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Acylation of Toluene with Acetic Anhydride over Beta Zeolites: Influence of Reaction Conditions and Physicochemical Properties of the Catalyst

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Acylation of toluene with acetic anhydride was carried out over Beta-type zeolites in a stainless steel autoclave. At low temperature, i.e., 150°C, and an arene/anhydride molar ratio 10–20, high yields of 4-methylacetophenone were obtained with selectivity close to 100%. The reaction is limited by the poisoning of the active sites by adsorption of the product and pore blockage due to "coke"-type products. Acid site accessibility is of paramount importance for this reaction, and the use of a nanocrystalline Beta zeolite as catalyst minimizes catalyst decay. This, combined with an optimum framework composition, allows the preparation of active and selective acylation catalysts based on Beta zeolite. © 2000 Academic Press

Key Words: **acylation; toluene; acetic anhydride; Beta zeolite; methylacetophenone.**

INTRODUCTION

Friedel–Crafts acylations are widely used in the manufacture of aryl ketones, which are of interest in the synthesis of a large number of fine chemicals such as drugs, fragrances, dyes, and pesticides (1, 2). This process has been carried out in industry by working under batch conditions using acyl halides as acylating agents and homogeneous Lewis acids such as anhydrous metal halides as catalysts (3). However, Lewis acids must be used in higher than stoichiometric amounts, and the catalyst must be destroyed at the end of the reaction with a significant production of undesirable wastes. Thus, it is highly desirable to develop new processes that can reduce the environmental and economic problems associated with the classical Friedel–Crafts acylation catalysts (4, 5). These new processes will require replacement of the homogeneous catalysts with friendly solid acids and use of less hazardous acylating agents, i.e., carboxylic acids and their anhydrides, instead of acyl halides.

Toward this purpose, different solid acids have been tested as catalysts for the acylation of low-molecular-weight aromatics. Materials such as pillared clays and rare-earth-exchanged pillared clays (6), Keggin-type heteropolyacids (7), Nafion-H and Nafion/silica composites (8–10), sulfated zirconia (6, 11), and graphite (12) have been proven to catalyze this reaction. Acid molecular sieves have also been widely used as acylation catalysts, and more specifically medium- and large-pore zeolites have been presented as the ultimate catalysts for the future industrial production of aromatic ketones (13). Basically, H-ZSM5 has been used in acylation of less substituted aromatic molecules such as benzene, phenol, and toluene (14–16), while zeolites with larger pores such as H-Beta and HY have been used extensively in acylation of arylethers such as anisole and polysubstituted aromatics such as xylenes and mesitylenes (13, 14, 17–21). A recent important development in this field has been reported by RHODIA, which has established the first industrial application of zeolites for the acylation of anisole and veratrole (22, 23). Bulkier molecules such as 2-methoxynaphthalene have also been efficiently acylated using large-pore zeolites as catalysts (24–26). However, it must be pointed out that while the acylation of phenols and aromatic ethers with alkyl/aryl chlorides is carried out with very good yields and selectivities on zeolites, the results obtained with low activated aromatic rings like toluene and benzene are poorer, especially when less reactive acylating agents, such as carboxylic acids and their anhydrides, are used. On the other hand, the fast catalyst decay, produced by "coke" deposition within the micropores (21, 27, 28), strongly limits the use of these materials in commercial processes. Nevertheless, we believe that it should be possible to improve the possibilities of using zeolites as acylation catalysts through a better catalyst design. We have tried in this work to optimize the physicochemical properties of a Beta zeolite catalyst by optimizing parameters such as framework Si/Al molar ratio, hydrophilic–hydrophobic properties, and crystallite size. Moreover, the effects of reaction conditions, i.e., temperature, catalyst concentration, and arene/anhydride molar ratio, on the catalytic performance have also been studied.

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TABLE 1

Physicochemical Characteristics of H-Beta Zeolites

					Acidity (μmol py)[c]					
					Brønsted			Lewis		
Sample	Si/Al[a]	Area BET ($m^2\ g^{-1}$)	Crystallinity (%)	Crystal size (μm)[b]	250°C	350°C	400°C	250°C	350°C	400°C
CP811	12.5	570	71	0.15	5	27	16	48	40	40
A13	13	549	72	0.2	33	15	7	32	26	25
A16	16	532	73	∼0.05	63	49	28	22	19	14
A27	27	548	77	0.2	27	13	8	31	25	19
A38	38	581	66	0.2	27	11	9	20	18	18
B15	15	519	85	0.4–0.6	45	22	14	38	38	38
B50	50	452	98	0.4–0.6	19	9	4	7	4	4
B93	93	463	100	0.3–0.5	11	10	2	5	4	2

[a] As-made molar ratio.
[b] Average size determined from the SEM images.
[c] Determined from the infrared spectra of adsorbed pyridine after evacuation at 250, 350, and 400°C.

EXPERIMENTAL

Catalysts

Several H-Beta zeolites have been tested as catalysts for the acylation of toluene. A commercial Beta was provided by P.Q. Industries (sample CP811), and the rest of the Beta samples were prepared in our laboratory. We have named them according to the preparation procedure (series A, B) and the as-made Si/Al framework molar ratio (A13, A16, A27, . . .). Samples of series A were synthesized hydrothermally at 140°C in basic medium in PTFE-lined stainless steel autoclaves under rotation, using amorphous silica (Aerosil 200, Degussa) as the silica source. Samples A13, A27, and A38 were prepared in the presence of alkali cations according to a reported procedure (29). Sample A16 is a nanocrystalline Beta zeolite synthesized in an alkali-free basic medium (30). Samples B15, B50, and B93 were synthesized in a similar way but using tetraethylorthosilicate (TEOS, Aldrich) as the silica source in a fluoride medium at nearly neutral pH, according to a previously described method (31).

The Al content in the samples was determined by atomic absorption spectrophotometry (Varian spectrAA-10 Plus). Crystallinity was measured by powder X-ray diffraction, using a Phillips PW1710 diffractometer with Cu$K\alpha$ radiation, and compared with a highly crystalline standard sample. The acidity of the samples was established by the standard pyridine adsorption–desorption method (32). The surface area of the catalysts was calculated by the BET/BJH method with N_2 adsorption/desorption performed at 77 K in a Micromeritics ASAP 2000 instrument. The crystal size was determined from the SEM images obtained in a JEOL 6300 scanning electron microscope.

Solid-state MAS NMR spectra were acquired in a Varian VXR-400S WB spectrometer, using a 7-mm RT CP/MAS Varian probe. ^{29}Si spectra were recorded at 79.5 MHz using a 55.4° pulse length of 4.0 μm and a recycle delay of 20 s, with the sample spinning at 5 kHz. ^{27}Al MAS NMR spectra were recorded at 104.214 MHz with a 10° pulse length of 0.5 μs and a recycle delay of 0.5 s, at spinning rates of 7 kHz. The ^{27}Al chemical shifts are reported relative to $Al(H_2O)_6^{3+}$. The most relevant physicochemical properties of these zeolites are summarized in Table 1.

Reaction Procedure

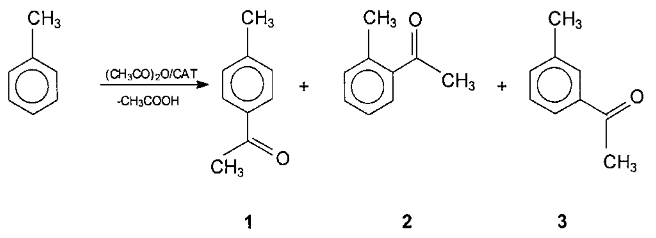
All experiments were carried out in a stainless steel stirred 150-ml autoclave (Autoclave Engineerings) in the 140–250°C interval (typically, 150°C). A 1.00-g portion of catalyst was activated *in situ* before the reaction by heating for 2 h at 150°C in N_2 flow (100 ml min^{-1}). A mixture of 400 mmol of water-free toluene (Aldrich) and 20 mmol of acetic anhydride (Riedel-de Häen) was then added. The amounts of reactants were also varied when necessary to provide different catalyst concentrations and arene/anhydride molar ratios. The time on stream (TOS) was 4 h, and samples were taken at different TOSs and analyzed. By recycling the catalyst, it was observed that some deactivation occurs during the reaction. Thus, in all experiments, a larger number of samples were taken during the first hour of reaction. Products were analyzed by GC in a Fisons 8000 Series instrument equipped with a 25-m capillary cross-linked 5% phenylmethylsilicone column and an FID detector, using nitrobenzene as an internal standard. The products were also identified by mass spectrometry in a Varian Saturn II GC–MS model working with a Varian Star 3400 gas chromatograph.

When the mass balances were performed at shorter times on stream, an excess of acetic acid was found. This was formed by hydrolysis of the anhydride, due to the small amounts of water retained in the catalysts even after the activation step (19). Such hydrolysis was taken into account in calculating the conversion of acetic anhydride, the yield of methylacetophenone, and the mass balance of anhydride, according to the equations proposed by Rohan *et al.* (27). Furthermore, "coke"-like products were adsorbed on the catalyst during the reaction, and the catalyst became dark brown. Catalysts were extracted in a micro-Soxhlet with $CHCl_3$ over 12 h. The solvent was evaporated and the remaining organic material was weighted, diluted with toluene, and analyzed by GC–MS. Among the adsorbed products we found acetic acid, methylacetophenone, and some minor compounds, basically diacyltoluene, coming from the consecutive acylation of monoacylated products. Although their percentages were usually very small, they were considered for the calculation of the total mass balance. Carbon determination in the used catalyst allowed us to quantify the nonextractable organic deposit by thermogravimetric and C-elemental analysis performed, respectively, in a NEST instrument using calcined Kaolin as reference material and in a Fisons EA 1108 CHSN-O apparatus. Ultraviolet–visible spectroscopy (Varian Cary 5G UV–vis-NIR spectrophotometer) was used to study the nature of the functional groups present in the coke. Taking into account all these fractions it was possible to obtain mass balances $\geq$95%.

RESULTS AND DISCUSSION

Friedel–Crafts acylation of toluene with acetic anhydride (AA) is a very selective process for the production of 4-methylacetophenone **1** (see Scheme 1). The reaction involves the production of one molecule of acetic acid (HAc) for every molecule of anhydride consumed. Small amounts of 2- and 3-methylacetophenone (**2** and **3**, respectively) were also found in the product mixture, especially at high conversions, due to the acylation of the less favored positions in the aromatic ring. Since the amount of these compounds was never above 2% of the total yield in acylated products, we have considered in those cases the total yield of methylacetophenones (MAP) calculated as the sum of yields of the three isomers.

As the first step we studied the influence of the reaction conditions on the yield of MAP, using a commercial Beta zeolite (CP811). Figure 1 shows the variation of the yield and selectivity to MAP with the reaction temperature at a time on stream (TOS) of 240 min. It can be seen that the yield of MAP shows a maximum at 150°C and decreases when the reaction temperature is further increased. We have found 100% selectivity to MAP when the reaction is carried out at low temperature, i.e., 150°C, but it decreases up to 80% at 250°C.



SCHEME 1

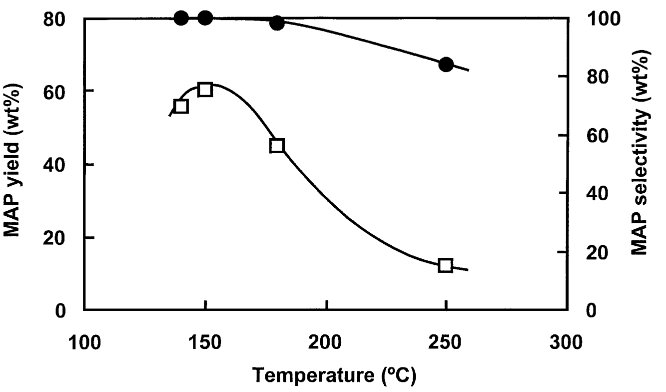


FIG. 1. Variation of yield (□) and selectivity (●) to MAP with reaction temperature obtained during acylation of toluene with acetic anhydride (AA) over Beta zeolite CP811. Experimental conditions: catalyst/AA weight ratio = 1; toluene/AA molar ratio = 20; TOS = 240 min.

The influence of TOS on the MAP yield is shown in Fig. 2. It can be seen that the yield of MAP first increases with increasing TOS but remains practically constant after 120 min. In addition, an increase in the yield of MAP is also observed when the catalyst/AA weight ratio is increased from 0.5 to 1. It is then apparent that an important deactivation of the catalyst occurs during the reaction.

With regard to the toluene/anhydride molar ratio (T/AA), Fig. 3 shows that the yield of MAP increases when the T/AA ratio is increased to ∼20, and then remains practically unchanged. This is probably due to the inhibiting effect of MAP, which can be strongly adsorbed on the catalyst (27).

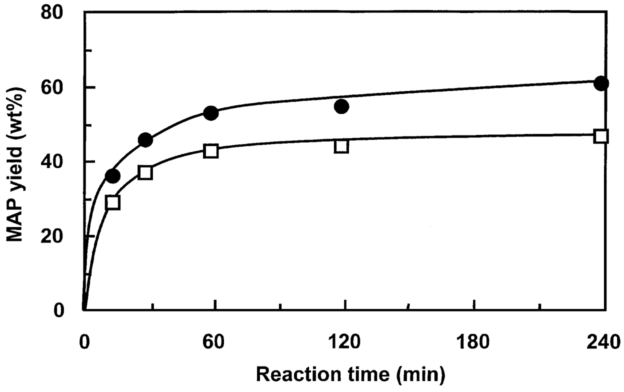


FIG. 2. Variation of yield of MAP with TOS obtained during acylation of toluene with acetic anhydride (AA) over Beta zeolite CP811 at a catalyst/AA weight ratio of 1 (●) or 0.5 (□). Experimental conditions: temperature = 150°C; toluene/AA molar ratio = 20.

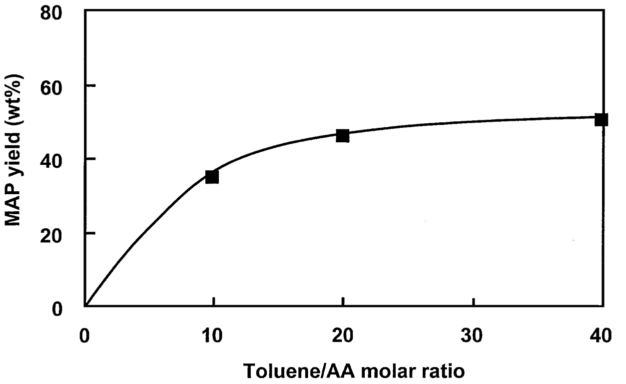
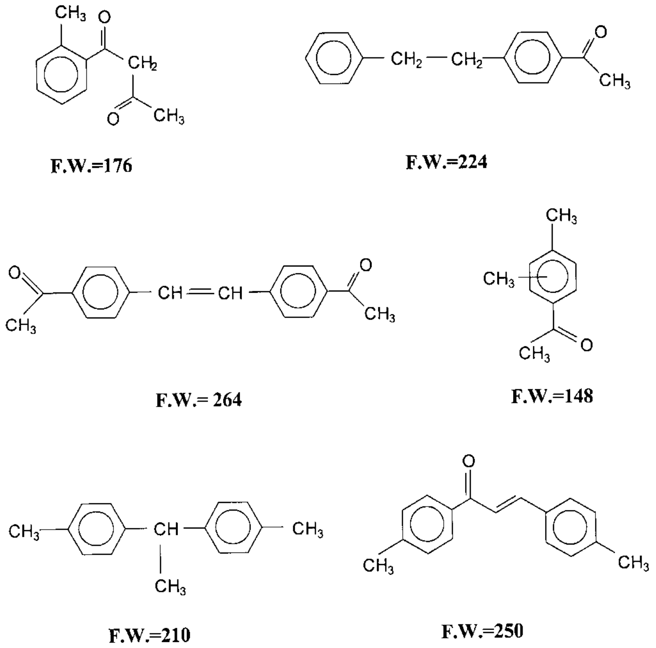


FIG. 3. Variation of yield of MAP with toluene/AA molar ratio obtained during acylation of toluene with acetic anhydride (AA) over Beta zeolite CP811. Experimental conditions: temperature = 150°C; catalyst/AA weight ratio = 0.5; TOS = 240 min.

This inhibiting effect would be less significant for mixtures richer in toluene, because the large excess of toluene helps to desorb the ketone formed. T/AA ratios larger than 20 do not improve significantly the yield in MAP and consequently we have used throughout this work a T/AA ratio of 20.

The acylated product is adsorbed on the acid sites due to its higher polarity and, consequently, the adsorption of the toluene on the surface and in the pores of the catalyst is restricted and the reaction rate decreases. Moreover, the adsorbed MAP can further react, giving larger by-products, which remain adsorbed and further increase the diffusion problems of reactants within the channels of the catalyst, producing a decrease of the catalytic activity. The formation of those bulkier products increases when the reaction temperature is raised from 150 to 250°C, since higher reaction temperature favors consecutive acylation, disproportionation, alkylation, and decarboxylation. Some of the by-products formed during acylation of toluene with Beta CP811 are indicated in Scheme 2. Those were barely seen in the liquid phase, but they were present in the zeolite pores and were analyzed and identified by GC–MS when the zeolite was subjected to Soxhlet extraction using chloroform. The diffuse reflectance spectrum of the catalyst used showed the typical band of acetophenones and polyaromatics, which were absent in the fresh sample (Fig. 4). Thermogravimetric and elemental analyses revealed that the products retained in the zeolite pores accounted for 5–8 wt%.

We then confirmed that methylacetophenone is strongly adsorbed in the zeolite pores and can undergo a number of consecutive reactions that produce bulkier molecules which cannot diffuse out of the zeolite. Those products not only block the acid sites but also produce pore blocking with the corresponding loss of catalytic activity. Soxhlet extraction with chloroform cannot extract all the by-products within the pores, and calcination in the presence of air becomes necessary to remove the organic residues. It is apparent that the Beta zeolite catalyst needs to be improved not only in activity but also in catalyst decay.



SCHEME 2

Influence of Zeolite Properties

From what we have observed up to now, we can conclude that both the total number of acid sites and the adsorption properties of the zeolite should have direct effects on the activity and decay of the catalyst. If this is so, one zeolite variable that influences both the total number of Brønsted acid sites and the adsorption properties of the catalyst is the framework Si/Al ratio. Indeed, increasing the framework Si/Al ratio decreases the total number of Brønsted

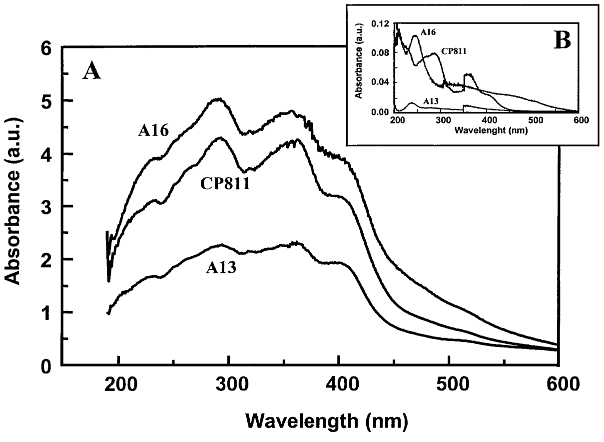


FIG. 4. UV–vis spectra of CP811, A13, and A16 samples before (B) and after (A) their use in the acylation of toluene with acetic anhydride. Experimental conditions: temperature = 150°C; catalyst/AA weight ratio = 0.5; toluene/AA molar ratio = 20; TOS = 240 min.

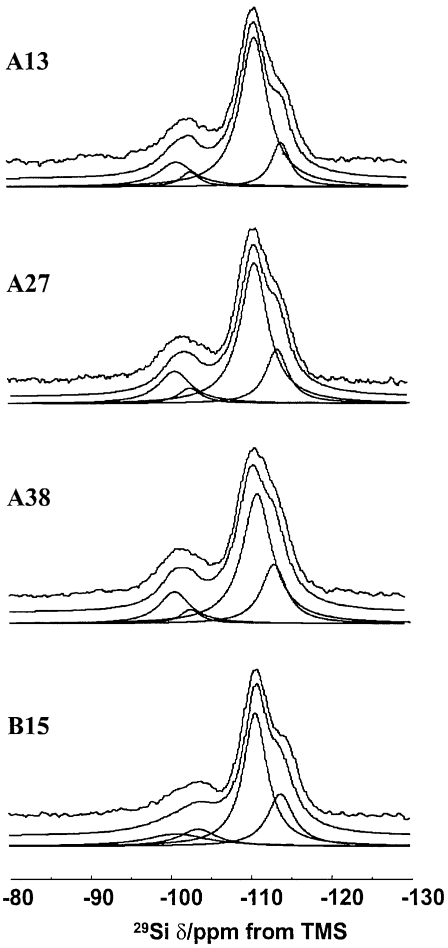


FIG. 5. ^{29}Si MAS NMR spectra of calcined samples A13, A27, A38, and B15. The band at −101 ppm is related to silanol groups present on zeolite surface.

acid sites and increases the hydrophobicity of the material. To explore the influence of the Si/Al ratio, three Beta samples with Si/Al ratios of 13 (A13), 27 (A27), and 38 (A38) were synthesized by a conventional method (29) that produces samples with a large number of defects. These are detected by ^{29}Si MAS NMR (Fig. 5) from the band at −101 ppm, which corresponds to Q^3Si (3Si, 1OH) groups. The presence of those groups strongly decreases the potential hydrophobicity of the zeolite and, consequently, we should not expect large variations in this property from sample A13 to sample A38. With respect to changes in acidity with the framework Si/Al ratio, we can see that the three zeolite samples suffer dealumination during the calcination process necessary to remove the structure-directing agent. This dealumination increases the framework Si/Al ratio while producing a certain amount of extraframework Al shown at ∼0 ppm in the ^{27}Al MAS NMR spectra (Fig. 6). The dealumination is also shown by the 1450 cm^{-1} IR band corresponding to pyridine coordinated to Lewis acid sites (Table 1), which corresponds to extraframework Al (33).

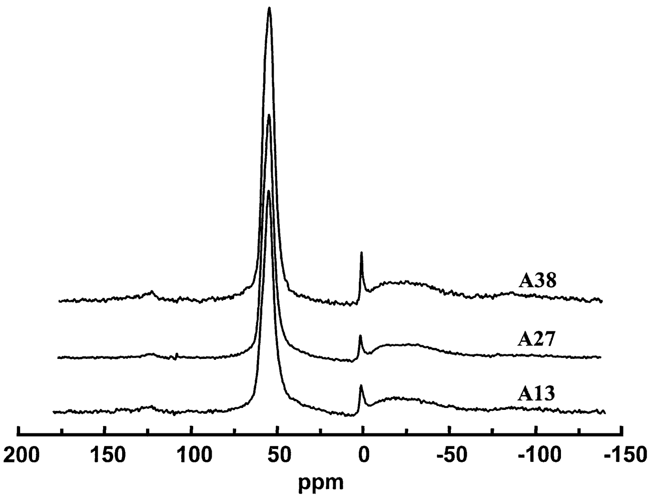


FIG. 6. ^{27}Al MAS NMR spectra of calcined samples A13, A27, and A38. The peak at ∼0 ppm is associated with octahedral nonframework Al present in the sample.

The higher the framework Al content of the as-synthesized zeolite sample, the higher the dealumination. Therefore, the differences in the final number of hydroxyl bridging groups, and consequently in the Brønsted acidity of the three samples studied, are smaller than expected taking into account the original framework Si/Al ratio (see pyridine results in Table 1). In any case, the acidity results are in good agreement with the catalytic activity of the three Beta samples, which, even though close, follows the order A13 > A27 ∼ A38 (see Table 2).

At this point, we prepared a more hydrophobic Beta zeolite by carrying out the synthesis in fluoride media (sample B15) (31). ^{29}Si MAS NMR results (Fig. 5) show that the number of defects is indeed lower in sample B15 than in the corresponding A13 sample. Moreover, both samples

TABLE 2

Friedel–Crafts Acylation of Toluene with Acetic Anhydride on H-Beta Zeolites[a]

Catalyst	AA conversion (wt%)[b]	MAP yield (wt%)	MAP selectivity (wt%)
CP811	58	46	100
A13	58	54	100
A16	83	80	100
A27	56	49	100
A38	55	50	100
B15	56	54	100
B50	38	35	92
B93	28	28	89

[a] Experimental conditions: $T = 150°$C; catalyst/AA weigth ratio = 0.5, 1 : 2; toluene/AA molar ratio = 20; TOS = 240 min.

[b] The difference between the conversion of acetic anhydride (AA) and the yield of MAP indicates the extension of the hydrolysis of the acetic anhydride.

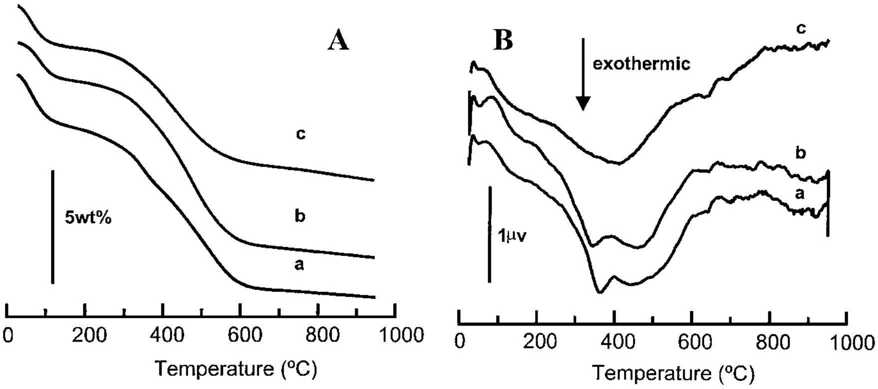


FIG. 7. Thermogravimetric (A) and thermodifferential (B) patterns of Beta zeolites obtained on samples used in catalytic tests: (a) CP811, (b) A13, and (c) A16. Conversion of AA and the yield of MAP obtained with these samples are comparatively shown in Table 3.

have practically the same Si/Al ratio as the as-made zeolite, but B15 should be more hydrophobic. In principle, a more hydrophobic zeolite should allow toluene to diffuse and adsorb better, thereby helping in the desorption of acetophenone. It is remarkable that, although the total number of Brønsted sites is higher in B15 than in A13 owing to the higher stability upon calcination of the former, the catalytic activity of B15 is similar to that of A13. "Defect-free" Beta samples with Si/Al ratios of 50 and 93 were also synthesized (Table 1), and these should have stability similar to that of B15 but should be more hydrophobic. We can see now (Table 2) that the catalytic activity and selectivity in the B series decrease when the framework Si/Al ratio is increased, regardless of the increase in hydrophobicity when the Si/Al ratio is increased. Therefore, we must conclude that neither the higher hydrophobicity nor the higher acidity of sample B15 produces an important increase in the catalytic activity for the acylation of toluene with acetic anhydride. This unexpected result can be explained by taking into account that even though sample B15 has a higher total number of acid sites than A13, it also has a larger crystal size (Table 1) and this may have a negative influence on the diffusion of reactants and products within the catalyst pores. Thus, since diffusion is an important issue during acylation reactions, at least in the liquid phase, we could expect (25) the zeolite crystallite size to have an important impact on the conversion and catalyst decay during acylation of toluene with Beta zeolites.

If we take this into account, the logical next step was to synthesize a Beta zeolite with smaller crystallites and high stability upon calcination. This was achieved through a special synthesis procedure (30) that produced one sample (A16) with very small crystallites and a high density of acid sites (Table 1). The small crystallites should allow faster diffusion of the products out of the catalyst and this, combined with the high acidity, should provide an important increase in the activity and a decrease in the rate of catalyst deactivation. The results presented in Table 2 clearly show that the activity of sample A16 is much higher than that of any of the other samples studied. Moreover, from what has been discussed before, it can be expected that the crystal size of the catalyst could also have an impact on the catalyst decay. In this way, the catalyst deactivation has been studied by comparing the amount of residues left in samples CP811, A13, and A16 after reaction.

The amount of coke deposited on the catalyst has been determined by thermogravimetric (TG) and differential thermal analyses (DTA), and the results are shown in Figs. 7a and 7b, respectively. From a comparative purpose, Table 3 shows the conversion of AA and the yield of MAP obtained on the studied zeolites. Similar coke deposits (7 wt%) were obtained by TG with CP811 and A13 samples, while the amount of coke in A16 is lower (5 wt%) at similar toluene conversions. On the other hand, when the DTA diagrams obtained in the presence of air are compared (Fig. 7b), both CP811 and A13 zeolites present two

TABLE 3

Coke Formation in H-Beta Zeolites during the Friedel–Crafts Acylation of Toluene with Acetic Anhydride at Different Levels of Conversion[a]

Catalyst	AA conversion (wt%)[b]	MAP yield (wt%)	Coke deposit (wt%)[c]
CP811	58	46	7.0[d]
	38	31	6.6
A13	58	54	7.0[d]
A16	83	80	6.9
	48	42	4.9[d]

[a] Experimental conditions: $T = 150^\circ$C; catalyst/AA weigth ratio = 0.5, 1 : 2; toluene/AA molar ratio = 20.

[b] The difference between the conversion of acetic anhydride (AA) and the yield of MAP indicates the extension of the hydrolysis of the acetic anhydride.

[c] The coke formed during the reaction has been determined from the TG experiments.

[d] Data corresponding to samples of Fig. 7.

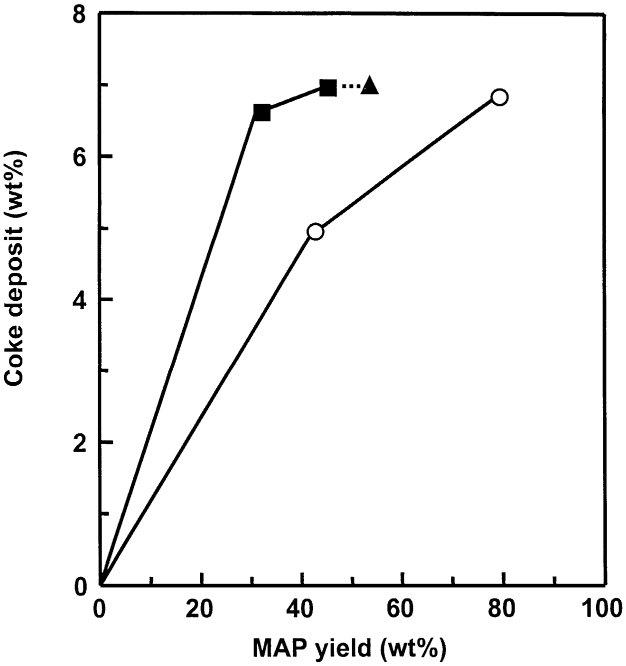


FIG. 8. Variation of coke deposit in used catalysts (determined from the TG patterns) with the corresponding MAP yield obtained during the acylation of toluene on Beta zeolites: CP811 (■), A13 (▲), and A16 (○). Experimental conditions are as in Fig. 3 except the TOS, which was varied in order to achieve different MAP yields.

exothermic bands at 360–370 and 460–480°C, while sample A16 presents a single broad band at 400°C with low intensity. This could indicate the presence of some coke that is more difficult to burn in the case of samples CP811 and A13. The greater difficulties in burning coke in these samples can be due to the more condensed nature of this coke (27) or to a diffusion-controlled regeneration process. If this is so, in the case of the nanocrystalline zeolite one should expect fewer consecutive reactions to occur, and consequently less-condensed coke-type products, and lower diffusional limitations for coke combustion.

Figure 8 shows the yield of coke at different yields of MAP with different Beta samples. It can be seen that for the same MAP yield, the nanocrystalline zeolite (sample A16) gives the lowest amount of coke. These results confirm the adequacy of thermally stable nanocrystalline Beta zeolites with a high density of acid sites (lower Si/Al ratios) as solid acylation catalysts.

CONCLUSIONS

Beta zeolite is a good catalyst with which to perform the acylation of toluene with acetic anhydride at low temperature (150°C). When an arene/anhydride molar ratio between 10 and 20 is used, reasonable conversions with very high selectivities to MAP are obtained. However, the poisoning of the acid sites by adsorption of the acetophenone formed and the production of coke deposits limits the extent of the reaction.

Catalytic activity is strongly influenced by the Brønsted acidity of the zeolite. In this way, low framework Si/Al ratios lead to better yields in MAP.

Considering the intrapore diffusion problems caused by the adsorption of different products, better results could be obtained with nanocrystalline stable Beta zeolite with lower nominal framework Si/Al ratios. This type of catalyst minimizes catalyst decay by coke deposition, with the corresponding improvements in activity and time of catalyst use.

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