JOURNAL OF CATALYSIS **175,** 70–79 (1998)
ARTICLE NO. CA981970

Use of Mesoporous MCM-41 Aluminosilicates as Catalysts in the Preparation of Fine Chemicals

A New Route for the Preparation of Jasminaldehyde with High Selectivity

M. J. Climent, A. Corma,[1] R. Guil-López, S. Iborra, and J. Primo

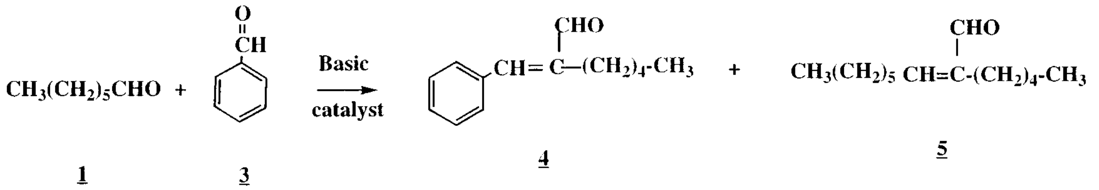
Instituto de Tecnología Química, Departamento de Química (CSIC-UPV), Avenida de Los Naranjos s/n 46022, Valencia, Spain

Received August 20, 1997; revised November 4, 1997; accepted November 4, 1997

α-*n*-Amylcinnamaldehyde (Jasminaldehyde) has been prepared with high selectivity and using low ratios of benzaldehyde/heptanal by means of mesoporous molecular sieve catalysts and a process which involves the acetalization of heptanal with methanol, followed, in the same pot, by a slow hydrolysis of dimethylacetal and the aldolic condensation of the two aldehydes as the final step. A large pore zeolite (Beta) as well as mesoporous silica-aluminas with regular pore sizes such as MCM-41 and SAM have been used as catalysts. The results indicate that mesoporous silica-aluminas with a very narrow range of pore diameter such as MCM-41 are the most adequate catalysts to produce in one pot the three consecutive reactions, avoiding in a very large extent the self-condensation of heptanal and undesired consecutive reactions. This new route allows us to achieve Jasminaldehyde with high selectivity and with a relative high global reaction rates. The influence of the concentration of acid sites on MCM-41, reaction temperature, and molar ratio of the reactants have been also studied.

INTRODUCTION

The synthesis of α-*n*-amylcinnamaldehyde (jasminaldehyde) (**4**),[2] a traditional perfumery material with violet scent, involves the condensation of 1-heptanal (**1**) with benzaldehyde (**3**).



[1]

This aldol condensation is carried out in the presence of alkali as catalyst (sodium or potassium hydroxide) (1, 2), heptanal being added slowly to the reaction mixture at moderate temperatures.

A general difficulty with aldol condensation reactions and, more specifically, in the condensation of 1-heptanal with benzaldehyde is that both reactants undergo side reactions which in this case reduce the yield of amyl cinnamic aldehyde and form undesired by-products. During the synthesis of (**4**) the most important undesired product comes from the autocondensation of heptanal to form 2-*n*-pentyl-2-*n*-nonenal (**5**) (Scheme [1] above). The formation of (**5**) can be inhibited, to some extent by maintaining a very low concentration of heptanal relative to benzaldehyde in the reaction mixture. This methodology requires long addition times in batch reactions and renders impractical the use of plug-flow continuous reactors for carrying out this process.

The formation of further by-products results from the limited stability of benzaldehyde under the reaction conditions which tends to disproportionate via the Cannizzaro reaction to yield benzyl alcohol and benzoic acid, forming the benzoate with the base catalyst and loosing, therefore, reactant and catalyst.

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 well known that this type of reaction can also be catalyzed by solid acids. However, the fact that lower selectivities are generally found when

---

[1] To whom correspondence should be addressed. Fax: 96-387 78 09.

[2] The bold face numbers in parentheses refer to the chemical formulas used in the schemes given throughout the paper. Schemes are denoted by bracketed numbers.

0021-9517/98 $25.00

using acid, instead of base, catalysts is responsible for the very few reports involving the use of heterogeneous acid catalysts in the production of Jasminaldehyde (6).

In this work we will present that, by working in a coupled way with the catalyst and the process, it was possible to develop a new route for the preparation of Jasminaldehyde using solid acid catalysts which gives higher selectivities than solid base catalysts. The new route is based on our previous observation that Al-MCM-41 materials were very active catalysts for the acetalization reaction and the hydrolysis of acetals (7). Then, we thought that these solids should be able to catalyze, in one pot, three consecutive reactions: acetalization of the aldehydes with methanol, followed by a slow hydrolysis of acetal, and finishing with aldolic condensation. By operating in this way, it was possible, with relatively high global reaction rates, to have low concentrations of heptanal at the surface of the catalyst, decreasing, therefore, the self-condensation of heptanal and achieving high selectivity to Jasminaldehyde.

EXPERIMENTAL

Materials

A large pore zeolite, H-Beta zeolite, was used, together with H-MCM-41 as the acid catalyst. The H-Beta zeolite was prepared starting from a TEA-Beta sample (Si/Al = 13) and heating at 773 K in N_2 stream, followed by calcination in air at 823 K. The sample thereafter was twice NH_4^+-exchanged and calcined at 823 K.

Three samples of Al-MCM-41 mesoporous material were synthesized following the procedure given in the literature (8) using hexadecyltrimethyl-ammonium (Panreac 98 wt%) cation as the template, and pseudoboehmite (Catapal B, Vista) as the aluminum source. The samples were activated by calcination in air at 813 K for 7 h, or calcination in N_2 for 1 h, and in air for 6 h at 813 K.

For comparison purposes, one amorphous silica-alumina, was prepared according to Ref. (9), and it is named SAM-144.

The main characteristics of the acid samples used are summarized in Table 1.

The solids were characterized by X-ray diffraction on a Phillips PW diffractometer using CuKα radiation. Surface area measurements were obtained on an ASAP-2000 apparatus following the BET procedure. Pore diameter distribution was obtained using argon as adsorbate and following the Horvath–Kawazoe method (10). IR spectra were recorded on a Nicolet 710 FTIR spectrophotometer, using 10 $mg \cdot cm^{-2}$ wafers. The Brönsted and Lewis acidity of the samples was measured by pyridine adsorption–desorption, and the resultant sample was monitored by IR. Thus, the samples were treated in an IR cell at 673 K and 15×10^{-3} Pa for 16 h. Pyridine was then admitted at room temperature and, after saturation, the samples were degassed at 423, 523, and 673 K and the IR spectra were recorded at room temperature.

TABLE 1

Main Structural Characteristics of the Catalysts

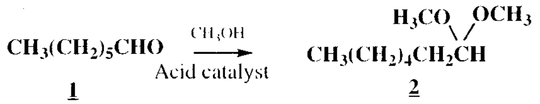
Catalysts	Surface[a] area ($m^2 \cdot g^{-1}$)	Pore[a] volume ($cm^3 \cdot g^{-1}$)	Si/Al ratio	Average[b] (Å) pore diameter
1.MCM-41	900	0.500	14	35
2.MCM-41	870	0.670	50	42
3.MCM-41	837	0.480	83	34
SAM-144	719	0.310	50	15
βH	607	0.175	13	7.6 * 6.4

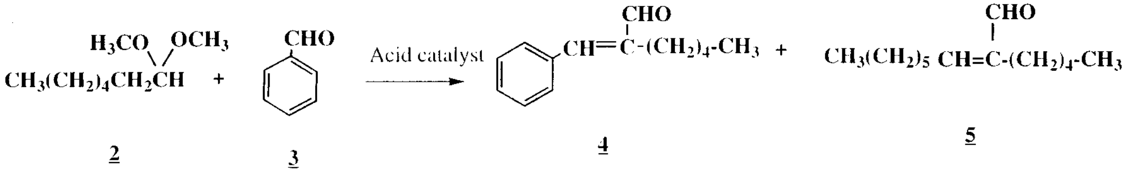
[a] Measured by N_2.
[b] Measured by Ar.

Reaction Procedure

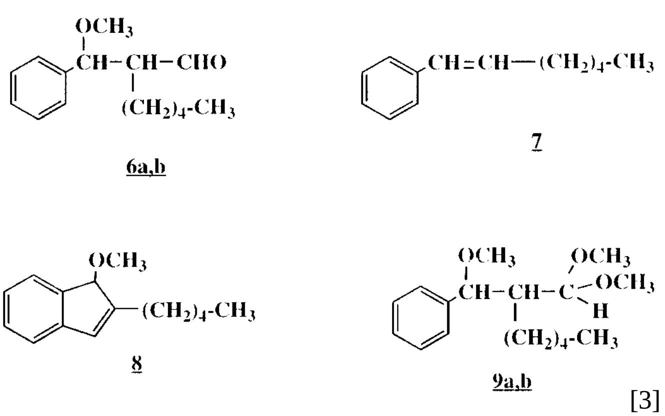
Activation of the catalyst, was performed by *in situ* heating at 373 K under vacuum (11×10^2 Pa) for 2 h. Thereafter the system was left at room temperature and a solution of 10 mmol of heptanal (Technical grade, from Fluka) in methanol (Technical grade, from Panreac) (15 ml) was poured onto the activated catalyst. The resulting suspension was magnetically stirred at reflux temperature until 80% conversion of the heptanal to dimethylacetal was achieved. At the end of the reaction the methanol was distilled in a vacuum, and the benzaldehyde (10–50 mmol) was added. The resulting suspension was magnetically stirred under N_2 atmosphere and the kinetics of the reaction was followed at different reaction temperatures (100–140°C). Liquid samples of this suspension were extracted at regular times with a filtering syringe and analyzed by gas chromatography using a capillary column. At the end of the reaction the catalyst was filtered and washed with dichloromethane and the filtrate was weighed and analyzed by gas chromatography–mass spectrometry (GC-MS) using a Hewlett–Packard 5988A spectrometer provided with a 25-m capillary column of cross-linked 5% phenylmethylsilicone; the ratios m/z and the relative intensities (%) are indicated for the corresponding peaks.

After the reaction was completed, the catalysts were submitted to continuous solid–liquid extractions with dichloromethane using a micro-soxhlet apparatus. After removal of the solvent the residue was analyzed by GC-MS and ^{1}H-NMR spectroscopy and included in the mass balance. In all cases the recovered products accounted for more than 90% of the starting material. Isolation of pure compounds was accomplished by high performance liquid chromatography, using an isocratic Waters apparatus provided with a semi-preparative Microprasil^R column and mixtures of hexane-ethyl acetate as eluent. The ^{1}H-NMR analyses of the products were carried out with a 400 MHz Varian VXR-400 S spectrometer in deuterated trichloromethane with TMS as the internal standard. Chemical shifts are reported in δ (ppm) and are referenced to TMS. The chemical structures of all the products obtained in this study are presented:





[2]



[3]

Spectroscopic-Spectrometry Data of the Reaction Products

*(E)-α-Pentylcinnamaldehyde (**4**).* ^{1}H-NMR: 9.54 (s, 1H, $-C\underline{H}O$), 1.70–7.38 (m, 5H, ArH), 7.20 (s, 1H, $Ph-C\underline{H}{=}C$), 2.52 (t, 2H, J = 8 Hz, $-C\underline{H}_2-(CH_2)_3-CH_3$), 1.50–1.39 (m, 2H, $-C\underline{H}_2-(CH_2)_2-CH_3$), 1.40–1.30 (m, 4H, $-CH_2-(C\underline{H}_2)_2-CH_3$), 0.89 (t, 3H, J = 8 Hz, $-C\underline{H}_3$); MS: 202 (M^+, 12), 145 (9), 129 (48), 115 (100), 105 (28), 91 (14).

*(E)-2-Pentyl-2-nonenaldehyde (**5**).* ^{1}H-NMR: 9.36 (s, 1H, $-C\underline{H}O$), 6.44 (t, 1H, J = 8 Hz, $-CH_2-C\underline{H}{=}CCHO-$), 2.45–2.29 (m, 2H, $-C\underline{H}_2-CCHO{=}CH-$), 2.29–2.10 (m, 2H, $-C\underline{H}_2-CH{=}CCHO-$), 1.60–1.10 (m, 14H, $C\underline{H}_2$), 1.10–0.80 (m, 6H, $C\underline{H}_3$); MS: 210 (M^+, 98), 153 (30), 139 (34), 125 (41), 41 (100).

*3-Methoxy-2-pentyl-3-phenyl propanaldehyde (**6**).* **6a**. ^{1}H-NMR: 9.71 (d, 1H, J = 4 Hz, $-C\underline{H}O$), 7.38–7.25 (m, 5H, ArH), 4.32 (d, 1H, J = 8 Hz, $-C\underline{H}OCH_3$), 3.16 (s, 3H, $-OC\underline{H}_3$), 2.65–2.55 (m, 1H, $-C\underline{H}-CHO$), 1.60–1.40 (m, 2H, $-C\underline{H}_2-(CH_2)_3CH_3$), 1.30–1.10 (m, 6H, $-(C\underline{H}_2)_3CH_3$); 0.80 (t, 3H, J = 7 Hz, $C\underline{H}_3$). **6b**. 9.64 (d, 1H, J = 3 Hz, $-C\underline{H}O$), 7.40–7.25 (m, 5H, ArH), 4.45 (d, 1H, J = 8 Hz, $-C\underline{H}-OCH_3$), 2.52–2.50 (m, 1H, $-C\underline{H}-CHO$), 1.80–1.60 (m, 2H, $C\underline{H}_2(CH_2)_3CH_3$), 1.40–1.10 (m, 6H, $CH_2(C\underline{H}_2)_3CH_3$), 0.83 (t, 3H, J = 6 Hz, CH_3); MS: 233 (M-1, 1), 174 (6), 121 (100), 104 (6), 91 (13).

*trans-1-Phenyl-heptene (**7**).* ^{1}H-NMR: 6.36 (d, 1H, $Ph-C\underline{H}{=}CH-CH_2$), 6.22 (dt, 1H, $Ph-CH{=}C\underline{H}-CH_2-$), 2.19 (dc, 2H, $Ph-CH{=}CH-C\underline{H}_2-$); MS: 174 ($M^+$, 61), 161 (12), 117 (100), 104 (96), 91 (44).

*2-Pentyl-3-methoxyindene (**8**).* ^{1}H-NMR: 7.43–7.12 (m, 5H, ArH), 6.45 (s, 1H, $Ph-C\underline{H}{=}C-$), 4.94 (s, 1H, $-C\underline{H}OCH_3$), 3.02 (s, 3H, $-OC\underline{H}_3$), 2.40–2.30 (m, 2H, $C\underline{H}_2-(CH_2)_3CH_3$), 1.80–1.10 (m, 2H, $C\underline{H}_2(CH_2)_2CH_3$), 1.45–1.20 (m, 4H, $CH_2(C\underline{H}_2)_2CH_3$), 0.91 (t, 3H, J = 6 Hz, CH_3); MS: 216 (M^+, 100), 185 (11), 159 (89), 131 (9).

*2-Pentyl-3-phenyl-1,1,3-trimetoxy propane (**9a, b**).* 7.50–7.20 (m, 5H, ArH), 4.47 and 4.36 (d, 1H, J = 4 Hz, $PhC\underline{H}-OCH_3$), 4.13 and 4.11 (d, 1H, J = 4 Hz, $-C\underline{H}(OCH_3)_2$), 3.47, 3.38, 3.36, 3.30, 3.24, and 3.16 (s, 3H, $-OCH_3$), 2.10–1.90 and 1.85–1.80 (m, 1H, $C\underline{H}(CH_2)_4CH_3$), 1.50–0.70 (m, 11H, *n*-pentyl); MS: 174 (10), 121 (100), 91 (10), 77 (15), 75 (100).

Preliminary experiments were carried out under the same experimental conditions on MCM-41 (Si/Al = 14) catalyst, but stirring at different speeds (500 and −1000 rpm), and no differences in the initial rate of the reaction was observed. Two series of experiments were also carried out at the same reaction conditions but using 1.7% and 5 wt% of MCM-41 (Si/Al = 14) catalyst, the initial rate of the reaction was seen to be directly proportional to the amount of catalyst, while no differences on product selectivity were observed.

RESULTS AND DISCUSSION

Reaction Mechanism

The production of Jasminaldehyde (**4**) in one pot from heptanal dimethyl acetal (**2**) and benzaldehyde (**3**) using heterogeneous solid acid catalysts, involves several reaction steps (Scheme [2]). In the first one, heptanal dimethyl acetal (**2**) is formed by refluxing heptanal (**1**) with an excess of methanol in the presence of the solid acid catalyst. In the second step and when the yield of (**2**) is around 80%, the

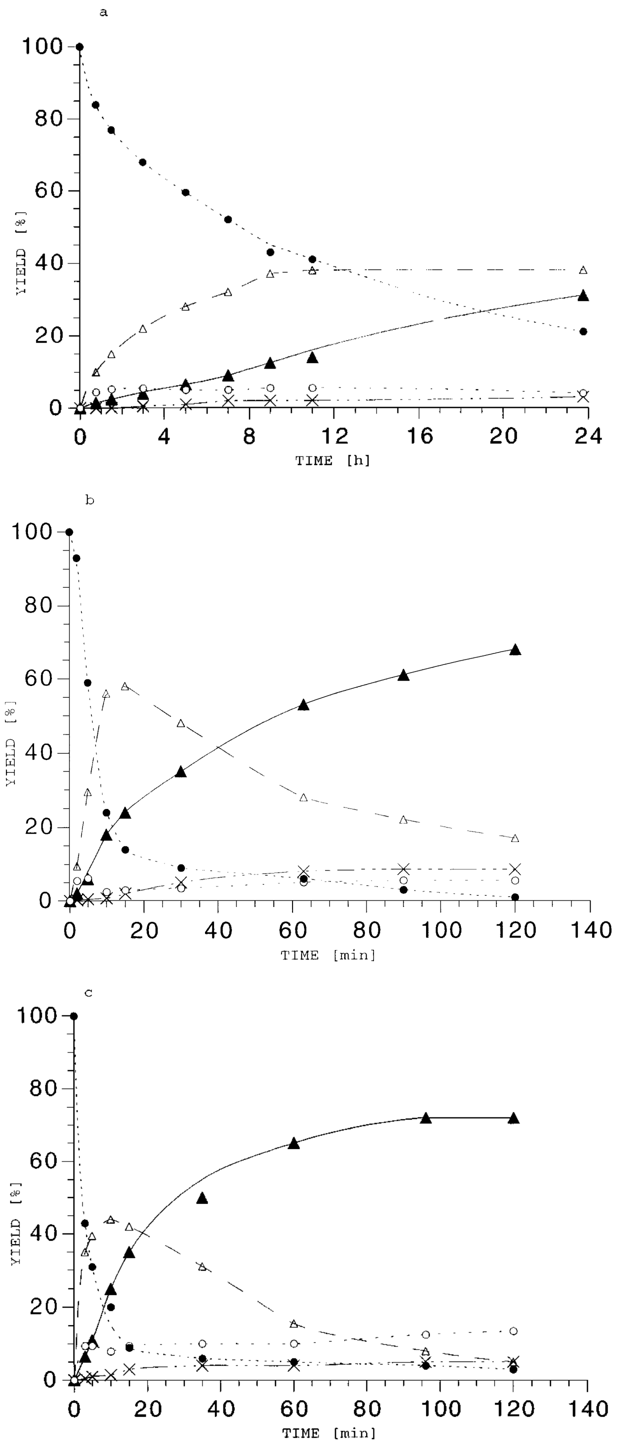
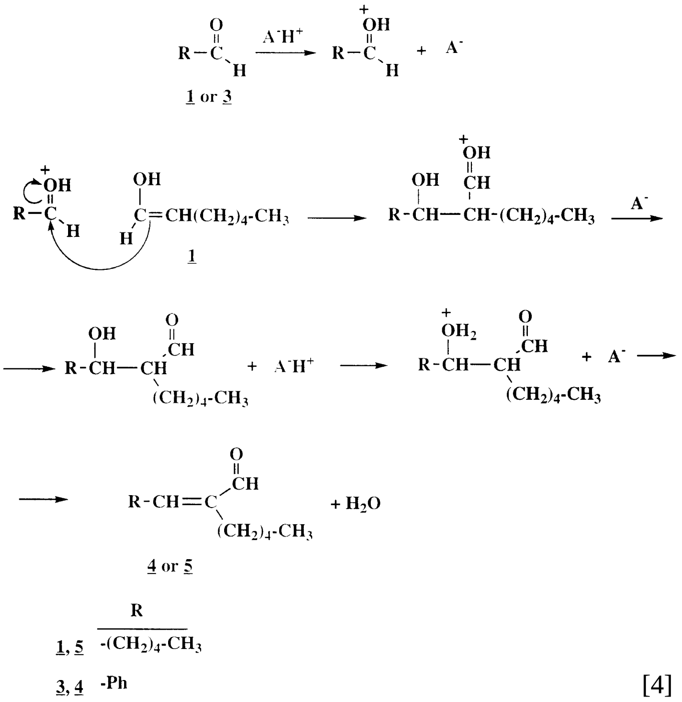


FIG. 1. Yields of different products (**1** + **2**) (●), **4** (▲), **5** (×), **6** (△), (**7** + **8** + **9**) (○) versus reaction time between benzaldehyde and heptanal dimethylacetal using 1.MCM-41 (1.7 wt%), a reactant molar ratio PhCHO : heptanal = 1.5 : 1 at (a) 373 K, (b) 398 K, (c) 413 K.

methanol is distilled in vacuum, benzaldehyde is added and the system is heated at the adequate temperature. Under these reaction conditions heptanal dimethyl acetal undergoes the deacetalization to (**1**), followed by the acid catalyzed aldolic condensation between heptanal (**1**) and benzaldehyde. Following this procedure and adjusting the rates of the hydrolysis of the acetal and the aldolic condensation, one can control the concentration of heptanal on the surface of the catalyst, and in this way it is possible to depress the extension of the unwanted self condensation of heptanal.

When the reaction was carried out in the presence of the mesoporous aluminosilicate 1.MCM-41 (Si/Al = 14) (1.7 wt%) using a molar ratio PhCOH/heptanal 1.5 : 1, at 398 K, we obtained after 2-h reaction time, a total conversion of 99% with a yield of (E)-α-*n*-amylcinnamaldehyde (jasminaldehyde) (**4**) of 68%. In the reaction mixture a 9% of self-condensation heptanal product (E)-2-*n*-pentyl-2-*n*-nonenal (**5**), 17% of 3-methoxy-2-pentyl-3-phenyl propanaldehyde (**6**), 2% of trans-1-phenylheptene (**7**) and 3% of 3-methoxy-2-pentyl indene (**8**) were also detected. Furthermore, we also observed at the beginning of the reaction the formation of a mixture of two diastereoisomers of the dimethylacetal of (**6**), that is 2-pentyl-3-phenyl-1,1,3-trimethoxy propane (**9a**, **9b**), which disappeared with the time (Scheme [3]). When the yields of the different products were plotted versus the reaction time (Fig. 1b), Jasminaldehyde (**4**) and the self-condensation product (**5**) appeared as primary products, 3-methoxy-2-pentyl-3-phenyl propanaldehyde (**6**) showed a primary but unstable character, while alkene (**7**) and indene (**8**) are secondary and stable products. The formation of (**4**) and (**5**) could be very easily 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,



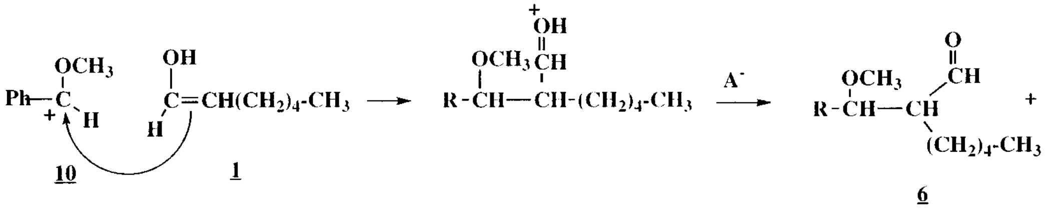
[4]

From Fig. 1b one can realize that the rate of the competitive self-condensation reaction is very slow. This effect being related to the low concentration of heptanal on the surface of MCM-41. The deacetalyzation process of heptanal dimethylacetal to produce the reactive heptanal can occur by two different routes, namely, by hydrolysis and/or by trans-acetalization between the two aldehydes involved in the process. In our case, the detection of benzaldehyde dimethyl acetal at the beginning of the reaction strongly indicates that, besides the direct hydrolysis of the heptanal dimethyl acetal, heptanal can also be formed by the trans-acetalization reaction. The choice of a catalyst such as MCM-41 with weak acid sites and large pores makes the hydrolysis and transacetalization to proceed slowly, maintaining in this way a low concentration of heptanal on the catalyst surface.

With respect to product (**6**) we found that this is a mixture of two diastereoisomers (**6a**, **6b**) and their formation could be explained, in a first approximation, by an acid catalyzed electrophilic Michael addition of methanol to Jasminaldehyde (**4**). However, if this was the mechanism, product (**6**) should appear as a secondary product, something which is not reflected in Fig. 2, in where it appears that product (**6**) has a primary character.

In order to obtain further confirmation on this, Jasminaldehyde was refluxed with methanol in the presence of 1.MCM-41 during 5 h. In these conditions, product (**6**) was not formed being Jasminaldehyde dimethyl acetal, the only product observed. From this it can be concluded that (**6**) should be produced by a reaction other than the Michael addition of methanol to Jasminaldehyde.

An alternative reaction which could explain the formation of (**6**), is the condensation between benzaldehyde and heptanal which involves the carbocation (as electrophilic species) (**10**) (Scheme [5]) which comes from the hemiacetal of benzaldehyde,



[5]

The high yield of product (**6**) observed at short reaction times (Fig. 1b) indicates that both the transacetalization between heptanal and benzaldehyde to produce the hemiacetal and the consecutive reaction of the carbocation (**10**) with the heptanal, should take place at a much faster rate than the condensation of the protonated benzaldehyde with heptanal to give Jasminaldehyde. This is not surprising if one takes into account that the mesomeric donor effect of the metoxy group is larger than that of a hydroxy group.

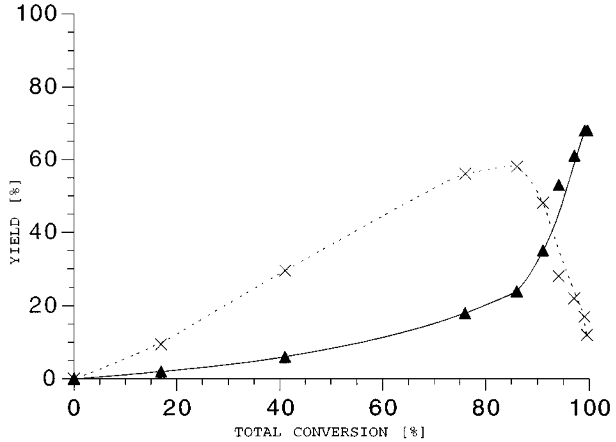


FIG. 2. Yield of Jasminaldehyde (**4**) (▲) and **6** (×) versus total conversion, obtained in the reaction between benzaldehyde and heptanal dimethylacetal using 1.MCM-41 (1.7 wt%), a reactants molar ratio PhCHO : heptanal = 1.5 : 1 at 398 K.

Then, it can be expected that the intermediate (**10**) is more stable than the intermediate formed by the direct protonation of benzaldehyde.

On the other hand, and as we indicated above, product (**6**) appeared as an unstable product (Fig. 1b) whose maximum yield is achieved after 15 min of reaction time, being at this point the conversion of the reactant close to 90%. After this point, the yield of product (**6**) decreases, while the yield to Jasminaldehyde (**4**) is still increasing. This effect can be better seen when plotting the yield of Jasminaldehyde versus total conversion (Fig. 2). It can be seen that, at a high level of conversion, Jasminaldehyde also forms, via an intermediate, once depletion of the product (**6**) has taken place. Thus, one can relate these two observations and propose that under our reaction conditions the acid catalyzed elimination of methanol from (**6**) occurs to give Jasminaldehyde (**4**) and that this is the main way to form Jasminaldehyde.

The minority products (**7**) and (**8**) clearly come from Jasminaldehyde. The former (1-phenylheptene) could be formed by oxidation of (**4**) followed by a fast decarboxylation, while the indene (**8**) should be formed through a mechanism which involves an intramolecular acid-catalyzed

TABLE 2

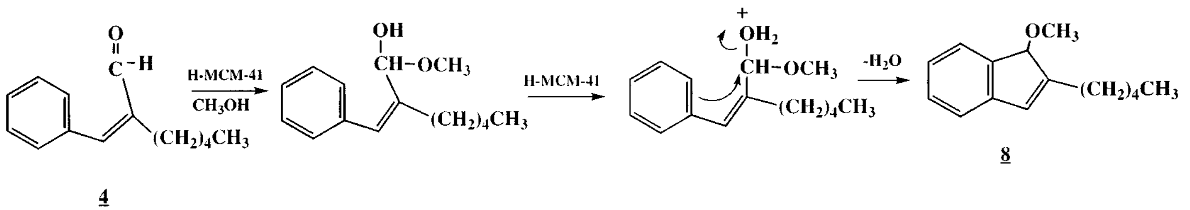
Results of the Reaction of Benzaldehyde with Heptanal Dimethylacetal (2) over Different Catalysts

Catalysts	Total[a] conversion (%)	$V_{\text{disappearance}} \times 10^{-3}$ (mol/min · g)	Yield[a] (%) to **4**	Yield[a] (%) to **5**	Yield[a] (%) to **6**	Yield[a] (%) to **7**	Yield[a] (%) to **8**	Yield[a] (%) to **9**
2.MCM-41	71	5.04	25	3	37	—	2	3
SAM-144	85	5.76	32	3	38	3	5	2
βH	51	2.08	6	4	26	11	—	4

Note. Reaction conditions: 1.7% w/w of catalyst/398 K/ratio PhCHO : heptanal = 1.5 : 1.

[a] Time of reaction: 2 h.

cyclization of the hemiacetal of Jasminaldehyde,



[6]

Finally, the very small amounts of product (**9**), i.e. 2-pentyl-3-phenyl-1,1,3-trimethoxy propane observed can be formed through a transacetalization between the dimethylacetal of heptanal and (**6**).

Influence of the Catalyst Structure

In order to study the influence of the catalyst structure on the rate of formation of Jasminaldehyde we have carried out the reaction using three different solid acid catalysts. In this way the behavior of a large pore a microporous zeolite such as Beta has been compared with that of a mesoporous molecular sieve (H-MCM-41) and, also, a mesoporous amorphous silica-alumina with a narrow pore size distribution (SAM).

The results given in Table 2 show that the rate of disappearance of heptanal on the different catalysts follows the order SAM ≥ H-MCM-41 > Beta. The similar initial rate observed for the two silica-alumina catalysts, i.e., SAM and H-MCM-41, is in agreement with the results given in the literature showing similar rates for the oligomerization of olefins (11) and acetalization of aldehydes (7). The lower rate observed on the microporous molecular sieve can be due to pore restrictions for the diffusion of the product out of the catalyst. The combination of large pores and mild acidity in the mesoporous materials makes these solids adequate catalysts to carry out the acetalization–hydrolysis–condensation reactions.

With respect to Jasminaldehyde selectivity (Table 3), it can be seen that at high levels of conversion H-MCM-41 is more selective than SAM, showing the better catalyst behavior of the former for the elimination of MeOH in product (**6**) to give Jasminaldehyde (**4**), while producing less decarboxylation of (**4**) on the former catalyst. Since we have not seen a large difference in the acidity of the two catalysts, we think that the observed behavior can be a consequence of the regular pore dimensions in H-MCM-41 which allow faster diffusion of Jasminaldehyde avoiding consecutive reactions, such as decarboxylation and cyclization to indene, to occur (Table 3). This hypothesis is in agreement with the fact that for Beta zeolite, where the diffusion of the product out is very slow, the autocondensation and decarboxylation of Jasminaldehyde is strongly enhanced.

In conclusion, it becomes clear that an adequate catalyst for the desired reaction involves the use of a mild acid catalyst with large regular pores which allow fast diffusion of the Jasminaldehyde decreasing and, therefore, the probabilities for consecutive reactions to occur.

Influence of the Concentration of Acid Sites on H-MCM-41

In the case of bimolecular reactions catalyzed by acid sites, not only the total number, but also the density of acid

TABLE 3

Yield of the Different Products and Selectivity to (4) in the Reaction of Benzaldehyde with Heptanal Dimethylacetal (2) at 80% Conversion over Different Catalysts

Catalysts	Selectivity (%) to **4**	Yield (%) to **4**	Yield (%) to **5**	Yield (%) to **6**	Yield (%) to **7**	Yield (%) to **8**	Yield (%) to **9**
2.MCM-41	52	41	6	29	—	2	2
SAM-144	35	28	3	37	3	5	4
βH	32	26	9	29	13	1	2

Note. Reaction conditions: 1.7% w/w of catalyst/398 K/ratio PhCHO : heptanal = 1.5 : 1.

TABLE 4

Results of the Reaction of Benzaldehyde with Heptanal Dimethylacetal (2) in the Presence of H-MCM-41 with Different Si/Al Ratios

Catalyst	Si/Al	Total[a] conversion (%)	$V_{\text{disappearance}} \times 10^{-3}$ (mol/min · g)	V_o/[Al/Al + Si]	Yield[a] (%) to **4**	Yield[a] (%) to **5**	Yield[a] (%) to **6**	Yield[a] (%) to **7**	Yield[a] (%) to **8**	Yield[a] (%) to **9**
1.MCM-41	14	99	19.71	0.35	68	9	17	2	3	—
2.MCM-41	50	70	5.04	0.30	25	3	37	—	2	3
3.MCM-41	83	83	1.11	0.33	29	5	43	—	2	4

Note. Reaction conditions: 1.7% w/w of catalyst/398 K/ratio PhCHO : heptanal = 1.5 : 1.

[a] Time of reaction: 2 h.

sites are important. These two parameters have a strong influence on both the total number of active sites and on the adsorption properties of the material.

It can be expected that for framework Si/Al ratios above 10, most of the acid sites will be isolated and, consequently, a further increase on the Si/Al ratio will only change the total number of acid sites and therefore total conversion, unless changes in the hydrophobic–hydrophillic properties of the sample can play an important role on the reaction.

In our case, we have studied the influence of the number of acid sites by carrying out the reaction on three H-MCM-41 samples with Si/Al ratios of 14, 50, and 83. The initial rates, and the turnover numbers calculated by dividing the initial rate by the ratio Al/Al + Si (Table 4) indicate that the activity is directly proportional to the amount of acid sites, and furthermore, the activity per site is the same regardless the amount of Al in the sample.

From the point of view of the product selectivity, the product distribution obtained on the three catalysts at the same level of conversion (80%) (Table 5) indicates that when increasing the framework Si/Al from 14 to 50, the selectivity to Jasminaldehyde increases, with the corresponding decrease in the molar ratio of product (**6**) to (**4**). This result can be explained by taking into account that the conversion of product (**6**) to Jasminaldehyde involves the elimination of a polar molecule (methanol), which certainly could be favored when increasing the hydrophobicity of the MCM-41 by increasing the Si/Al ratio. Despite the beneficial effect of hydrophobicity, there is no doubt that if one increases further the framework Si/Al ratio, the moment arrives when the concentration of active sites is so small that the reaction rates are strongly influenced, so that the consecutive elimination reaction is proportionally influenced. This hypothesis could explain the observation that the ratio of product (**6**) to (**4**) increases, decreasing, therefore, the selectivity to Jasminaldehyde.

Influence of the Reaction Temperature

Taking into account the nature of the products formed during the studied reaction, it can be expected that the reaction temperature will have a strong influence on product selectivity. Indeed, an increase in the temperature of reaction, besides increasing the rate of disappearance of the reactant, should strongly favor the consecutive reactions of Jasminaldehyde such as oxidation–decarboxylation and the cyclization to indene, as well as the elimination of methanol from product (**6**). The two first reactions will tend to decrease the final selectivity to Jasminaldehyde, while the elimination reaction will increase its final yield and selectivity. These expectations are confirmed by the experimental results given in Figs. 1a–c and Table 6. It can be seen there that with the amount of catalyst used (1.7 wt%), the maximum selectivity is observed at 373 K, but under these conditions 24 h of reaction time are needed to achieve only 80% conversion. Then, in order to increase the rate of the reaction while still working at lower temperatures (373 K),

TABLE 5

Yield of the Different Products and Selectivity to 4 at 80% Conversion Obtained in the Reaction of Benzaldehyde with Heptanal Dimethylacetal (2) over H-MCM-41 with Different Si/Al Ratio

Catalyst	Si/Al	Selectivity (%) to **4**	Yield (%) to **4**	Yield (%) to **5**	Yield (%) to **6**	Yield (%) to **7**	Yield (%) to **8**	Yield (%) to **9**	Ratio **6**/**4**
1.MCM-41	14	25	20	2	57	—	1	—	2.85
2.MCM-41	50	52	41	6	29	—	2	2	0.71
3.MCM-41	83	30	24	4	46	—	2	4	1.92

Note. Reaction conditions: 1.7% w/w of catalyst/398 K/ratio PhCHO : heptanal = 1.5 : 1.

TABLE 6

Results of the Reaction of Benzaldehyde with Heptanal Dimethylacetal (2) at 80% Conversion at Different Reaction Temperatures

Temperature (K)	Selectivity (%) to **4**	$V_{\text{disapp.}} \times 10^{-3}$ (mol/min · g)	Yield (%) to **4**	Yield (%) to **5**	Yield (%) to **6**	Yield (%) to **7**	Yield (%) to **8**	Yield (%) to **9**
373	40	0.73	32	3	42	—	1	2
398	25	19.71	20	2	57	—	1	—
413	29	36.06	23	3	44	2	4	4

Note. Reaction conditions: 1.7% w/w of 1.MCM-41/ratio PhCHO : heptanal = 1.5 : 1.

an experiment was done using 5 wt% of catalyst, since as it was shown before that the amount of catalyst does not have a direct influence on selectivity but only on conversion. The results obtained (Fig. 3) show that it is now possible to achieve conversions above 90% and in all cases the selectivity achieved at 373 K is larger than when working at higher temperatures. This is especially notorious at higher conversions, where the consecutive reactions of Jasminaldehyde have a strong impact on the final selectivity observed.

Finally, it is worth pointing out that an increase in the reaction temperature has little effect on the condensation product, while it strongly affects the decarboxylation and cyclation to indene.

Influence of the Benzaldehyde/Heptanal Ratio

It was said in the Introduction that when the condensation reaction is catalyzed by base catalysts, the concentration of heptanal in the reaction media should be kept very low in order to decrease the rate of the autocondensation reaction. This is achieved in two ways: by decreasing the rate of addition of heptanal and consequently involving very long reaction time, or by directly working with a relatively high ratio of benzaldehyde to heptanal, which requires larger reactors.

We have shown here that through our reaction system it is possible to work with almost equimolecular mixtures of benzaldehyde and heptanal while producing very little of the self-condensation product. Nevertheless, we have also studied the influence of the ratio of benzaldehyde to heptanal and the results obtained are given in Table 7.

Interestingly, when increasing the ratio of benzaldehyde to heptanal from 1.5 to 5 mol · mol^{-1}, the initial rate for the disappearance of heptanal (or even better for the corresponding acetal) decreases by threefold. This result could be explained on the basis of a competitive adsorption of benzaldehyde on the acid sites responsible for the transacetalization and ulterior condensation, decreasing therefore, the concentration of the available active sites for the desired reaction. This hypothesis is supported by the changes in selectivity observed when increasing the benzaldehyde/heptanal ratio. Indeed, while the selectivity for the self-condensation decreases, as was expected, the selectivity to Jasminaldehyde decreases at conversions below 80% (Fig. 4). This is mainly due to the higher concentration of product (**6**) (Fig. 5), possibly due to the competitive

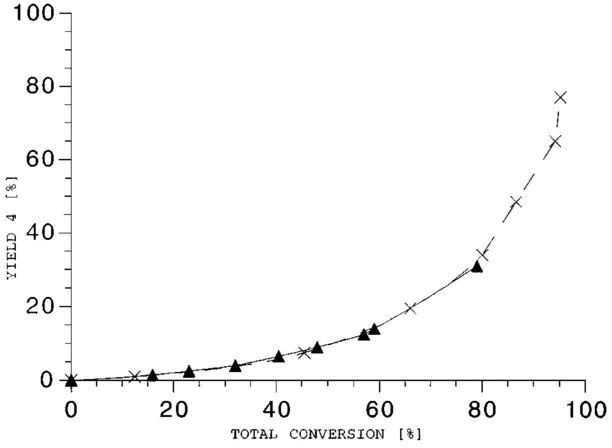


FIG. 3. Yield of Jasminaldehyde versus total conversion obtained in the reaction between benzaldehyde and heptanal dimethylacetal with a reactants molar ratio PhCHO : heptanal = 1.5 : 1, using different amounts of catalyst (1.MCM-41): 1.7 wt% (▲) and 5 wt% (×) at 373 K.

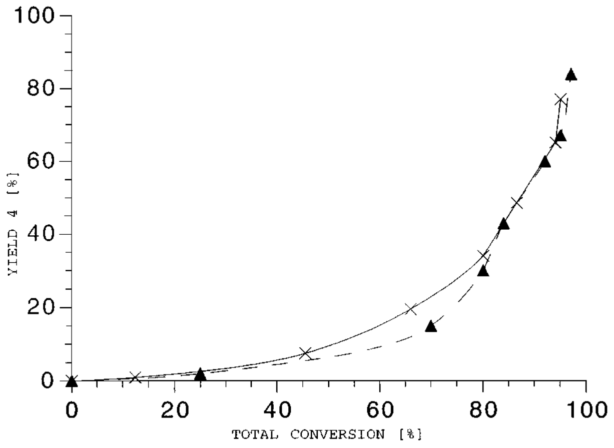


FIG. 4. Yield of Jasminaldehyde versus total conversion obtained in the reaction between benzaldehyde and heptanal dimethylacetal using different molar ratios of the reactans: PhCHO : heptanal = 1.5 : 1 (▲), and 5 : 1 (×), in the presence of 1.MCM-41 (5 wt%) at 373 K.

TABLE 7

Results of the Reaction of Benzaldehyde with Heptanal Dimethylacetal (2) at 80% Conversion Using Different Reactant Ratio

PhCHO : heptanal ratio	Selectivity (%) to **4**	$V_{\text{disapp.}} \times 10^{-4}$ (mol/min · g)	Yield (%) to **4**	Yield (%) to **5**	Yield (%) to **6**	Yield (%) to **7**	Yield (%) to **8**	Yield (%) to **9**	Selecti. **4** + **6**
1.5 : 1	42	9.9	35	4	36	—	1	4	83
5 : 1	37	3.4	30	—	48	—	—	2	97

Note. Reaction conditions: 5% w/w of 1.MCM-41/373 K.

adsorption of benzaldehyde on the acid sites, which decreases the rate of elimination of MeOH from product (**6**) to give Jasminaldehyde. Nevertheless, by increasing the ratio of benzaldehyde to heptanal, we decrease the autocondensation and increase the yield of products (**6**) + (**4**) which finally will end up giving product (**4**) as the only one, increasing the selectivity to Jasminaldehyde (**4**). Indeed this is observed from the results in Fig. 4, where the selectivity to Jasminaldehyde can be as high as 90% for conversions larger than 80%.

At this point it is reasonable to ask what will be the product distribution under acceptable reaction conditions if one tries to carry out the synthesis of Jasminaldehyde by direct condensation of benzaldehyde and heptanal, without forming in the same pot the acetal of the heptanal.

When this reaction was carried out on 1. MCM-41 using a molar ratio of benzaldehyde to heptanal of Fig. 5, the results given in Fig. 6 show that the process was much less selective with more than 20% of self-condensation being produced. If one uses Beta zeolite instead of MCM-41 (Fig. 7), the selectivity to the self-condensation product is much higher, being the resultant selectivity to Jasminaldehyde of order 25%.

The results obtained with the Beta zeolite are a clear consequence of the faster diffusion of heptanal with respect to benzaldehyde, and especially of the smaller size of the transition state for the self-condensation reaction with respect to that necessary to form the Jasminaldehyde, and the better fit of the former in the pores of the zeolite.

CONCLUSIONS

We have shown here that it is possible to carry out the synthesis of Jasminaldehyde, an industrially important product, with high selectivities to the desired product and using low ratios of benzaldehyde to heptanal by the combination of the appropriate process and catalyst. In this case it is possible by adjusting the acidity of the catalyst to carry out the reaction using a unique catalyst in a single pot reaction and forming the acetal of the heptanal in a first step. Then, by using the adequate catalyst one can balance the rates of the hydrolysis of the acetal and the condensation of the two aldehydes, avoiding to a very large extent the self-condensation. Meanwhile, if the pores of the catalyst are in a very narrow range of pore diameter and in the mesoporous region (MCM-41) the product can readly diffuse

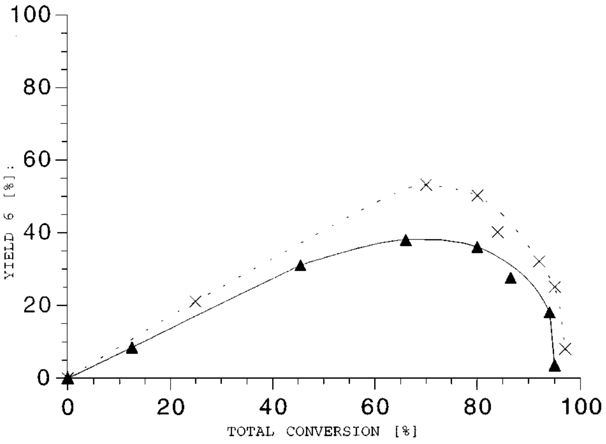


FIG. 5. Yield of product (**6**) versus total conversion obtained in the reaction between benzaldehyde and heptanal dimethylacetal using different molar ratios of the reactants: PhCHO : heptanal = 1.5 : 1 (▲), and 5 : 1 (×) in the presence of 1.MCM-41 (5 wt%) at 373 K.

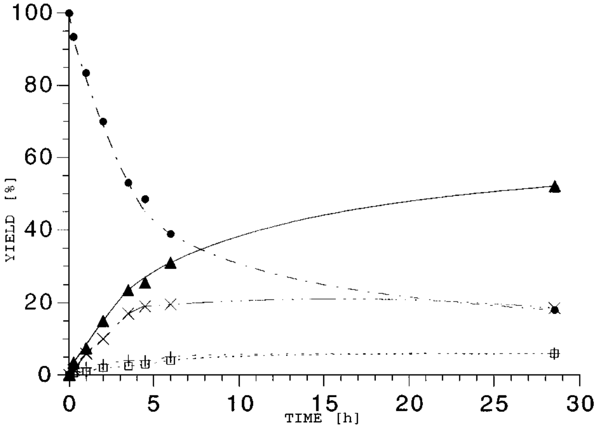


FIG. 6. Time-conversion plot for reaction of benzaldehyde (5 mol) and heptanal (1 mol) in the presence of 1.MCM-41 (1.7 wt%) at 398 K: 1 (●), **4** (▲), **5** (×), **7** (+), heptanoic acid (☐).

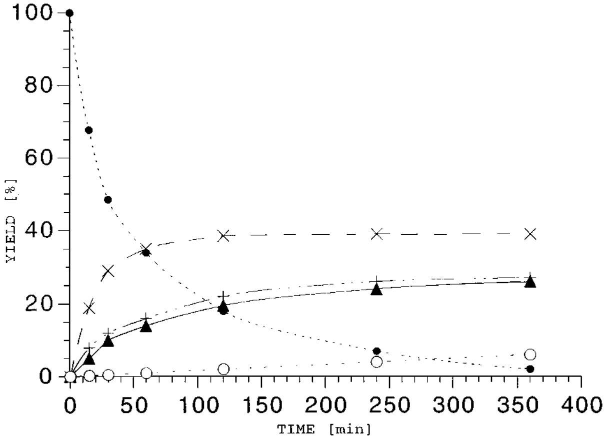


FIG. 7. Time-conversion plot for reaction of benzaldehyde (5 mol) and heptanal (1 mol) in the presence of Beta zeolite (10 wt%) at 398 K: **1** (●), **4** (▲), **5** (×), **7** (+), heptanoic acid (○).

out, avoiding consecutive reactions which can decrease the final yield of Jasminaldehyde.

ACKNOWLEDGMENTS

Financial support by the Direccción General de Investigacion Científica y Técnica of Spain (Projects MAT94-0359-C02-02 and MAT97-1016-C02-01) is gratefully acknowledged.

REFERENCES

1. Farbenindustrie, I. G., DRP, 284, 458/1927.
2. Payne, L. S., E.P. 0 392 579 A2 (1990).
3. Mastagli, P., and Durr, G., *Bull. Soc. Chim. France*, 268 (1955).
4. Sarkar, A., Dey, P. K., and Datta, K., *Indian J. Chem. B* **25**, 656 (1986).
5. Abenhaim, D., Ngoc Son, C. P., Loupy, A., and Ba Hiep, N., *Synthetic Comm.* **24**, 1199 (1994).
6. Mastagli, P., and Lagrange, G., *Compt. Rend.* **244**, 207 (1957).
7. Corma, A., Climent, M. J., Iborra, S., Navarro, M. C., and Primo, J., *J. Catal.* **161**, 783 (1996).
8. Corma, A., Fornés, V., Navarro, M. T., and Perez-Pariente, J., *J. Catal.* **148**, 569 (1994).
9. Bellusi, G., Perego, C., Carati, A., Peratello, S., Previde Massara, E., and Perego, G., *Stud. Surf. Sci. Catal.* **84**, 85 (1994).
10. Horvath, G., and Kawazoe, K., *J. Chem. Eng. Jpn* **16**, 470 (1983).
11. Bellusi, G., Cavani, F., Arrigoni, V., and Ghezzi, R., E.P. 463 673 (1992).