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Improved performance of nano-size H-BEA zeolite catalysts for the Friedel–Crafts acetylation of anisole by acetic anhydride

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Nano-size zeolite H-BEA (n-H-BEA) prepared by "confined space synthesis" (CSS) within the pores of a carbon black matrix shows improved activity without loss in para-selectivity for the Friedel–Crafts acetylation of anisole by acetic anhydride. The turnover frequency (TOF) of n-H-BEA exceeds that of a conventional H-BEA catalyst of similar aluminum and thus acid site content by a factor of about three at intermediate conversion. The latter observation is attributed to enhanced access and better utilization of the whole zeolite intracrystalline volume by the reactants as well as to the easier desorption of the acetylated product, *p*-methoxyacetophenone.

KEY WORDS: zeolite; H-BEA; particle size; acid catalysis; Friedel–Crafts; acetylation; anisole; nanotechnology.

1. Introduction

The most important routes for the synthesis of aromatic ketones that are intermediates in manufacturing fine and specialty chemicals as well as pharmaceuticals are the Friedel–Crafts aromatic acylation and the related Fries rearrangement reaction [1,2]. Present industrial practice requires a stoichiometric amount of soluble Lewis acids (e.g. $AlCl_3$) or mineral acids (e.g. HF) as catalysts, which results in substantial amount of waste and corrosion problems [3]. In view of the increasingly strict environmental legislation, the application of heterogeneous catalysis has become attractive. In the last couple of decades, considerable effort has been put into developing heterogeneously catalyzed Friedel–Crafts chemistry using solid acid catalysts such as zeolites, clays modified by transition metal ions, Nafion-H, etc. [3] with zeolites being the most studied catalysts for both the Friedel–Crafts acylation [3–6] and the Fries rearrangement reactions [3,7,8].

Recent reports have demonstrated that the performance of zeolite catalysts for liquid phase acid-catalyzed reactions, among which Friedel–Crafts acylation, was not only determined by their pore size leading to well-documented molecular shape selectivity effects and by their strong and tuneable acidity (amount and strength of their Brønsted acidic sites) but also by confinement effects governing the competitive adsorption of reactants and products in the zeolite that behaves as a solid solvent [5,6].

Although classical tests indicated that mass transfer limitations (intra- and inter-particle) appeared not to be critical, at low conversion, for the acetylation of anisole by acetic anhydride (AA) using zeolite H-BEA as catalyst [9], it was not excluded that competitive adsorption effects, in particular for the bulkier acetylated product, could result in diffusional limitations at intermediate and high conversions.

Andy *et al.* [10] and Botella *et al.* [11] pointed out that zeolite particle size could affect the performance of zeolites used as catalysts for Friedel–Crafts acylation. Moreau *et al.* [12] showed that different secondary meso-porosities in the pore diameter range 2–15 nm, resulting from different modes of aggregation of individual zeolite crystallites, affected substantially the activity and selectivity of H-BEA catalysts for the acetylation of 2-methoxynaphthalene.

Here, we report a quantitative comparison of the behavior of conventional H-BEA and nano-size H-BEA (n-H-BEA) catalysts [13] for the acetylation of anisole by AA, aiming at identifying possible particle size effects over a broad range of conversions using catalysts differing by their Si/Al ratio.

2. Experimental

2.1. Catalysts

Two parent H-BEA catalysts were selected for this study. One was a conventional zeolite H-BEA (H-BEA-18) from Zeolyst (the last two digits correspond to a Si/Al atomic ratio of 18). The other was a nano-size H-BEA zeolite (n-H-BEA-32, ref. KJO 060, Si/Al

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atomic ratio of 32) from Haldor Topsøe A/S, prepared by the "confined space synthesis" (CSS) method whereby the zeolite is synthesized in the pores of a carbon black matrix that is eventually removed by oxidative calcination [13].

As both parent catalysts differ by their Si/Al ratio, two other partially dealuminated H-BEA catalysts were prepared by stirring at room temperature 4 g of H-BEA-18 with 400 mL of HNO_3 solutions of various concentrations for different times. The suspension was then filtered and the collected solid calcined at 823 K overnight. The following materials were obtained: H-BEA-60 ($Si/Al = 60$) and H-BEA-77.5 ($Si/Al = 77.5$). The protonated forms of the three H-BEA and n-H-BEA-32 catalysts were calcined in air at 823 K for 2 h and allowed to cool to ambient temperature prior to reaction, all necessary precautions being taken to avoid their contact with moist air before the transfer of the catalysts into the reaction vessel as described previously [5,6].

The characteristics of the four catalysts mentioned above are summarized in table 1. Characteristics and performance of other H-BEA catalysts used previously for the acetylation of toluene and obtained by progressive dealumination of a H-BEA zeolite ($Si/Al = 12.5$) obtained from Zeolyst have been reported elsewhere [6].

2.2. Characterization of the catalysts

A very good agreement was observed between the Si/Al ratios for the various catalysts as determined by ICP-AES (total chemical analysis), ^{27}Al MAS NMR (framework Al in tetrahedral coordination), and NH_3-temperature programmed desorption (TPD, a measure of the Brønsted acid site concentration), from which the framework Al molar fractions reported in table 1 were obtained (within 5% experimental error). X-ray diffraction confirmed that the structural integrity of the zeolite framework was retained after dealumination. Transmission electron microscopy showed that both H-BEA and n-H-BEA catalysts were agglomerates of crystals, with crystal sizes in the range 0.1–0.4 ìm and 0.01–0.02 μm, respectively. The sizes of the agglomerates were ca. 2 μm for H-BEA and 5 μm for n-H-BEA-32. Figure 1 shows the morphology of n-H-BEA-32 used in the present investigation.

Table 1
Catalysts characteristics

Catalyst	Al molar fraction in the frame work	Origin
H-BEA-18	0.0526	Parent material (Zeolyst)
H-BEA-60	0.0164	Dealuminated H-BEA-18 (HNO_3, 1 M, 2 h, RT)
H-BEA-77.5	0.0127	Dealuminated H-BEA-18 (HNO_3, 0.25 M, 3 h, RT)
n-H-BEA-32	0.0303	CSS method(KJO 060)

2.3. Catalytic tests

The catalysts were re-calcined in air at 823 K for 2 h and allowed to cool in a desiccator prior to reaction. The reactants, AA (Aldrich, purity higher than 99%): 0.0496 mol (5.05 g) and anisole (AN, Avocado Research Chemicals, purified by distillation over CaH_2): 0.0992 mol (10.71 g), achieving an AN/AA molar ratio of two, were introduced into the batch reactor (glass flask) fitted with a condenser and a septum, allowing samples to be removed and analyzed as a function of time. The system was flushed with nitrogen and preheated to 353 K, then further heated to 363 K. The catalyst (10 wt% relative to AA, i.e., 0.505 g) was weighted and introduced into the batch reactor. The acetylation of anisole on the H-BEA and n-H-BEA catalysts was then conducted for 5 h at 363 K. Samples were taken at regular time intervals and analyzed by gas chromatography as described previously [5,6].

Experimental details for the acetylation of toluene by BEA-x catalysts referred to herein are described in ref. [6]. Turnover frequency (TOF) values for the acetylation of toluene, used in the discussion section of this paper, are for a reaction system consisting of 0.2591 mol (23.84 g) of toluene (TOL) and 0.0267 mol (2.72 g) of AA corresponding to a TOL/AA molar ratio of 9.7, and 0.495 g (18 wt% relative to AA) of BEA, BEA1 or BEA5 catalyst.

2.4. Analysis and data interpretation

All analytical procedures and data interpretation procedures were reported previously [5,6]. Samples were removed periodically to follow conversion as a function of time and analyses made with reference to an internal standard. *p*-Methoxyacetophenone (*p*-MOAP) was the main reaction product with less than 2% of the ortho-isomer being observed. Conversions are expressed with

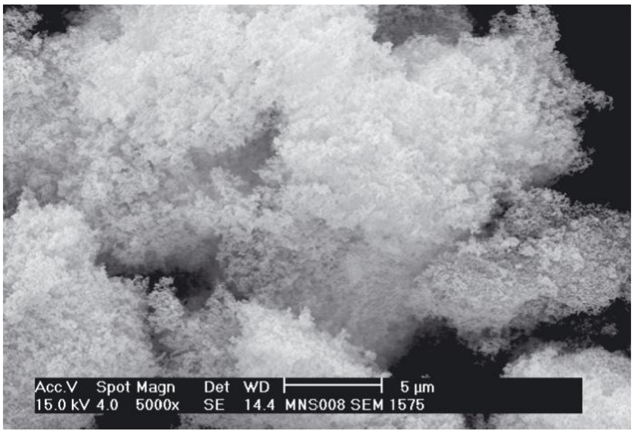

Figure 1. TEM picture of n-H-BEA-32.

respect to the reactant in default, i.e., AA. Reactions rates are calculated as the number of moles of *p*-MOAP produced per minute and per gram of catalyst.

3. Results and discussion

3.1. Comparison of the catalysts performance: *p-MOAP* yield versus. time

Figure 2 compares the variation with time of the yield (in mole units) in *p*-MOAP for the three H-BEA and the n-H-BEA catalysts used in the present investigation. 100% yield in *p*-MOAP with respect to the reactant in deficit (AA) corresponds to the production of 0.0496 mole of *p*-MOAP. Conversions achieved after 300 min for the four catalysts are in the range 50–60% with respect to AA.

As reported and discussed previously, the rate of production of *p*-MOAP is initially very high and rapidly decreases after about 1 h on stream when conversion of the limiting reactant, AA, has reached about 50%. This time-on-stream dependence of the *p*-MOAP yield was explained by competitive adsorption effects, the equilibrium adsorption constant for the *p*-MOAP product being higher than those of anisole or AA (relative to $K_{AA} = 1.0$, $K_{p\text{-MOAP}} = 11.8$ and $K_{AN} = 1.7$), resulting in product inhibition (i.e., retention of the more strongly adsorbed component, *p*-MOAP, in the intracrystalline volume of the zeolite preventing the access of the reactants) [5,6].

It appears, at first sight, that the order of catalyst activities, as measured by the yield in *p*-MOAP, is as expected on the basis of the catalysts Si/Al ratios, i.e., the concentration of their acid sites. However, because the four zeolite catalysts used in the present investigation differ by their Si/Al ratio, their intrinsic performances are best compared in terms of the TOF that they can achieve, initially and at intermediate and high conversions, respectively.

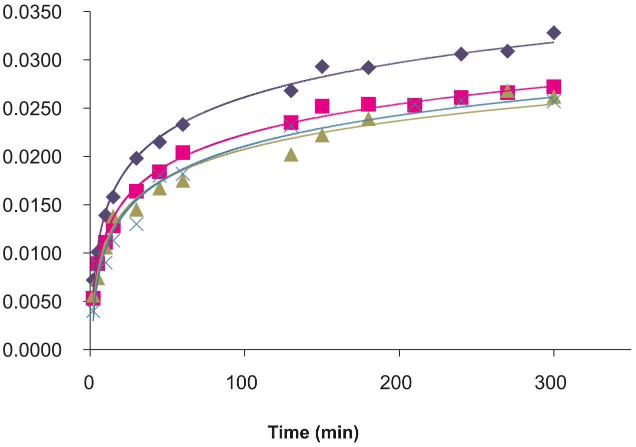

Figure 2. *p*-MOAP yield (moles) versus time using H-BEA and n-H-BEA zeolites with different Si/Al ratios.

3.2. Comparison of TOF values for the H-BEA and n-H-BEA catalysts

It has been demonstrated that the TOF of H-BEA catalysts used in the acetylation of toluene depends on both their Si/Al ratio and conversion (reaction time) [6]. The Si/Al ratio affects the zeolite polarity and thus the adsorption equilibrium constants of the reactants and products, as well as the strength of the acid sites, but its effect becomes smaller and even negligible at low Al content; for example, TOF values (from initial rates measurements) increase with decreasing Al content and remain constant when the Al molar fraction is less than about 0.015 (i.e., Si/Al > 66) for the acetylation of toluene by AA. TOF values at intermediate and quasi-stationary-state conversion are also affected by product inhibition as mentioned above and discussed in refs. [5] and [6].

Initial reaction rates (RRs) for the four catalysts were derived by fitting a quadratic equation to the low conversion (20% maximum, $t < 10$ min) data whose value of the first derivative at $t = 0$ is the initial RR [5,6]. RRs at intermediate conversion were derived in a similar manner using data for $t = 15$–60 min. RRs at quasi-stationary state were determined from a linear fit of the data for $t = 150$–300 min.

TOF values (min^{-1}) are easily calculated from RR ((mol/(min × g catalyst)), considering the molecular weight of $Si(Al,H)O_2$ (60) and the molar fraction of Al in the zeolite, as shown in eqn. (1):

$$\text{TOF}\ (\text{min}^{-1}) = [\text{RR} \times 60/(\text{Al}/(\text{Al} + \text{Si})] \qquad (1)$$

RRs and TOF values reported in table 2 were calculated at $t = 0$ (initial rate), 36% conversion (intermediate rate), and 52% conversion (quasi-stationary state rate) of AN relative to the reactant in deficit, AA.

TOF values for all catalysts increase with decreasing Al content at zero and quasi-stationary state conversion, as there is less competition by the reactants and products for the intracrystalline volume of the zeolite [6]. However, catalyst n-H-BEA-32 has a higher TOF at intermediate conversion.

3.3. TOF as a function of Si/Al ratio

As mentioned above, previous results for the acetylation of toluene (TOL) by AA using H-BEA catalysts demonstrated that TOF was dependent on the Si/Al ratio of the zeolite [6]. Therefore, it is of interest to compare the present results with those obtained for the former reaction, performed in nearly similar conditions, in order to assess if this dependence is "reaction sensitive".

Figures 3–5 compare, for both reactions, the TOF dependence on the Al molar fraction of the H-BEA catalysts, at $t = 0$ (initial TOF), intermediate conversion, and quasi-stationary state conversion. As both acetylations were performed at different temperatures,

Table 2
Rates (mol min^{-1} g^{-1}) and TOFs (min^{-1}) for conventional and nano-HBEA catalysts with different Si/Al ratio at various conversion (CON, %) levels

Catalyst	Rate (mol min^{-1} g^{-1})			TOF (min^{-1})		
	CON = 0	CON = 36	CON = 52	CON = 0	CON = 36	CON = 52
H-BEA-18	0.0061	0.00020	0.00006	7.0	0.23	0.07
n-H-BEA-32	0.0051	0.00040	0.00004	10.3	0.79	0.08
H-BEA 60	0.0046	0.00020	0.00004	16.7	0.72	0.15
H-BEA-77.5	0.0046	–	–	21.5	–	–

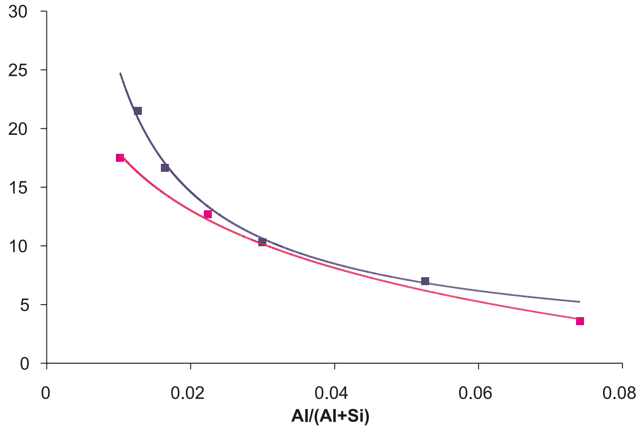

Figure 3. Initial TOF values for the acetylations of anisole and toluene with AA with conventional and nano-HBEA zeolites as a function of their Al molar fraction.

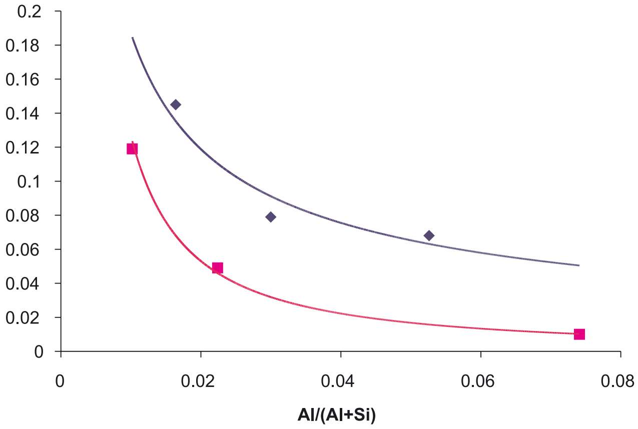

Figure 5. TOF values at quasi-stationary state (250 min) for the acetylations of anisole and toluene with AA with conventional and nano-HBEA zeolites as a function of their Al molar fraction.

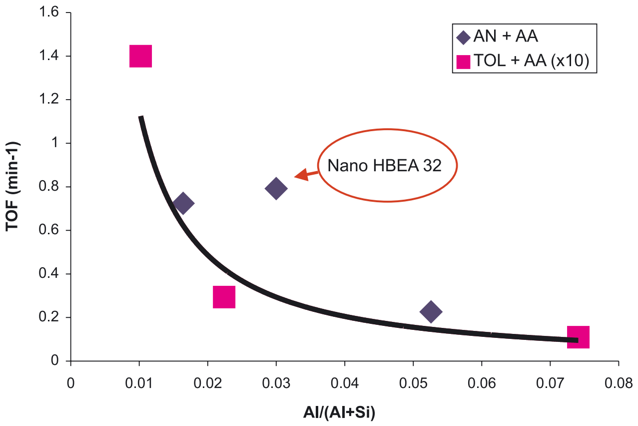

Figure 4. TOF values at intermediate conversions for the acetylations of anisole and toluene with AA with conventional and nano-HBEA zeolites as a function of their Al molar fraction.

i.e., 90 °C for AN + AA and 115 °C for TOL + AA, and as the acetylation of a non-activated substrate (TOL) is more difficult than that of an activated one (AN), TOF values for the acetylation of toluene (table 8 in ref. [6]) were multiplied by a factor of 10 to allow an easier comparison of the results. This factor accounts reasonably for the difference in intrinsic RRs (table 7 in ref. [6]) and reaction temperature for both substrates, assuming an activation energy of about 13–15 kcal mol^{-1} [5].

As shown in figure 3, the dependence of the initial TOF values (with adjusted values for TOL as mentioned above) on the Al molar fraction are similar for both reactions, with the TOF value for n-H-BEA-32 fitting the general trend of the other three H-BEA catalysts for the acetylation of anisole. It confirms that the initial TOF depends on the Si/Al ratio which affects the zeolite polarity and acid sites strength. It also demonstrates that no intra-crystalline mass transfer limitations are present in the initial stage of the reaction as the behavior of n-H-BEA is in line with that of the other catalysts. This is expected as both anisole and AA are molecules that should diffuse rather freely within the large pores of zeolite H-BEA. In addition, it can also be concluded that the CSS preparation method, inclusive of synthesis and calcination, does not affect detrimentally the chemical and catalytic properties of the zeolite.

Figure 4 is a similar type of plot for TOF values obtained at intermediate conversion. Again a similar trend is observed for both reactions when conventional H-BEA catalysts are used. However, the n-H-BEA-32 catalyst shows a TOF that is about three times greater than the expected value, which is interpreted as being the result of reduced diffusion limitations. Indeed, at intermediate conversion, the access of the reactants to the active sites is restricted by the presence of the bulkier and more strongly adsorbed *p*-MOAP product [5,6] that should have therefore a smaller diffusivity within the zeolite pores. Consequently, the concentration of *p*-MOAP in the intracrystalline volume of larger H-BEA crystallites will be greater than in nano-size H-BEA when *p*-MOAP is still produced at a reasonable rate.

Figure 5 compares TOF values at quasi-stationary state conversion. Similar dependences on the Al molar fraction are again observed for both reactions, with the TOF of n-H-BEA-32 following the expected trend for the AN + AA reaction. Obviously, the nano-size zeolite catalyst does not show improved performance in these conditions, which is expected. Indeed, at quasi-stationary state, the RR is low and should not depend on crystal size as the partitions of the reactants and product(s) between the zeolite intracrystalline volume and the surrounding liquid phase should be at equilibrium, in batch conditions, as discussed previously [5,6]. Although both trends are similar for the AN + AA and the TOL + AA reactions, it is interesting to note that adjusted TOF values for the TOL + AA reaction are about 2–3 times smaller than those for the AN + AA reaction, which we tentatively attribute to the much smaller adsorption equilibrium constant of toluene. Indeed, the adsorption equilibrium constants relative to AA ($K_{\mathrm{AA}} = 1$) are $K_{\mathrm{p\text{-}MOAP}} = 11.8$, $K_{\mathrm{AN}} = 1.7$, and $K_{\mathrm{TOL}} = 0.19$ (table 7 in ref. [6]) and a stronger product inhibition effect is thus expected at the quasi-stationary state for the TOL + AA reaction.

Although it is recognized that such plots are only indicative in the absence of (1) detailed kinetics describing the quantitative interplay between intrinsic kinetics and diffusional limitations, and (2) a strict comparison of the performance of catalysts with similar Si/Al ratio, the results demonstrate nevertheless that n-H-BEA catalysts have superior performance at intermediate conversion, as product inhibition resulting from diffusional limitations is decreased when using zeolite crystals of smaller size as suggested earlier [10,11].

4. Conclusions

It has been demonstrated that n-H-BEA has superior performance at intermediate conversion for the acetylation of anisole by AA when the reaction is operated batch-wise. The use of zeolite nano-crystals decreases the diffusional constraints limiting the egression of the bulkier *p*-MOAP product from the intracrystalline volume of the zeolite in conditions where it still can be produced at a reasonable rate, and thus product inhibition as discussed earlier [5,6].

No improvement is observed at initial or quasi-stationary state conversions. In the first instance, product inhibition is nil. In the second case, adsorption equilibria rule the distribution of the reactants and products between the liquid phase and the zeolite intracrystalline volume.

It has been further demonstrated that the TOF dependence on Si/Al ratio previously reported for the acetylation of toluene is of a general nature. Increasing the Al content of the zeolite increases its polarity and thus competitive adsorption effects when the reactants and/or products have different polarities, in addition to decreasing the strength of the acid sites.

As nano-size zeolites show improved performance for organic synthesis reactions operated at intermediate conversion in the liquid phase, it is likely that product yield could be best improved by using such catalysts in continuous reactor systems (CSTR or PFR, with or without direct recycling) rather than conventional batch reactors as commonly practiced today in the fine and specialty chemicals industry.

The above conclusions are relevant to many reactions using zeolites as catalysts in fine and specialty chemical organic synthesis when one of the products is strongly adsorbed by the zeolite or when steric constraints exist, both leading to diffusional limitations. Developing further the synthesis of a broad variety of nano-size (as used herein) and/or mesoporous zeolites (materials containing mesopores in addition to the conventional micropores, [14]) with lower Si/Al ratio is certainly an objective that should be pursued to support and expand research and developments in this field.

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