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.

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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 octa-hedral/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,
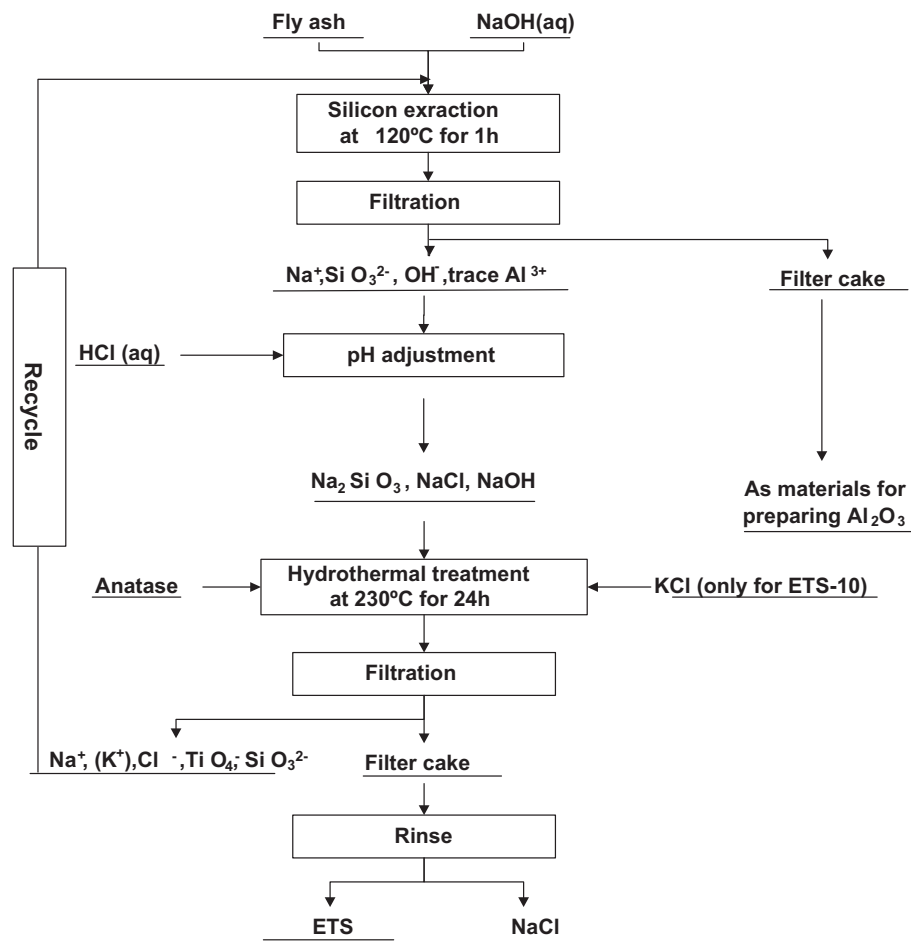

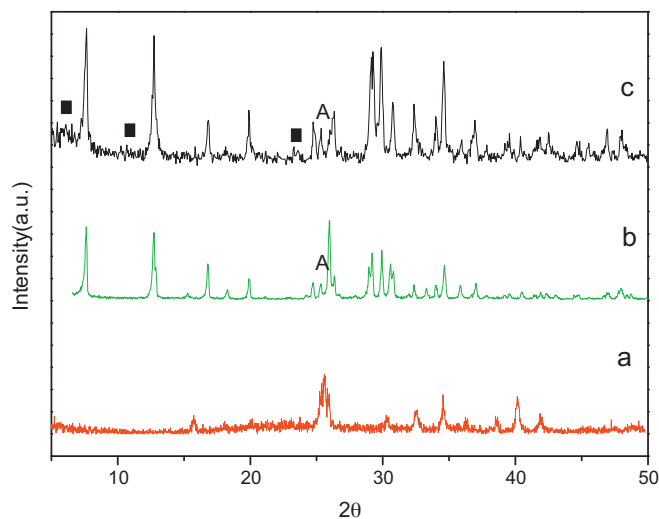**Fig. 1.** Flowchart for synthesis of ETS-4 and ETS-10 from fly ash.

Fig. 2. X-ray diffraction patterns for: (a) fly ash, (b) as-synthesized ETS-4(FA) obtained at pH 12.5, (c) as-synthesized ETS-4(FA) obtained at pH 11.6, circles represents anatase impurity, while squares indicate ETS-10 impurity.

26.5 wt% SiO_2, BDH) was diluted with 20 g of water. Then 6.9 g NaCl, 1.3 g KCl and 1.3 g anatase were added and the solution was homogenized by continuous stirring for 30 min. In both synthesis procedures, the gel was heated in an autoclave at 230 °C for 24 h under static conditions. The final products were filtered, washed three times with deionized water and dried at 70 °C overnight. The samples were labeled as ETS-4(T) and ETS-10(T), respectively.

2.2. Measurement and characterization

The chemical composition of the fly ash, as-synthesized ETS-4 and ETS-10 were determined by Inductively Coupled Plasma-mass Spectrometry (ICP-AES, Ultratrace, Perth). The crystalline properties of the samples were examined by X-ray diffraction (XRD) using a Philips PW1140/90 diffractometer with Cu Kα radiation (λ = 1.5404 Å). FE-SEM (Field Emission Scanning Electron Microscopy) analysis was conducted by employing a JEOL 6300F/7001F scanning electron microscope operated at 15 kV. All samples were platinum coated prior to measurement. BET and Langmuir surface areas measurements were conducted on an ASAP 2020 analyzer (Micromeritics, USA) using N_2 and H_2 as probe gases at 77 K in the relative pressure range of 0.05–0.25. The total pore volume was evaluated with a single point method at a relative pressure of 0.995. CO_2, N_2, CH_4 adsorption isotherms were measured on an ASAP 2010 gas adsorption analyzer. Prior to measurements, all the samples were degassed under vacuum (90 °C for ETS-4 and 330 °C for ETS-10), for 8 h.

3. Results and discussion

3.1. Structure and morphology

The X-ray diffraction pattern for fly ash (Fig. 2a) indicates that the crystalline phases are mainly α-quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$), identified by the sharp peaks, with coexistence of an amorphous phase in the range of about 2θ = 15–30°.

XRD patterns of as-synthesized ETS-4(FA) at pH 12.5 and pH 11.6 are shown in Fig. 2b and c respectively. The overall X-ray diffraction patterns show distinct peaks, which are consistent with those reported for ETS-4. As expected, the ETS-4(FA) sample synthesized at pH > 12 shows better crystallinity [36]. However, in all samples, a small peak attributed to anatase phase is seen at about
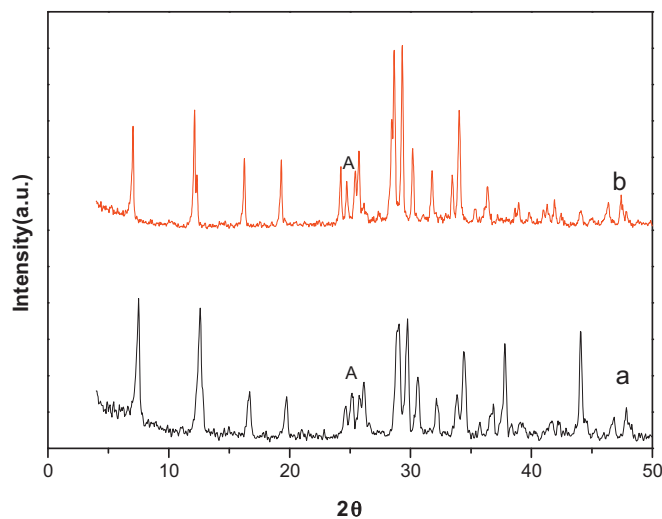
25°, which indicates incomplete conversion of anatase into the ETS-4 product. The intensity of the peak corresponding to anatase can be reduced by decreasing the amount of the anatase in the gel, however, the yield of ETS-4 reduces consequently. Furthermore, the ETS-4(T) sample, prepared from colloidal silica source also shows anatase impurity (Fig. 3a), suggesting that when anatase is used as a Ti-source, the conversion is usually incomplete and it is difficult to get pure ETS materials [35,37], although product purity can be improved by adjusting the ratio of Si/Ti.

Hydrothermal reaction conditions are also critical in controlling the purity of the synthesized ETS materials [36]. The XRD results show that when the pH value is in the range of 12–12.5, high purity ETS-4 can be obtained. However, ETS-10 impurity is detected when the pH is around 11.6 (Fig. 2c) and when the pH is below 11, ETS-10 became the main product. Fig. 3b shows the X-ray diffraction patterns for ETS-4(FAR) sample prepared by recycling the effluent. It is clear from the pattern that high-quality ETS-4 can be prepared by recycling the gel solution and suggests that there is no additional solid formed during this recycling process. As expected, the yield of ETS-4 increased with the number of cycles due to more efficient utilization of the reactants. However, with the increase of recycle cycles, NaCl in the liquid phase accumulates and eventually reaches saturation and co-precipitates with ETS-4, which can be easily removed by rinsing the solid. Hence, from environmental
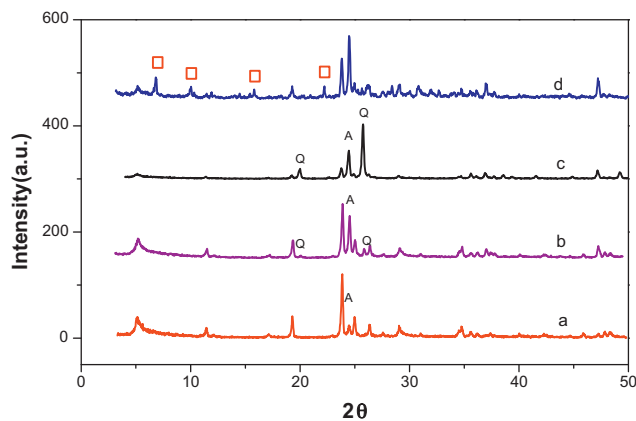

Fig. 3. X-ray diffraction patterns for: (a) ETS-4(T), (b) ETS-4(FAR), "A" represents anatase impurity.

Fig. 4. X-ray diffraction patterns for: (a) ETS-10 (T), ETS-10(FA) obtained at pH of (b) 11.2, (c) 10.6, (d) 11.6, A corresponds to unreacted anatase, Q represents quartz impurity, hollow square represents ETS-4 impurity.

perspective, this process is eco-friendly because the only waste generated is NaCl (a by-product).

Fig. 4a–d shows the X-ray diffraction patterns for both ETS-10 samples prepared using colloidal silica source as well as fly ash. ETS-10(T) has the distinct peaks (Fig. 4a), corresponding with the characteristic signatures of ETS-10. However, an incomplete transformation of ETS-10 was observed, which can again be attributed to the commercial anatase source [35,37]. Similarly, all the ETS-

10(FA) samples contain a small amount of unreacted anatase in addition to quartz (Fig. 4b and c). According to the XRD results, the best ETS-10(FA) was obtained at pH 11.2, with a small amount of quartz (Fig. 4b). At pH 10.6, ETS-10(FA) was contaminated with a large amount of quartz (Fig. 4c), while at pH 11.6, ETS-10(FA) was heavily contaminated with ETS-4 impurity (Fig. 4d). In agreement with past observations in the literature we observe that pure ETS-10 could not be obtained using commercial anatase as titanium
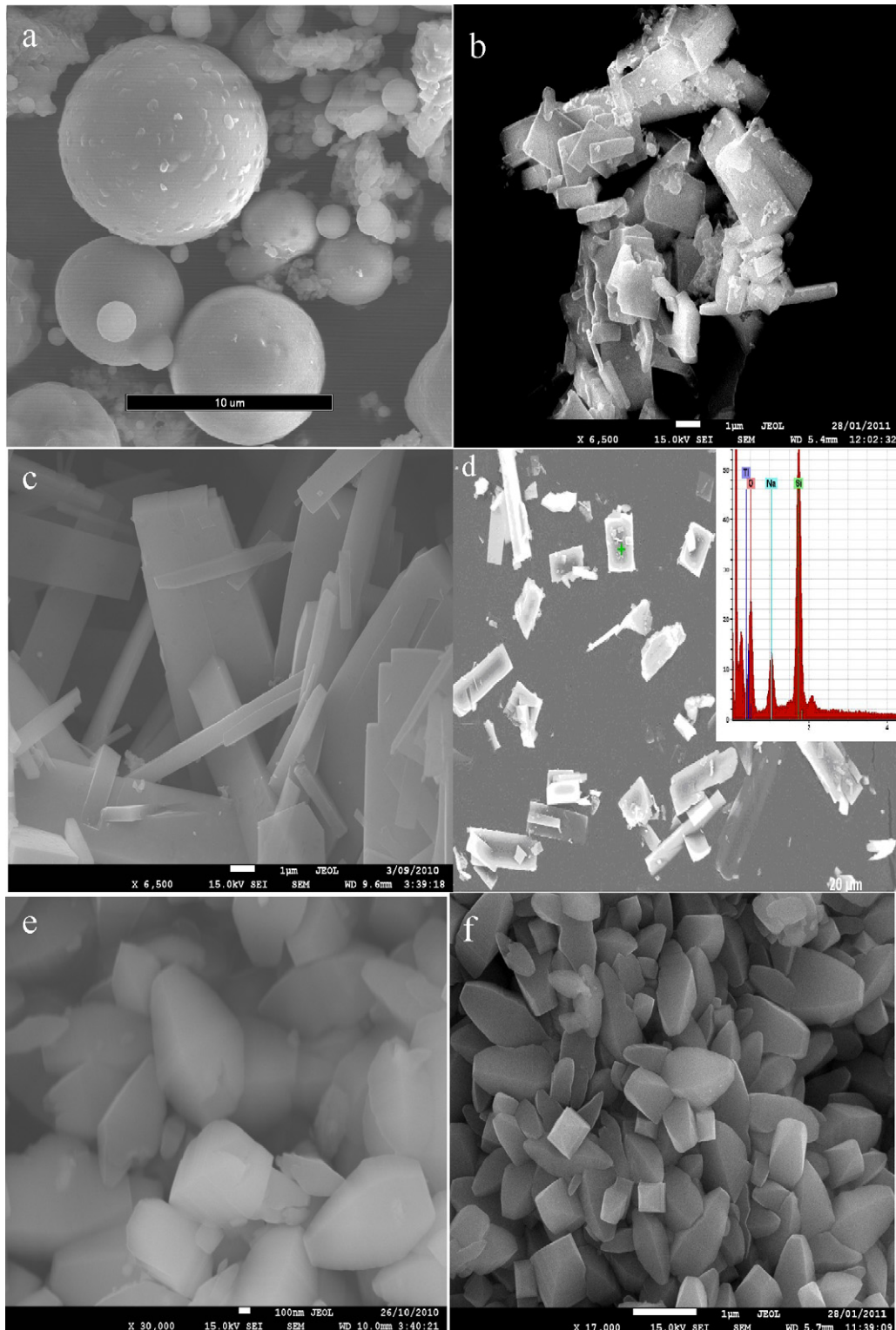

Fig. 5. FE-SEM images of: (a) original fly ash, (b), ETS-4(T), (c) ETS-4(FA), (d) inset EDX spectra of ETS-4(FA), (e), ETS-10(T), (f) ETS-10 (FA).

Table 2
Chemical composition of as-synthesized ETS-4 and ETS-10.

Component (wt%)	ETS-4(T)	ETS-4(FA)	ETS-10(T)	ETS-10(FA)
Si	21.1	17.5	26.3	22.1
Al	0.02	0.6	0.1	0.19
Ti	13.6	19	11.9	19.3
Na	6.47	9.53	6.6	4.66
K	0.2	0.2	2.9	3.3

Table 3
The structural properties of ETS-10 samples using sodium silica solution and fly ash.

Samples	Surface area (m^2/g)	The total pore volume
Fly ash	2.2[a]	0.005
ETS-4(T)	203[b]	0.08
ETS-4(FA)	5.2[a]	0.01
ETS-4(FA)	210[b]	0.10
ETS-10(T)	313[a]	0.20
ETS-10(FA)	304[a]	0.19

[a] Denotes BET surface area obtained by N_2 adsorption.
[b] Denotes Langmuir surface area obtained by H_2 adsorption.

source, as the particle size of anatase is too large compared with other titanium sources such as P25 or nano-anatase [35,37]. The particle size of anatase is known to be the controlling factor in the purity of the resultant ETS materials [33].

The chemical composition by ICP of the as-synthesized ETS samples is displayed in Table 2. Fly ash contains a considerable amount of Al (20.9%), as shown in Table 1. ICP data reveals that ETS-4(FA) and ETS-10(FA) contain a very small amount of Al impurity, about 0.6% and 0.19%, respectively. This suggests that most of the alumina from the fly ash is removed during the process.

Fig. 5 shows the scanning electron micrographs of fly ash and ETS samples. SEM for fly ash (Fig. 5a) shows particles with a wide size distribution and spherical morphology. ETS-4(T) and ETS-4(FA) (Fig. 5b and c) samples show inter-grown aggregates of plate-like crystals with rectangular morphology, with approximately 5.0 ($\pm$2.0) $\times$ 1.8 ($\pm$0.2) μm in size. The elemental analysis using EDX (inset) gave high intensity signals for Ti, Si, Na and O, and does not show presence of any additional elements, suggesting that ETS-4(FA) contains only traces of elemental impurity of Al_2O_3. The morphology of as-synthesized ETS-10 samples is shown in Fig. 5e–f. Regardless of the silica source, both ETS-10(T) and ETS-10(FA) samples display truncated bipyramid structure suggesting that the morphology of ETS-10 materials is dependent on Ti source rather than silica source. The particles of ETS-10(FA) show uniform distribution approximately 1.5 ($\pm$0.2) $\times$ 0.6 ($\pm$0.1) μm in size. The elemental analysis using EDX (not shown) showed high intensity signals corresponding to Ti, Si, Na and O, and do not show the presence of any additional elements, suggesting that the trace impurities were removed during the fusion and extraction process.

3.2. Adsorption properties

Specific BET surface area and total pore volume of the ETS-4(FA) sample measured with liquid nitrogen are quite low as expected, about 5.2 m^2/g and 0.01 cm^3/g, respectively as N_2 has practically no access to the micropore system [38]. In order to investigate the details of textural properties of as-synthesized ETS-4(FA), smaller diameter H_2 gas adsorption isotherm was measured at 77 K. A typical Type I isotherm (Fig. 6a) was measured, confirming presence of only micropores. Single-point total pore volume estimated from the amount adsorbed at a relative pressure P/P° of 0.995 was 0.10 cm^3/g. The Langmuir surface areas of ETS-4(T) and ETS-4(FA) (Table 2) are 203 m^2/g and 210 m^2/g, respectively, and are slightly lower than the reported values (247 m^2/g) in the literature [39], which may be attributed to the small amount of impurity such as unreacted anatase.

The N_2 adsorption isotherm (77 K) of ETS-10(FA) shows a typical Type I isotherm and a narrow pore size distribution centered at the value of 0.7 nm (not shown). The specific BET surface area of ETS-10(T) and ETS-10(FA) shown in Table 3 were nearly similar viz 313 m^2/g and 304 m^2/g, respectively, well within experimental error. Single-point total pore volumes estimated from the amount adsorbed at a relative pressure P/P° of 0.995 was 0.20 cm^3/g and 0.19 cm^3/g, respectively.

The single-component equilibrium isotherms for N_2 and CH_4 were also measured at 30 °C for the ETS-4(T) and ETS-4(FA) and are shown in Fig. 6b and c. All the isotherms were reversible. The adsorption loadings of both gases on ETS-4(FA) and ETS-4(T) were in agreement suggesting that ETS-4 prepared from fly ash was similar to ETS-4 prepared from traditional sources. CH_4 adsorption capacity was higher as compared to N_2, which could be attributed
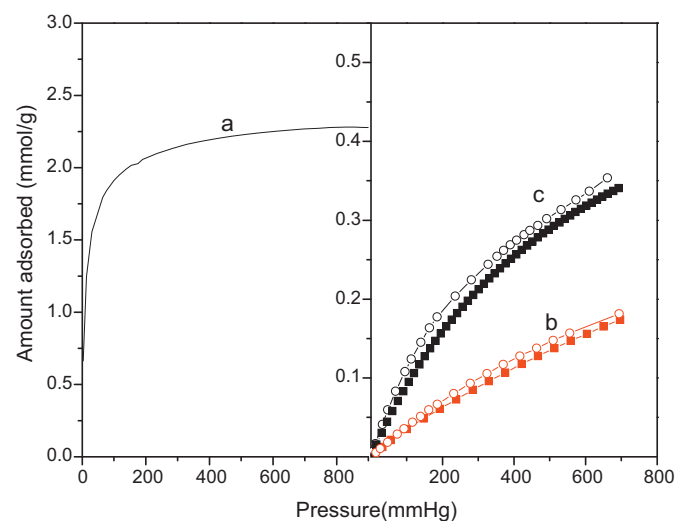

Fig. 6. (a) Hydrogen adsorption isotherm of synthesized ETS-4(FA) at 77 K. Adsorption isotherms of (b) N_2 and (c) CH_4 in the ETS-4(T) and ETS-4(FA) at 30 °C, where the square denotes ETS-4(T) and circles denotes ETS-4 (FA).
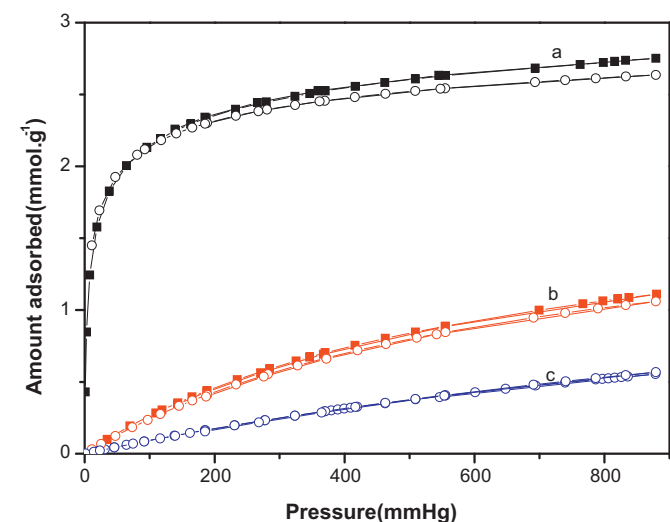

Fig. 7. Adsorption isotherms of: (a) CO_2, (b) CH_4, (c) N_2 in ETS-10(T) and ETS-10(FA) at 25 °C, where the square denotes ETS-10(T) and circle denotes ETS-10 (FA).

to the induced octopole moment that CH_4 exhibits and its large polarizability [40].

The representative adsorption isotherms measured at 25 °C for pure CO_2, N_2 and CH_4 on the ETS-10(T) and ETS-10(FA) samples were shown in Fig. 7. The adsorption loadings of CO_2, CH_4 and N_2 on ETS-10(T) and ETS-10(FA) are comparable. CO_2 adsorption capacity was the highest followed by methane and nitrogen. Furthermore, selectivity of methane over nitrogen was caused by the higher polarizability [40]. ETS-10(FA) showed good selectivity for CO_2 over N_2 at 25 °C. Thus, prepared ETS-10 (FA) could be an appropriate adsorbent for CO_2 separation in the future. Furthermore, the adsorption loadings of gases on ETS-10(FA) were comparable with the data published by Anson et al. [21], suggesting the ETS-10 prepared with fly ash has similar adsorption properties with counterparts obtained with commercial sources.

4. Conclusion

Fly ash was successfully utilized for production of ETS for the first time in the absence of an organic template. High purity ETS-4 and ETS-10 can be obtained at pH of 12.5 and 11.2, respectively. ETS-4 and ETS-10 obtained using fly ash exhibit high surface areas and pore volumes, in spite of trace impurities. The properties of ETS prepared from fly ash are comparable with those from commercial sources. The recycling of the effluent after removal of solids ensures efficient use of the reactant materials, while maintaining high product purity, and most importantly this process is extremely beneficial from an environmental perspective.

Acknowledgements

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