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Synthesis and adsorption properties of titanosilicates ETS-4 and ETS-10 from fly ash

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ABSTRACT

ETS-4 and ETS-10 titanosilicates were prepared from fly ash and anatase, as silica and titanium sources respectively, via a hydrothermal procedure for the first time. The fusion of fly ash by alkali was carried out at a relatively low temperature and the use potassium fluoride salt was avoided in the synthesis of ETS. The by-product of this process is mainly NaCl, which is a useful source material for industry. The energy efficiency and yield of the synthesis process was improved by directly recycling the final filtrate after recovering the product viz ETS-4. All the ETS materials were characterized in terms of structural morphology, thermal stability and surface/pore properties. The properties of ETS-4 prepared from fly ash by the filtrate recycling method were comparable to that from commercial sources. The results show that ETS type materials can be prepared from cheaper resources, with good purity, comparable physico-chemical properties as well as excellent adsorption properties with lower environmental impact.

1. Introduction

A large amount of fly ash is produced from coal-fired power stations annually. As a solid waste, more than 65% is disposed of in landfills and ash ponds. Recycling coal fly ash has received extensive attention due to increasing landfill costs and negative environmental impact. Fly ash usually is rich in Si and Al, hence, converting fly ash into a useful commodity (e.g. cement) has a number of benefits from both economic and environmental aspects. In particular, a large number of patents and technical articles have proposed different methods for zeolites synthesis from fly ash [1,2], using hydrothermal processes. Various types of zeolites have been prepared from fly ash including Na–A, Na–X, Na–P1, K-chabazite, ZSM-5, MCM-41, etc. These adsorbents can be used for removal of heavy metals from waste water or as adsorbents for the removal of SO_2, NH_3, and CO_2 from industrial gas sources [3–10].

Titanosilicate materials possess zeolite-like properties and find numerous applications in catalysis, adsorption and separation [11–14], since first reported by Chapman and Rod [15]. Titanosilicates ETS-4, ETS-10 and ETS-14 were later developed and patented by Engelhard Corporation. ETS-4 has a mixed octahedral/tetrahedral structure, with small pores between 0.3 and 0.4 nm, which can be easily tuned by progressive dehydration (Molecular Gate Effect). Hence, ETS-4 could be optimized as an adsorbent for separation of gases of close size, for example methane/nitrogen, oxygen/argon, etc. [16,17]. The Na form of ETS-4 is known to be thermally unstable, however, ion exchanging Na^+ with bivalent ions such as Sr^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, etc., results in improved thermal stability, which can be then be exploited practically for gas separation [14,18,19]. Pressure Swing Adsorption (PSA) processes using Sr-ETS-4 has already been commercialized for the important N_2/CH_4 separation [20]. Additionally, adsorption based separation of CO_2, CH_4 and C_2H_5 as well as O_2 and Ar have also been examined [21,22] by PSA with titanosilicates. ETS-10 on the other hand is a large pore titanosilicate with an effective pore size of approximately 8 Å with high thermal stability and good cation exchange capacity [23]. ETS-10 materials generally find application in catalysis viz acid–base catalysis, photocatalysis, etc. ETS-10 has gained considerable attention as an ionic sieving material for heavy and radioactive metal ions [24–26]. Furthermore, cation exchanged ETS-10 can demonstrate separation selectivity and it has been reported as a suitable adsorbent for PSA-based CO_2 separation from methane [21] and for the separation of ethylene/ethane or propylene/propane mixtures [27,28]. Additionally, ETS-4 and ETS-10 membranes have been prepared and their performance was tested in water: ethanol separation [29–32].

ETS-4 and ETS-10 can be synthesized by a hydrothermal process, wherein the titanium source can be $TiCl_3$ or $TiCl_4$ in HCl, anatase, rutile, etc. and the silica source is normally fumed silica, sodium silicate, rice husk, etc. in the presence of an alkali, fluoride or chloride [27], as described in the literature. Additionally, the effect of seeds

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Table 1
Chemical composition of fly ash in wt%.

SiO_2	Al_2O_3	Fe_2O_3	CaO	C	TiO_2	MgO
53.1	39.5	3.37	1.76	0.43	1.32	0.37

on the particle size [33], synthesis time, pH [24,35], etc. in case of ETS-10, has also been studied. Although ETS-10 has been prepared using rice husk as silica source [37], to the best of our knowledge, synthesis of titanosilicate ETS-4 and ETS-10 using fly ash as silica source has not been examined, perhaps due to the large portion of Al in the fly ash (as shown in Table 1). Moreover, in the case of ETS-4, we demonstrate that the supernatant liquid after recovering the product can be recycled to reproducibly synthesize ETS-4 thus minimizing waste. The ultimate aim of this work was to demonstrate that ETS-4 and ETS-10 can be prepared from low cost, eco-friendly starting materials (use of KF was avoided) and the un-reacted materials in the filtrate can be reused and the produced material can be used for adsorption of green house gases such as CO_2, CH_4, etc.

2. Experimental

2.1. Synthesis

Fly ash used for this study was provided by Shoutou electricity plant (China) and its composition is described in Table 1. The synthesis procedure for both ETS-4 and ETS-10 is summarized schematically in the flow diagram (Fig. 1). In a typical procedure, 60 g of fly ash and 48 g of NaOH (Ajax Fine Chemicals) were mixed with 120 g of water, followed by heating the slurry (in a Parr autoclave) at 120 °C for 2 h under continuous stirring. The mixture was diluted by adding 80 g of water, followed by filtration. Then, concentrated HCl solution (32 wt%) was added drop wise to the resulting filtrate for pH adjustment. To synthesize ETS-4, 0.5 g of ETS-4 seeds and 2.5 g of commercial anatase (99.8% Sigma–Aldrich) was added to the above filtrate with vigorously stirring for 30 min. To synthesize ETS-10, 3.6 g of anatase and 13.3 g of KCl (Ajax Fine Chemicals) were added to the fly ash slurry. In both of the cases, the mixture was transferred into a 300 mL stainless steel autoclave (Parr Instruments, USA) and heated at 230 °C for 24 h under static conditions. After cooling to room temperature, the resultant solid was filtered, washed three times with deionized water, and dried at 70 °C overnight. The samples prepared from fly ash were labeled as ETS-4(FA) and ETS-10(FA), respectively.

The filtrate containing unreacted Na^+, Cl^-, TiO_4^-, SiO_3^{2-} after the hydrothermal treatment stage in the case of ETS-4 was recycled for the next synthesis batch as demonstrated in the flow diagram. In a typical procedure, the filtrate was evaporated to 120 mL. Then, 30 g of fly ash and 24 g of NaOH were added to the filtrate, followed by the same procedure detailed above, and the resulting samples were labeled as ETS-4(FAR).

For comparison purposes, ETS-4 and ETS-10 were also prepared by reported methods using commercial silica sources [34,35]. In a typical synthesis of ETS-4, 12.5 g of colloidal silica (30 wt.% SiO_2, Ludox) solution, 2.5 g of NaOH, 2 g of NaCl, 1 g of anatase were mixed with 12.5 g of water, followed by vigorously stirring for 30 min. To prepare ETS-10, 20 g of sodium silicate solution (8.5 wt% Na_2O,

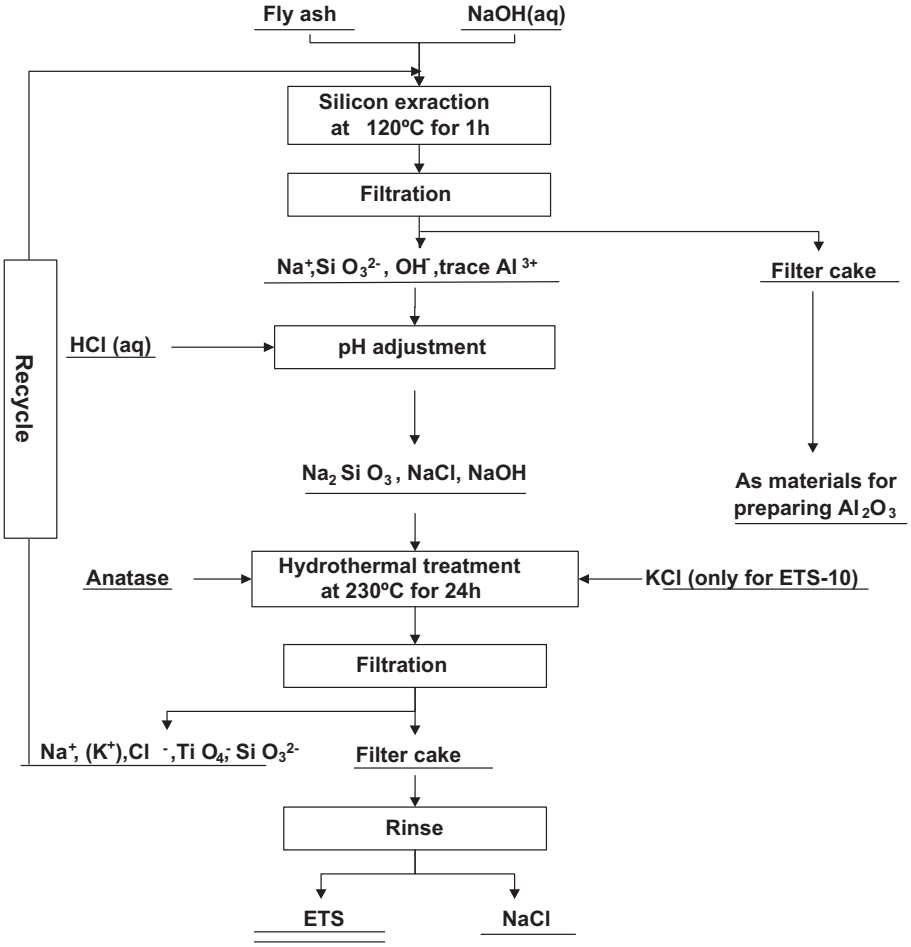

Fig. 1. Flowchart for synthesis of ETS-4 and ETS-10 from fly ash.