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Beta zeolite supported on a macroscopic pre-shaped SiC as a high performance catalyst for liquid-phase benzoylation†

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Preparation and characterisation of a highly active and stable beta zeolite supported on a pre-shaped silicon carbide catalyst for the benzoylation reaction in liquid phase.

Zeolite materials have been widely employed in several industrial processes, *i.e.* catalysis, absorption, separation.[1] Zeolites are typically obtained by hydrothermal synthesis in aqueous solution.[2] In general, the unsupported beta zeolite has a colloidal form. The small size of the particles renders their recovery and purification difficult, and ultracentrifugation is needed for the subsequent separation. The macroscopic shaping of the zeolite into extrudates or tablets for industrial use requires the introduction of binders such as α-Al_2O_3 or alumina–silica materials. The presence of binders increases the diffusion barrier between the reactants and the zeolitic active sites, especially for reactions with high intrinsic activity. For all these reasons, during the last decade, much research has been focused on the synthesis of supported zeolites over several supports to obtain a macroscopic shaping in order to facilitate their recovery from the synthesis solution and their subsequent catalytic use.[3–6]

Silicon carbide exhibits high thermal conductivity, high resistance towards oxidation, high mechanical strength and chemical inertness, properties required for heterogeneous catalyst supports. It was expected that silicon carbide could be efficiently used as a support for zeolites.

The aim of the present communication is to report the synthesis of nanosized beta zeolite supported on macroscopic SiC of various size and shape[7] and its subsequent use as catalyst in a liquid-phase benzoylation reaction. The catalytic activity is compared with that obtained on unsupported beta zeolite.

SiC in an extrudate form (diameter, 2 mm, length, 6 mm), synthesized according to the Shape Memory Synthesis (SMS),[8] with a specific surface area of 23 $m^2\ g^{-1}$ was employed. The solid is mainly mesoporous and no trace of microporosity was ever observed.

The beta zeolite synthesis solution was prepared by dissolving a silica source (Aerosil 200) in an aqueous solution of tetraethylammonium hydroxide (TEAOH) at 50 °C under vigorous stirring. At the same time, the aluminium source (aluminium powder) was dissolved in a solution of TEAOH at room temperature. This solution was then added to the silica source. After one hour of aging under vigorous stirring, a known amount of SiC (10 g) was slowly added to the zeolite precursor gel (*ca.* 30 ml) at atmospheric pressure and ambient temperature. The resulting mixture was then transferred into a Teflon-lined stainless steel autoclave, and heated at 140 °C (autogeneous pressure) for 17 h. The solid obtained was washed with distilled water several times in order to remove the unreacted soluble fraction and dried at 100 °C for 5 h. Finally, it was calcined at 550 °C in flowing argon for 10 h in order to decompose the organic template. The zeolite was exchanged with ammonium choride (150 ml, 1 M) and calcined in order to obtain the acidic form (HBEA).

XRD pattern carried out with Cu Kα radiation (Fig. 1A) shows the presence of diffraction lines corresponding to the HBEA zeolite along with those of the SiC support. A low magnification SEM image (inset of Fig. 1A) shows the gross morphology of the SiC extrudate after zeolite synthesis. According to the figure the shape of the support was not modified during the synthesis even in a high basic medium. High-magnification SEM image of the zeolite supported on the SiC carrier is presented in Fig. 1B which clearly shows the presence of small zeolite particles homogeneousely dispersed on the entire surface of the support. The high magnification SEM image (inset) shows the homogeneous size of the zeolite particles centered at around 50 nm. The zeolite deposit, determined by HF treatment, was 8 ± 2 wt%. The supported zeolite has a Si/Al ratio of around 50 according to the elemental analysis of the composite after HF dissolution.

The deposition of zeolite on the SiC surface significantly increases the overall surface area of the material from 25 (for

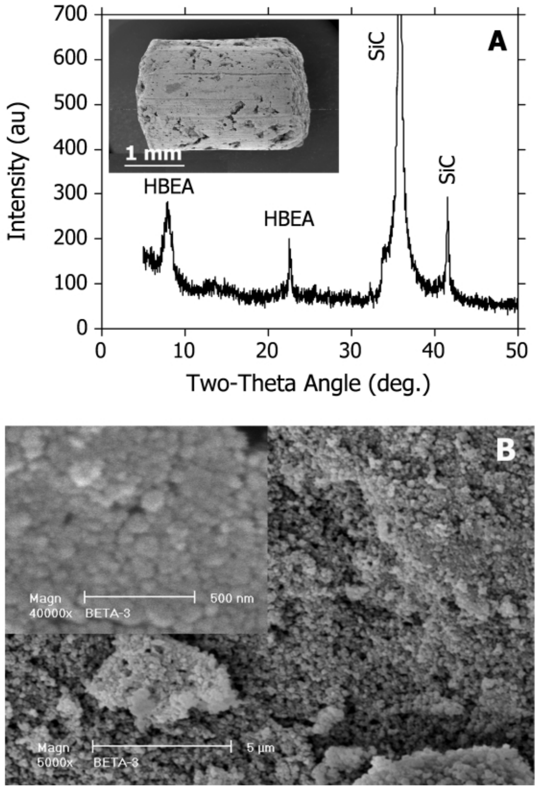

Fig. 1 (A) XRD pattern of the as-synthesised zeolite beta supported on SiC composite. Inset: low magnification SEM image showing the complete conservation of the support shape after synthesis. (B) SEM images of the composite showing the homogeneous coverage of the SiC surface by the zeolite. The synthesis duration was 17 h at 140 °C. Inset: high magnification SEM image showing the zeolite particles with an average particle size of *ca.* 50 nm.

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† Electronic supplementary information (ESI) available: TPO spectra. See http://www.rsc.org/suppdata/cc/b2/b206805m/

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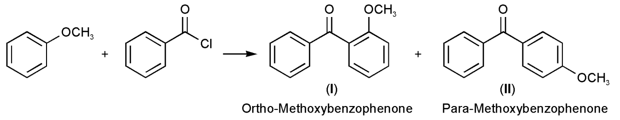

Scheme 1

pure SiC) to more than 100 m^2 g^{-1} along with a large microporous contribution (*ca.* 60 m^2 g^{-1}) according to the N_2 adsorption isotherm. Taking into account the unmodified surface area of the starting SiC support the real surface area of the zeolitic deposit amounted to about 500 m^2 g^{-1} with a microporosity surface area contribution of about 350 m^2 g^{-1} which was in good agreement with the surfaces generally obtained with zeolitic materials.

Catalytic tests were carried out under the following reaction conditions: catalyst weight, 0.2 g of zeolite (for the supported zeolite the total catalyst weight was 2 g with about 8 ± 2 wt.% zeolite loading), reaction temperature, 120°C, anisole (0.03 mmol), benzoyl chloride (0.02 mmol). The benzoylation (see Scheme 1) catalytic results obtained on the supported beta zeolite catalyst are reported in Fig. 2A and compared with those obtained on an unsupported HBEA zeolite (Fig. 2B). On the SiC supported catalyst the benzoylation activity was relatively high with a total conversion of 71% after 24 h on stream. The selectivity towards aromatic ketone I, *para*-methoxybenzophenone, reached about 95% (Fig. 2A) while isomer II, *ortho*-methoxybenzophenone, only amounted to less than 5%. It is significant to note that no trace of ester has been observed. The catalyst was then washed several times with dichloromethane in order to remove the trapped products inside its pores and then re-tested for benzoylation under the same reaction conditions. The conversion and ketone selectivity remained almost unchanged for the second and third tests on the supported zeolite catalyst as show in Fig. 2A.

The benzoylation activity and selectivity obtained under the same reaction conditions on the commercial bulk beta zeolite catalyst with higher acidity strength (Zeolysts International, with a Si/Al ratio given by the supplier of 12.5 and an average particle size of *ca.* 10 nm) are reported in Fig. 2B. The post-reaction treatment (washing) was identical to that used for the supported catalyst. During the first cycle, similar activity and ketone selectivity were observed. However, significant deactivation was observed during the second cycle on the unsupported catalyst. Similar results have been reported earlier by different authors[9,10] during the benzoylation of anisole by acetic anhydride in a batch reactor over HBEA. The loss of catalytic performance was due to several factors: coke formation during the test by acidic condensation of the products inside the zeolite pores[9,10] and/or de-alumination of the catalyst by the product, *i.e.* acetic acid, based on ^{27}Al MAS NMR spectroscopy.[11] The similar rates of benzoylation as a function of time on stream shown in Fig. 1A and B indicate that supported zeolite displays a higher benzoylation activity compared to that of the commercial zeolite regarding the difference in the Si/Al ratio, *i.e.* Si/Al ratio of 50 for the supported zeolite instead of 12.5 for the commercial zeolite. The dispersion of the zeolite on the support surface which leads to a higher contact surface with the reactants was advanced to explain the observed results.

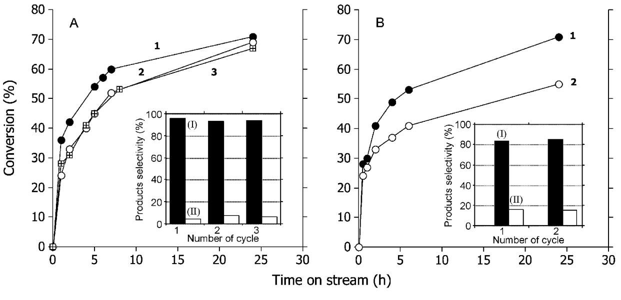

Fig. 2 Alkylation results, conversion and *ortho*-methoxybenzophenone (labelled I) and *para*-methoxybenzophenone (labelled II) selectivity, obtained after 24 h of reaction as a function of the catalytic cycling over the SiC supported beta zeolite (A) and the unsupported one (B).

Larger zeolite particles are more sensitive to deactivation due to the formation of heavier coke inside the micropore. From the results obtained, one should thus expect that the deactivation of the commercial zeolite originated from another factor. The difference in activity observed between the supported and unsupported HBEA catalysts can be attributed to the bigger apparent size of the bulk zeolite due to the easy aggregation between the different zeolite particles on the commercial catalyst. The apparent particle size of the active supported zeolite was expected to be smaller than that of the unsupported one due to its dispersion on the support surface. The bigger apparent size of the commercial zeolite probably decreased the rate of the reactant and product diffusion in and out of the zeolite pores leading to irreversible deactivation by heavier compounds formed later within the pores. It is though that the partition between the reactants and products inside the zeolite pores and the bulk solvent plays an important role in the maintenance of the catalytic activity and prevents deactivation by the formation of coke or heavier products.[12]

Temperature-Programmed Oxidation (ESI†) carried out on the catalysts after reaction clearly indicates that a higher amount of coke was formed inside the commercial zeolite compared to the supported one. Such results are in line with the low Si/Al ratio of the commercial zeolite which is more sensitive to coke formation. The range of combustion temperature on the commercial unsupported zeolite was also broader and significantly shifted towards high temperatures, *i.e.* 100 °C, indicating the presence of coke with heavier molecular weight.

In summary, beta zeolite activity and stability in the benzoylation reaction can be greatly improved by supporting it on a silicon carbide carrier using classical hydrothermal synthesis. In addition, the macroscopic shaping of the zeolite renders recovery and cleaning easier as compared to the unsupported material. Work is ongoing in the laboratory to investigate the physico-chemical properties of the supported zeolite, before and after reaction, using more sensitive techniques such as NMR (^{27}Al and ^{29}Si) and to evaluate its activity directly in a fixed-bed configuration which is commercially more attractive.

Notes and references

1 H. L. Hoffman and L. Riddle, *Hydrocarbon Process., Int. Ed.*, 1988, **67**, 41.
2 R. M. Barrer, in *Hydrothermal Chemistry of Zeolites*, Academic Press, London, 1987.
3 V. Valtchev, J. Hedlund, B. J. Schoeman, J. Sterte and S. Mintova, *Microporous Mater.*, 1997, **8**, 93.
4 J. C. Jansen, J. H. Koegler, H. van Bekkum, H. P. A. Calis, C. M. van den Bleek, F. Kapteijn, J. A. Moulijn, E. R. Geus and N. van der Puil, *Microporous Mesoporous Mater.*, 1998, **21**, 213.
5 M. Xu, M. Cheng and X. Bao, *Chem. Commun.*, 2000, 1873.
6 J. Garcia-Martinez, D. Cazorla-Amoros, A. Linares-Solano and Y. S. Lin, *Microporous Mesoporous Mater.*, 2001, **42**, 255.
7 S. Basso, J. P. Tessonnier, C. Pham-Huu and M. J. Ledoux, *Fr. Pat. Appl.* No. 02-00541, 2002.
8 M. J. Ledoux and C. Pham-Huu, *CaTTech*, 2001, **5**, 226.
9 U. Freese, F. Heinrich and F. Roessner, *Catal. Today*, 1999, **49**, 237.
10 E. G. Derouane, C. J. Dillon, D. Bethel and S. B. Derouane-Abd Hamid, *J. Catal.*, 1999, **187**, 209.
11 T. Jaimol, A. K. Pandey and A. P. Singh, *J. Mol. Catal. A: Chem.*, 2001, **170**, 117.
12 E. G. Derouane, *CaTTech*, 2001, **5**, 214.