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Novel honeycomb structure: a microporous ZSM-5 and macroporous mullite composite

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We have developed a novel honeycomb composite structure consisting of microporous ZSM-5 and macroporous mullite by *in-situ* crystallization of ZSM-5 utilizing glass from a sintered kaolin honeycomb. This *in-situ* crystallization of ZSM-5 leads to better adhesion and mechanical strength for the zeolite film and results in a graded structure with three layers consisting of strongly adhered ZSM-5 film at the surface, a composite ZSM-5 and mullite layer below the pure ZSM-5 layer and porous mullite at the core. These novel composite structures are expected to have major applications in the areas of automotive and other catalysts, pervaporation membranes, cation exchange separations, *etc*.

A novel composite honeycomb consisting of microporous ZSM-5 and macroporous mullite is developed with many potential applications. The automotive industry utilizes cordierite ceramic honeycomb structures in catalytic converters of gasoline-powered cars to reduce carbon monoxide, nitrous oxide and hydrocarbon emissions. The macroporous honeycomb structures are also used in diesel-powered cars to trap and burn particulate carbon from the exhaust gases. In gasoline-powered cars a significant amount of the total emissions that a vehicle emits in a single trip are emitted in the first few minutes of operation[1] because the operating temperature of the catalytic converter is below 300 °C at the very beginning of the trip. Below a 300 °C, the catalytic converter is ineffective in decomposing the various emissions while it has a maximum efficiency in the range 400–800 °C. A great deal of effort at present is being devoted to reduce the emissions in the first few minutes by using electrically-heated catalysts. An alternative approach is to trap the hydrocarbon emissions until the catalytic converter reaches an operating temperature of 300 °C by using microporous adsorbents such as zeolites. Here we report the fabrication of a novel ZSM-5 (microporous)–mullite (macroporous) composite honeycomb structure which can be located at the entrance of the three-way catalyst and is potentially useful to trap the emissions until the catalytic converter reaches its operating temperature. There is also a great deal of interest in the preparation of composite materials containing continuous zeolite films for other applications such as catalysis, pervaporation, adsorption, cation exchange, *etc.*.[2–9] However, most of these studies led to limited success because of the problems of zeolite adhesion to the ceramic substrate. Here we overcome the adhesion problems by *in-situ* crystallization of ZSM-5 zeolite.

Monolithic honeycomb was prepared from a commercially available New Zealand kaolin clay. The kaolin (halloysite) powder supplied by New Zealand Clay Company has the following chemical composition: SiO_2, 50.07; Al_2O_3, 35.76; Fe_2O_3, 0.26; TiO_2, 0.07; CaO, trace; MgO, 0.08; Na_2O, 0.07; K_2O, 0.01 and ignition loss, 13.79 wt%. This powder was first calcined at 500 °C for 3 h to remove adsorbed water and hydroxyls to reduce the deformation during final sintering at 1650 °C. The calcined clay was ball-milled, dried and then thoroughly mixed with 10 wt % methyl cellulose binder and 25 wt% water before extrusion forming of a honeycomb of $15 \times 15 \times 100$ mm (cell size, 1.4×1.4 mm; wall thickness, 510 μm). This extruded honeycomb was heated initially at 300 °C for 2 h to remove the binder and heated to 1650 °C at the rate of 2.2 °C min^{-1} followed by sintering at 1650 °C for 2 h. The sintered body was determined to be composed of 58 wt% mullite and 42 wt% silica glass. The silica glass in this sintered body was transformed to ZSM-5 zeolite *in-situ* by hydrothermal treatment at 190 °C for 14–28 days in Teflon-lined hydrothermal vessels at autogenous pressure. The molar ratios of the starting chemicals for hydrothermal synthesis were as follows: SiO_2 in honeycomb : NaOH : tetrapropylammonium bromide (TPAB) : $H_2O = 100 : 12.8$ (or 25.5) : 5 : 2800.

First, a sintered honeycomb body of mullite and silica glass was produced. By hydrothermally treating this honeycomb in alkaline solutions, one can convert it into a porous mullite honeycomb,[10,11] by dissolving silica into the solution. By treating this honeycomb with NaOH in the presence of TPAB template at 190 °C for two weeks, we converted the silica in

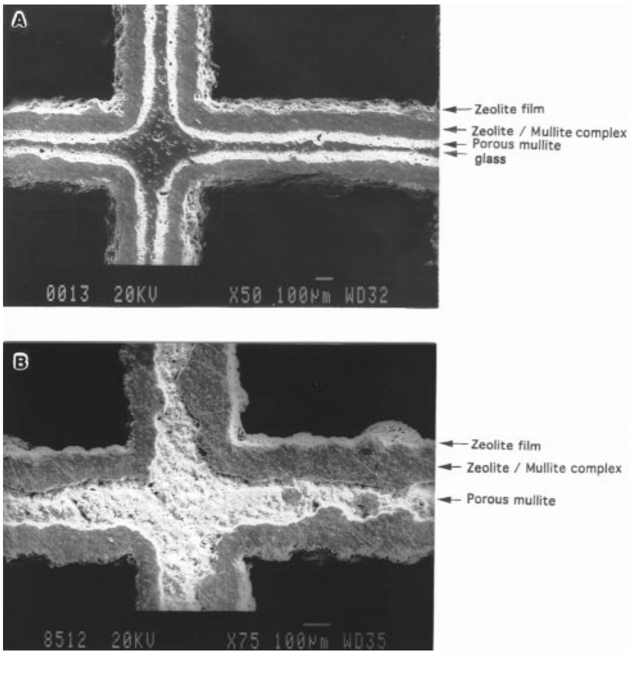

Fig. 1 Cross-section of honeycomb body showing (A) four layers of ZSM-5, ZSM-5 + mullite, porous mullite and mullite + glass upon hydrothermal treatment with 12.8 M NaOH at 190 °C, 14 days and (B) three layers of ZSM-5, ZSM-5 + mullite and porous mullite upon hydrothermal treatment with 25.5 M NaOH at 190 °C, 14 days.

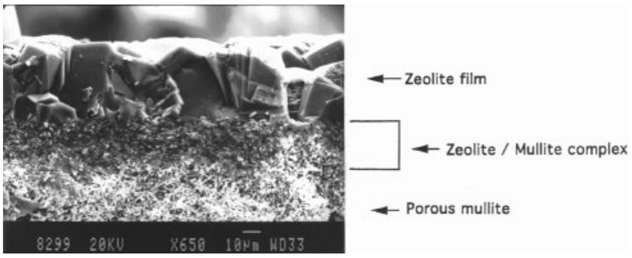

Fig. 2 Cross-section at higher magnification showing ZSM-5 layer, ZSM-5 plus mullite layer and porous mullite after hydrothermal treatment at 190 °C, 21 days.

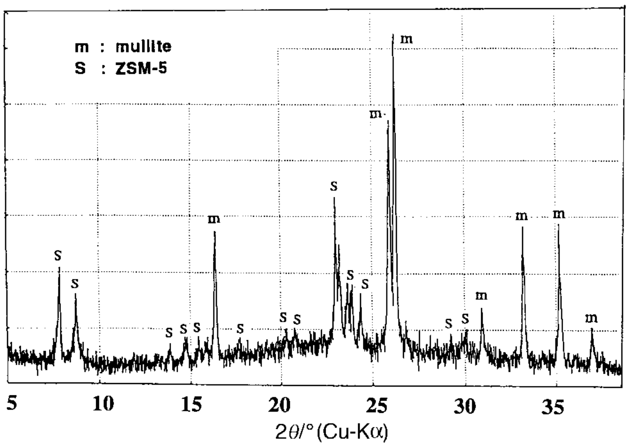

Fig. 3 Powder X-ray diffraction pattern of ZSM-5 and porous mullite composite prepared at 190 °C for 14 days.

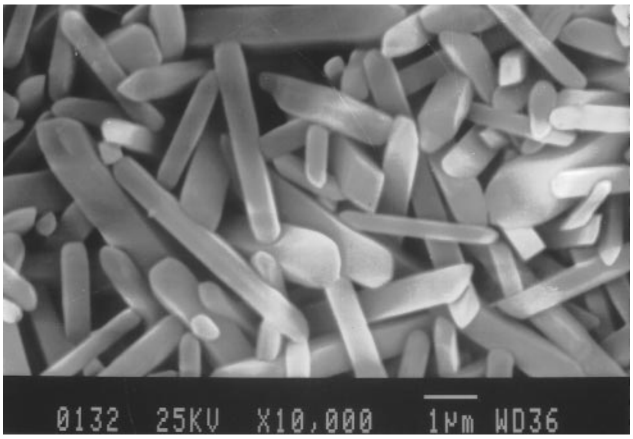

Fig. 5 Morphology of porous mullite after hydrothermal leaching of glass at 190 °C, 21 days.

Table 1 The effect of time and concentration of NaOH on the surface area of zeolite–mullite composites

Hydrothermal conditions[a]		
Time/days	Amount of NaOH/mol	Surface area/m^2 g^{-1}
7	25.5	43.7
14	25.5	76.2
21	25.5	92.2
7	12.8	60.9
14	12.8	78.3
21	12.8	82.7
28	12.8	110.8

[a] Hydrothermal conditions: 190 °C; autogeneous pressure and molar ratios, SiO_2 in kaolin : NaOH : TPABr : H_2O = 100 : (12.8, 25.5) : 5 : 2800.

the honeycomb to ZSM-5 zeolite. Fig. 1A shows the initial conversion of the honeycomb to four layers from the surface to the core as follows: ZSM-5 on the surface, ZSM-5 + mullite below the surface, porous mullite and mullite + glass at the core. By continuing the treatment for three weeks, we completely converted all the glass to ZSM-5 zeolite with a sequence of three layers as follows: ZSM-5 layer on the surface, ZSM-5 + mullite below the surface and porous mullite at the core (Fig. 1B). A cross-section of this novel composite clearly shows ZSM-5 on the surface followed by ZSM-5 + mullite complex and porous mullite (Fig. 2). Powder X-ray diffraction patterns of the composite showed mullite and ZSM-5 crystalline phases only (Fig. 3). Scanning electron micrographs of ZSM-5 from the surface show that a continuous layer of this phase had formed (Fig. 4). The size of the ZSM-5 crystals ranged from 20 to 60 µm. Fig. 5 shows the needle-like morphology of the porous mullite with an average pore size of about 0.57 µm.[10] The results presented here clearly show that a novel microporous–macroporous composite was prepared with a very high surface area (Table 1). The adhesion and compressive strengths of a zeolite film with a thickness of 200 µm on the surface of the porous mullite were found to be very good and are in the ranges of 9–17 MPa and 319–483 MPa, respectively.

We heated this porous mullite with a zeolite film of 200 µm at 900 °C for 60 h to determine its thermal stability and found it to be very stable with no cracks or pinholes. The surface areas of several samples heated at 900 °C were determined to be in the range of 80–100 m^2 g^{-1}. Thus we have fabricated a

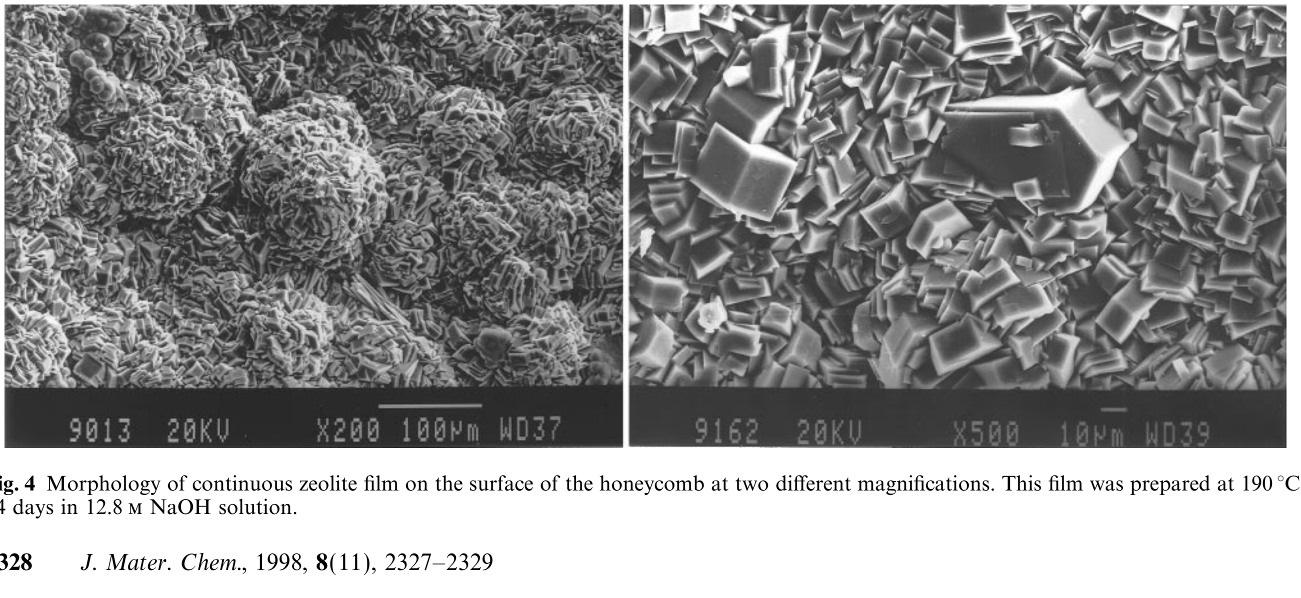

Fig. 4 Morphology of continuous zeolite film on the surface of the honeycomb at two different magnifications. This film was prepared at 190 °C, 14 days in 12.8 M NaOH solution.

novel microporous ZSM-5 and macroporous mullite composite with excellent mechanical properties and very high surface areas. This combination of mechanical properties, micro- and macro-porosities with a high surface area has never been achieved before and these composites are expected to find applications as automotive catalysts, adsorbents, cation exchangers, pervaporation membranes, *etc.* Such application studies are now in progress.

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