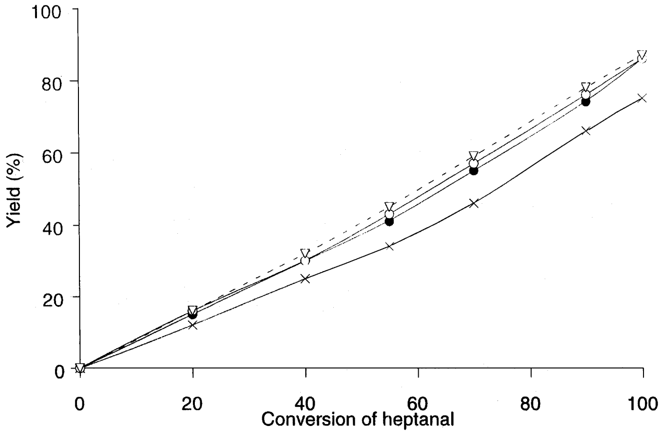

FIG. 11. Yield of **3**–heptanal conversion plot using benzaldehyde to heptanal molar ratios of **3** (×), **5** (●), **7** (○), and **9** (▽) in the presence of ALPO catalyst at 398 K.

out at 383 K and 413 K, using ALPO (10 wt%) as catalyst. The results are presented in Figs. 12a and 12b. As was expected, a decrease of temperature causes a decrease in the heptanal disappearance rate, whereas an increase of temperature leads to a total heptanal conversion within 1 h of

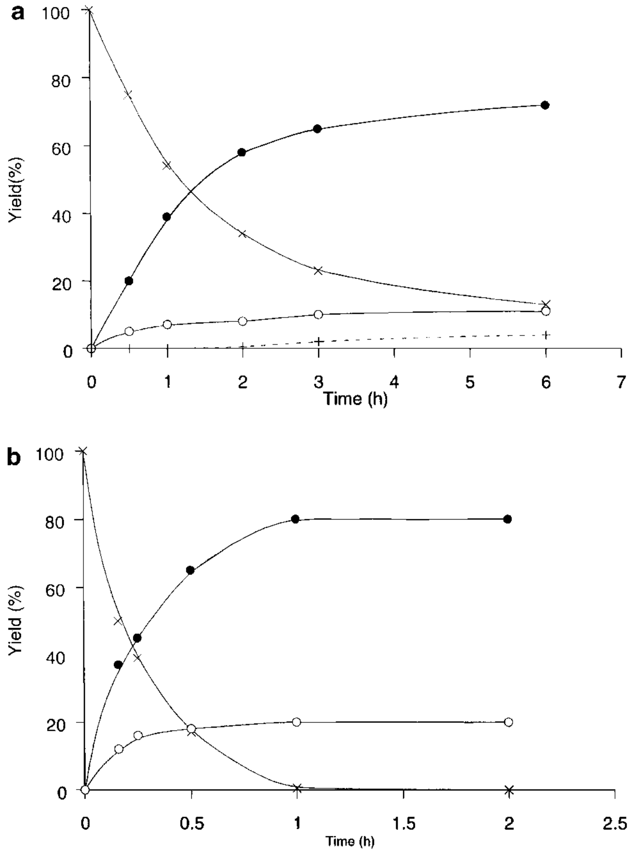

FIG. 12. Yields of the different products **2** (×), **3** (●), **4** (○), and **6** (+) versus reaction time in the condensation of benzaldehyde and heptanal using ALPO catalyst (10 wt%), a reactant molar ratio PhCHO : heptanal = 5 : 1 at 383 K (a) and 413 K (b).

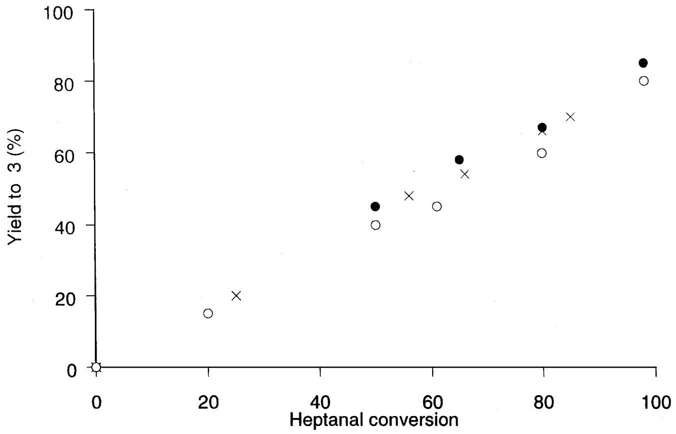

FIG. 13. Yield of **3**–heptanal conversion plot using a benzaldehyde to heptanal molar ratio of 5 in the presence of ALPO catalyst at 388 K (×), 398 K (●), and 413 K (○).

reaction time. However, when the yield of jasminaldehyde is compared at same level of conversion (Fig. 13), the selectivity is practically the same at temperatures between 383 K and 398 K, while at 413 K or higher a decrease in the selectivity should be expected.

CONCLUSIONS

It has been shown that the use of zeolites as catalysts for the condensation of benzaldehyde and heptanal leads to low selectivities to jasminaldehyde and fast deactivation of the catalyst. These results are 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 heptanal self-condensation product as well as to consecutive reactions occurring within the pores, which end with the formation of persistent diphenyl allyl cation. Whereas mesoporous aluminosilicate (AlMCM-41) exhibits better activity and selectivity to jasminaldehyde than zeolites, the best results are obtained using amorphous aluminophosphate as catalyst. This finding was explained on the basis of the acid–base bifunctional character of the ALPO, where the role of the weak acid sites is the activation of benzaldehyde by protonation of the carbonyl group favoring then the attack of the enolate heptanal intermediate generated on the relatively weak basic sites of ALPO. This hypothesis is supported by the fact that the IR band of the carbonyl group of benzaldehyde shifts toward lower wavelength when the benzaldehyde is adsorbed on ALPO, indicating that a certain polarization of the carbonyl group occur. Moreover, when acid sites on ALPO are neutralized by treating with sodium acetate it is found that Na-ALPO gives lower activity and worse selectivity to jasminaldehyde than ALPO.

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