

## Beta zeolite supported on silicon carbide for Friedel–Crafts fixed-bed reactions†

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**Beta zeolite supported on silicon carbide, with high thermal conductivity and high mechanical strength, was successfully used as an active and stable catalyst for Friedel–Crafts reactions in a fixed bed configuration.**

The Friedel–Crafts reactions of aromatics represent one of the most important methods of production of aromatic ketones which are intermediate products in several fine chemical domains, *i.e.* the pharmaceutical, agrochemical and fragrance industries. Several reports have been published on the replacement of traditional  $\text{AlCl}_3$  or  $\text{FeCl}_3$  homogeneous catalysts by the heterogeneous solid acid zeolites in order to reduce the waste produced by the reaction and also to improve the catalyst/products separation.<sup>1–6</sup>

During the last decade, supporting zeolite onto a carrier has been a hot research subject in order to replace the bulk form, according the following advantages: lower pressure drop, lower diffusion rate, especially in liquid medium, and avoidance of the use of binders for the final macroscopic shaping which considerably limit the reactants access.<sup>7–11</sup> Recently, it has been reported that silicon carbide supported beta zeolite exhibits a high and stable catalytic activity for the Friedel–Crafts reaction in a slurry mode.<sup>12</sup> The aim of the present work is to report the use of such a catalyst directly in a fixed-bed reactor which allows the obtention of a significantly higher product yield without deactivation due to product adsorption or inhibition.

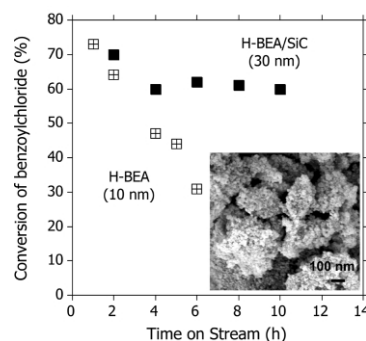
Silicon carbide in an extrudate form (diameter, 2 mm, length, 6 mm) with a specific surface area of  $23 \text{ m}^2 \text{ g}^{-1}$  and a mesopore distribution centered at around 40 nm was used as support for the zeolite. The support was synthesized according to a gas–solid reaction between  $\text{SiO}$  and carbon according to the Shape Memory Synthesis method.<sup>13</sup> The supported zeolite synthesis was carried out in a hydrothermal mode according to the method already described previously.<sup>12</sup> The resulting HBEA had a Si:Al ratio of 50. For comparison, a commercial HBEA zeolite (Zeolysts International, Si:Al ratio of 12.5 according to the information given by the producer) was also tested under the same reaction conditions. The commercial HBEA was obtained by calcinating the  $\text{NH}_4\text{-BEA}$  in air at  $550 \text{ }^\circ\text{C}$  for 10 h. The powder was then pasted and crushed in order to obtain grains between 0.4 and 1 mm in diameter. The average particle size deduced from the X-ray line broadening was about 30–40 nm for the SiC supported HBEA and 10–20 nm for the commercial HBEA catalysts.

The first advantage of the SiC supported zeolite was that the post-synthesis centrifugation of the crystallised zeolite which is a time and energy consuming step, could be omitted.<sup>14</sup> SEM observations have revealed that the as-deposited zeolite homogeneously covered the surface of the SiC support and had an average particle size of around 50 nm (not shown). The formation of zeolite on the surface of the SiC support also significantly increased the overall specific surface area (BET

measured using  $\text{N}_2$  as adsorbant at liquid nitrogen temperature) of the composite from  $25 \text{ m}^2 \text{ g}^{-1}$  to about  $120 \text{ m}^2 \text{ g}^{-1}$ .

The Friedel–Crafts reaction was carried out in a fixed bed downflow glass reactor (diameter, 10 mm, length, 300 mm). The catalyst was maintained in the reactor between quartz wool plugs. The anisole (A) and benzoyl chloride (B) mixture (A:B molar ratio of 8) were fed into the reactor by a HPLC pump (Varian 9002) with different liquid rates. Anisole is used in the present work as solvent in order to favour the extraction of the products formed from the catalyst cavity. The reactor temperature was kept at  $120 \pm 2 \text{ }^\circ\text{C}$  using a thermocouple placed in the oven, linked to an electronic controller. The liquid products were collected at regular intervals and analysed with gas chromatography (Varian GC-3400CX with a HP-PONA column,  $50 \text{ m} \times 0.2 \text{ mm} \times 1.05 \text{ } \mu\text{m}$  film thickness).

A blank test carried out on the SiC support alone shows no conversion which indicates the complete inactivity of the support which is in line with the chemical inertness of SiC. The catalytic results obtained by the Friedel–Crafts fixed bed reaction on the supported HBEA at a WHSV (weight hourly space velocity) of  $4 \text{ h}^{-1}$  are shown in Fig. 1 as a function of time on stream at  $120 \text{ }^\circ\text{C}$ . The initial benzylation activity was relatively high after 1 h on stream, *i.e.* 73% of conversion, with a selectivity towards *p*-methoxybenzophenone amounting to about 96%. These results are in line with those already reported in the literature in the slurry reactor configuration over zeolite catalysts where the main product is the *p*-substituted ketone.<sup>15</sup> The other reaction products, *i.e.* *o*-methoxybenzophenone and ester (phenyl benzoate) were formed in small amounts, 3 and 1% of the total reaction products. No trace of other compounds, *i.e.* phenol, has been detected among the products due to the lack of water in the catalytic system. The mechanism of the phenyl benzoate formation without the participation of phenol is depicted in Scheme 1 in the ESI†. The results obtained on the commercial beta zeolite (Zeolysts International) are shown in the same figure for comparison. The initial benzylation activity of the unsupported zeolite was similar to that observed with the supported catalyst, *i.e.* 70%. The benzylation activity drastically decreased with time on stream from 70% to about



**Fig. 1** Fixed bed Friedel–Crafts reaction of anisole and benzoyl chloride on beta zeolite supported on SiC and on a commercial bulk beta zeolite at  $120 \text{ }^\circ\text{C}$  and with a WHSV of  $4 \text{ h}^{-1}$ . Inset: The average zeolite particle size, *i.e.* 50 nm, observed by SEM on the H-BEA/SiC catalyst.

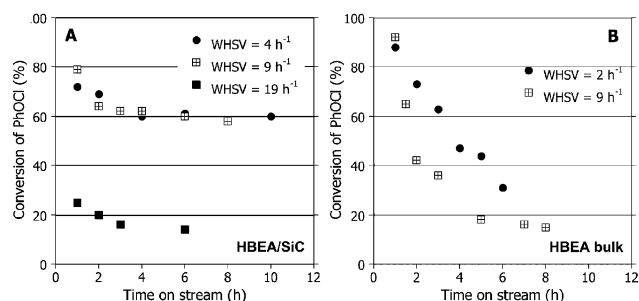
† Electronic supplementary information (ESI) available: Temperature-pressure oxidation spectra and mechanism of phenyl benzoate formation without the participation of phenol. See <http://www.rsc.org/suppdata/cc/b2/b209858j/>

30% after 6 h of test indicating a strong inhibition of the active site. It should be noted that the *p*-methoxybenzophenone selectivity remains unchanged, *i.e.* >90%, on both catalysts which indicates that the nature of the catalysts was not modified during the run.

Larger zeolite particles are more sensitive to deactivation due to the formation of heavier coke inside the intra-microporosities. However, according to the average particle size measured, more deactivation would be expected to occur on the supported zeolite because of the higher average size, *i.e.* 50 instead of 10 nm. From the results obtained one would expect that the deactivation which occurred on the commercial zeolite was originated from another factor. The difference of stability observed between the supported and unsupported HBEA can be attributed to the apparent size of the zeolite particles. On the supported catalyst these zeolite particles are smaller than the particles of the unsupported zeolite because of the dispersion on the support surface, while on the commercial catalyst aggregation between the different zeolite particles can result in bigger apparent particle sizes. The zeolite apparent particles influenced the rate of diffusion of the reactants and products which in turn, modified the real stoichiometry of the different reactants inside the zeolite cavity which in turn, lowered the catalytic activity. The difficulty in evacuating the heavier products formed inside the zeolite cavity also probably increased the coke formation inside the zeolite porosities, thus leading to deactivation. Temperature-programmed oxidation (Electronic Supplementary Information†) analyses carried out on the two catalysts after reaction clearly evidence a higher coke accumulation inside the bulk zeolite compared to that of the supported zeolite.

It has been reported by several authors in the literature that the aromatic ketone formed is the main inhibitor for the Friedel–Crafts reaction in a slurry reactor due to its strong adsorption on the active sites. Derouane and co-workers<sup>5,6</sup> have reported that the acylation activity significantly decreased as the amount of aromatic ketone in the reactant mixture increased. A similar deactivation has also been reported by Jaimol *et al.*<sup>4</sup> in a fixed-bed reactor during the acetylation of toluene over H-ZSM5 catalyst. At 453 K the conversion decreased from 70% to 30% after about seven hours on stream. The deactivation observed was attributed by the authors to coke formation inside the zeolite microporosity. Freese *et al.*<sup>15</sup> have reported that the acylation activity on dealuminated H-Beta was higher than that observed on initial H-Beta. This was attributed to the modification of the porosity in the dealuminated H-Beta, which favours the diffusion of the products from the core of the catalyst to the surface for desorption. It is expected that on the supported zeolite the dispersion of the zeolite particles on the support surface favours the evacuation of the ketone products. The higher diffusion rate of ketones out of the zeolite porosity probably allows the initial activity of the supported catalyst to be maintained despite the slight deactivation observed. This initial deactivation could be due to the equilibrium adsorption of a part of the formed ketone and the reactants inside the zeolite intraporosity.

The supported HBEA was also able to work in a large range of WHSVs without appreciable activity loss except at extremely high WHSV values which was probably due to a too short contact time between the reactants and the catalytic sites (Fig. 2A). The high Friedel–Crafts activity observed on the HBEA/SiC catalyst was attributed to the high dispersion of the zeolite as individual particles on the support surface which can offer a high effective surface contact to the reactants. Similar reactions carried out on the commercial bulk zeolite showed a drastic activity loss as a function of the WHSV (Fig. 2B). Formation of aggregates of several zeolite particles, leading to a bigger



**Fig. 2** Influence of the WHSV, *i.e.* 4 to 19 h<sup>-1</sup>, on the benzoylation activity, expressed in terms of conversion, on the H-BEA/SiC (A) and on the commercial bulk H-BEA (B) catalysts at 120 °C.

apparent size which could affect the reactants diffusion and/or products back-diffusion, was advanced to explain these results when increasing the WHSV, on the commercial unsupported zeolite. Again, the selectivity remained unchanged as a function of the WHSV.

In summary, silicon carbide synthesised by a gas–solid reaction can be efficiently used as support for dispersing beta zeolite. The supported beta zeolite catalyst was active for the benzoylation of anisole by benzoyl chloride and was very stable in a fixed bed reactor configuration when compared to that of the commercial unsupported beta zeolite. The high thermal conductivity of the SiC support can also allow use of the catalyst in highly exothermic reactions where a rapid dispersion of heat through the catalyst bed is necessary to avoid the formation of hot spots. Finally, the possibility of preparing SiC with a more open shape, *i.e.* monolith, allows the use of these supported catalysts for a high rate reaction, with a minimum diffusion limitation, which is not easy with a traditional support shape, for an extremely high space velocity process.

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