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Hierarchically structured meso-macroporous aluminosilicates with high tetrahedral aluminium content in acid catalysed esterification of fatty acids

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ABSTRACT

A simple synthesis pathway has been developed for the design of hierarchically structured spongy or spherical voids assembled meso-macroporous aluminosilicates with high tetrahedral aluminium content on the basis of the aqueous polymerisation of new stabilized alkoxy-bridged single molecular precursors. The intimate mixing of an aluminosilicate ester $(sec\text{-BuO})_2\text{–Al–O–Si(OEt)}_3$ and a silica co-reactant (tetramethoxysilane, TMOS) with variable ratios and the use of alkaline solutions (pH 13.0 and 13.5) improve significantly the heterocondensation rates between the highly reactive aluminium alkoxide part of the single precursor and added silica co-reactant, leading to aluminosilicate materials with high intra-framework aluminium content and low Si/Al ratios. The spherically-shaped meso-macroporosity was spontaneously generated by the release of high amount of liquid by-products (water/alcohol molecules) produced during the rapid hydrolysis and condensation processes of this double alkoxide and the TMOS co-reactant. It has been observed that both pH value and Al–Si/TMOS molar ratio can strongly affect the macroporous structure formation. Increasing pH value, even slightly from 13 to 13.5, can significantly favour the incorporation of Al atoms in tetrahedral position of the framework. After the total ionic exchange of Na^+ compensating cations, catalytic tests of obtained materials were realised in the esterification reaction of high free fatty acid (FFA) oils, showing their higher catalytic activity compared to commercial Bentonite clay, and their potential applications as catalyst supports in acid catalysed reactions.

1. Introduction

Recent studies highlight the promising superiority of hierarchical meso-macrostructured materials in large series of catalytic reactions [1–11], thanks to improved diffusion and mass transfer properties as well as limitation of poisoning and coking, especially when large molecules are used and reactions are performed in viscous liquid phase [12,13]. A large panel of original strategies, often quite tedious to achieve, have been developed to allow the incorporation of desirable porosities at different length scales into one single body. These strategies can be summarised into two categories. One concerns the use of templates such as polymeric beads and silica opals [14–16], soft sacrificial template [17], foam [18,19], emulsions [20,21], ice crystals [22], natural structures [23] such as bacterial threads [24] with the combination of amphiphilic molecules or zeolite crystal seeds [25–28]. Other one is related to post-synthesis treatments [29]. Lately, a self-formation phenomenon of porous hierarchy has been discovered [30–48]. This new strategy is based on the very fast polymerisation of metal alkoxides in aqueous solution, yielding hierarchical meso-macroporous oxide and metallosilicate materials. The macrostructure consists of typically well organised parallel macrochannels of funnel like shape whereas mesoporosity results from the aggregation of inorganic nanoparticles. This strategy has been extended to metal alkyls as precursor [49].

Aluminosilicate composition is heavily involved in catalytic reactions and separation processes [50,51]. Its chemical activity arises from the insertion of trivalent aluminium atoms into a tetrahedral silicate framework, implying charge deficiencies and compensating cations. This creates Lewis and Brönsted acid–base sites which are catalytically active for cracking, isomerisation or alkylation reactions. Synthesised porous aluminosilicate materials with low Si/Al ratios are rare [52] and the preparations from two separated precursors, an aluminium alkoxide and an alkoxysilane, results in hierarchical meso-macroporous aluminosilicates that are

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chemically heterogeneous due to their construction from binary oxides [53–55]. In fact, aluminium alkoxides polymerise faster than alkoxysilanes, forming octahedrally co-ordinated extra-framework aluminium species that may exist in separated bulk, inducing the important loss of selectivity. The synthesis of porous aluminosilicate materials with high aluminium content and a molecular and a homogeneous distribution of the Si–O–Al linkages in the final frameworks still remains a great challenge.

One promising strategy relies on the use of single molecular precursors [56–59]. These molecules, constructed from a preformed M–O–Si linkages, are able, under controlled hydrolysis and condensation reactions, to form unequalled chemically homogeneous metallosilicate materials. An Al–Si ester type precursor which already contains an Al–O–Si linkage, the di-*sec*-butoxyaluminoxytriethoxysilane (*sec*-BuO)$_2$Al–O–Si(OEt)$_3$ has been used in pioneer works [60–63]. More importantly, this single-source molecular precursor possesses, in addition to the preformed Al–O–Si bond, two alkoxide functionalities that are able to undergo fast hydrolysis and polycondensation reactions, rendering possible the auto-generation of a hierarchical meso-macroporosity with unmatched chemical homogeneity, thus, introducing unprecedented acid–base properties with a totally controlled stoechiometry and improved diffusion properties. Previous works have revealed that the Al–O–Si linkage rupture prevention of the single molecular precursor in aqueous solution requires the use of some aluminium selective chelating agents [64] or silica co-reactants such as TMOS, TEOS, TPOS and TBOS [65] in highly alkaline medias. High alkaline condition favours the conversion of aluminium precursors into monomeric tetrahedral $\mathrm{O{-}Al[OH]_3^-}$ species, which is known to preferentially co-polymerise with the silicate anions to form an Al–O–Si network [66–68].

In this work, in order to synthesise a panel of materials with finely tuned Si/Al ratios (1 < Si/Al < 2) without the rupture of the Al–O–Si linkage, tetramethoxysilane (TMOS) as a silica co-reactant in reduced amount were mixed with the di-*sec*-butoxyaluminoxytriethoxysilane due to its high efficiency to favour co-polymerisation between highly reactive aluminium functionalities and the silicon functionalities from the Al–Si ester and TMOS co-reactant [69]. The influence of the (*sec*-BuO)$_2$Al–O–Si(OEt)$_3$/TMOS ratio on the macroporous morphology, textural properties, and aluminium incorporation were studied. The obtained aluminosilicate materials were ion exchanged to obtain acidic form of aluminosilicate materials. Newly synthesised acid-type aluminosilicate materials were then used in acidic catalytic transesterification reactions of a palmitic acid/oleic acid mixture with ethanol to assess their performance [70,71]. Their catalytic behaviour was compared with commercial Bentonite clay, which is a well known FCC catalyst support. These results indicate that a new generation of more efficient catalyst supports has been prepared from the promising single-source molecular precursor route.

2. Experimental

2.1. Preparation of meso-macroporous materials

The Al–Si ester, di-*s*-butoxyaluminoxytriethoxysilane ((Bu-^{s}O)$_2$Al–O–Si(OEt)$_3$), was purchased from Gelest, and other chemicals from Aldrich. They were used without any further purification. Aqueous alkaline solutions (pH = 13.0 and 13.5) were prepared by dissolving NaOH in 60 mL of bidistilled water (at a pH of 6.5). Subsequently, 5.0 g of the Al–Si ester were intimately mixed with tetramethoxysilane (TMOS) (molar ratios Al–Si ester/TMOS = 1/1, 2/1 and 4/1) under vigorous stirring (700 rpm) and inert N$_2$ atmosphere for 5 min, resulting into the formation of unique transparent aluminosilicate phase, made by new stabilized alkoxy-bridged single molecular precursors. This mixture was slowly added dropwise into the NaOH solution under very mild stirring (<100 rpm). After 1 h the mixture was transferred into a Teflon-lined autoclave and heated to 80 °C for 24 h. The solid product was filtered, washed with water, and dried in an oven at 40 °C. Materials are labelled as Al–Si-TM. The number following immediately Al–Si-TM prefixes indicates the pH value used for the synthesis and the following number after the dash (–) represents the ratio of single precursor/silica co-reactant (TMOS). Informations are compiled in Table 1.

Reference materials, prepared without TMOS silica co-reactant at ph 13.0 and 13.5 are named Al–Si-13 and Al–Si-13.5 respectively.

Catalytic tests were achieved by using H$^+$ form of aluminosilicate materials obtained by successive ionic exchange. The ion exchange was made by nine consecutive ion exchange procedures by the immersion of the Al–Si-TM13-1 sample in 0.12 M NH$_4$NO$_3$ ethanol solutions at 80 °C during 1 h.

2.2. Characterisation

Transmission electronic microscopy (TEM) experiments were performed on a Philips TECNAI-10 microscope at an acceleration voltage of 80 kV with sample powders embedded in an epoxy resin and sectioned with an ultramicrotome. The N$_2$ adsorption and desorption isotherms were measured at −196 °C with a volumetric adsorption analyzer, Micromeritics Tristar 3000. The morphology as well as the macroporous array was studied using a Philips XL-20 scanning electron microscope (SEM) and a JEOL JSM 7500 field emission scanning electron microscope (FE-SEM) with conventional sample preparation and imaging techniques. The environments of the Al and Si atoms were studied via ^{27}Al MAS NMR and ^{29}Si MAS NMR respectively, with a Bruker Avance 500 spectrometer and the Si/Al ratio was investigated with the help of a Philips PU9200X atomic absorption spectrometer. Na$^+$ ions exchange process was observed by ^{23}Na MAS-NMR (Bruker Avance 500 spectrometer) and the generation of NH_4^+ ions was studied by FTIR with KBr pellets loaded with 1 wt.% of material, using a Perkin–Elmer Spectrum 2000 spectrometer.

2.3. Catalytic runs and analysis

To evaluate the performance of the catalysts for the high free fatty acid (FFA) oil esterification, palmitic acid was modified with 17% oleic acid. The esterification of palmitic acid with ethanol was performed in a 25 mL magnetically stirred round-bottomed flask fitted with a reflux condenser and an arrangement for digital temperature controller. The mixture of reaction was composed of a 60/1 ethanol/acid weight ratio and 0.6 wt.% catalyst was used. The reaction temperature was 130 °C and the stirring speed was 700 rpm. At the end of the experiment, the catalyst was separated from the reaction mixture by repeated centrifugation. The final acidity was measured by titration with 0.5 M sodium hydroxide solution. The conversion of FFA (x_{FFA}, in percents) was calculated by the acidity ratio using below formula:

$$x_{\mathrm{FFA}} = \frac{a_s - a_t}{a_s} \times 100,$$

where a_s is the starting acidity of the reactant and a_t is the acidity at a “t” time. As reference, commercial Montmorillonite [Al$_2$O$_3$·4SiO$_2$·H$_2$O] clay purchased from Aldrich has been used.