Modification in Properties of Fly Ash through Mechanical and Chemical Activation

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Authors' contributions

This work was carried out in collaboration between all authors. Senior and corresponding author AR supervised and designed the study, Author AS performed the experimental and analytical study, wrote the protocol, and wrote the first draft of the manuscript. Authors KS and VD managed the literature search and some experimental part. All authors read and approved the final manuscript.

Research Article

ABSTRACT

This paper is a critical overview on chemical, structural, and morphological changes in fly ash properties with mechanical activation using high energy planetary ball mill and chemical activation by digesting with various mineral acids (HCl, HNO_3, H_2SO_4 and $HClO_4$) at 110ºC. Mechanical activation results in increase in silica percentage, amorphous nature, specific surface area and surface roughness, as evident by analytical measurements using XRF, XRD, FT-IR, BET surface area and SEM techniques. The chemical activation of Fly ash performed by different acids results in increased silica content and surface area due to leaching of several metal ions from silico-aluminate skeleton. The surface silanol groups responsible for generating Brönsted acidity are enhanced as evident by pyridine adsorbed FT-IR. Activation with $HClO_4$ is also evident to generate surface active Lewis acid sites due to formation of Al-OH phases on the surface. The mechano-chemical activation can generate sufficient activity on fly ash surface rendering its potential application in heterogeneous acid catalysis.

Keywords: Fly ash; mechanical activation; chemical activation; acid treatment; ball milling.

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1. INTRODUCTION

Fly ash (FA) is a micro spherical particulate by product of coal burning power plants, produced approximately 420 million tons per year globally (Naggar et al., 2008). It consists of silica, alumina, iron oxide, lime, magnesia and alkali in varying amounts with some unburned activated carbon (Dogan et al., 2006; Fan et al., 2001). Due to environmental regulations, new ways of utilizing fly ash have to be explored in order to safeguard the environment and provide cost effective ways for its bulk utilization. Now, there is an urgent and imperative need to adopt technologies for gainful utilization and safe management of FA on sustainable basis.

FA has a number of useful applications that serves to utilise some of the large amount being produced all over the world. Main applications of FA are in the field of manufacturing of cement and other construction materials (Sear et al., 2001), agriculture, metal recovery, water and atmospheric pollution control (Blanco et al., 2006) etc. FA contains high silica content, which helps in converting it as an active catalytic material like other silica sources. After suitable activation and modified surface activity, FA is used as heterogeneous catalyst for various organic transformations viz. Friedal-Crafts acylation (Khatri et al., 2010 a), benzylation (Khatri et al., 2010 b), chlorination (Leer et al., 1989) and condensation (Jarmohamed et al., 1994; Jain et al., 2010; Jain et al., 2011; Jain et al., 2012) etc.

FA is transformed from micron sized to nano structured through high energy planetary ball milling (Rao et al., 2010). Such mechanical activation not only improves degree of fineness but also involves breaking of bonds, dispersion of solids, generation and migration of chemical moieties in the bulk thus results in increased surface roughness and specific surface area (Kumar et al., 2007). The modification of morphology and size of FA experienced with milling confreres a great degree of reactivity to the FA as a catalyst or catalyst support material which can be further improved by combining the effects achieved with acid activation (Blanco et al., 2005).

Acid activation of FA is widely used for developing acidic sites for catalytic applications as solid acid (Koehl et al., 2006). Treatment of minerals with inorganic acids of rather high concentrations and usually at elevated temperatures, as referred to as 'acid activation', is commonly used for production of sorbents or catalysts in industries or in environmental protection measures (Bergaya et al., 2001; Ravichandran et al., 1997). Treatment of FA with mineral acids induces remarkable changes in the crystal structure of alumino-silicate minerals due to dissolution of structural ions and/or rearrangement of the structure (Jozefaciuk et al., 2002). Acid activation involves leaching of several metal oxides and aluminium ions from the silico-aluminate layers of the FA thus increases high amorphous silica content and specific surface area of FA (Flessner et al., 2001).

The present work elaborates how to improve the capability of fly ash in order to increase its silica content and surface activity by mechanical activation and chemical treatments using various types of acids viz. HCl, HNO_3, H_2SO_4 and $HClO_4$. In this paper an attempt has been made to modify the chemical, structural and morphological properties of FA through synergistic mechano-chemical activations. Development of sufficient surface acidity on FA surface provides an innovative pathway for its bulk utilization as a solid acid catalyst in industrial scale organic synthesis.

2. EXPERIMENTAL DETAILS

2.1 Materials and Reagents

Class-F type fly ash having ($SiO_2+Al_2O_3>80\%$) produced from combustion of bituminous coal, was collected from Kota Thermal Power Plant, Kota (Rajasthan). The components of fly ash are SiO_2 (62%), Al_2O_3 (23%), Fe_2O_3 (7%), CaO (1.6%), MgO (0.8%), TiO_2 (1.3%), Na_2O (2.8%) and trace elements (1.5%). All chemicals $HClO_4$ (98%), H_2SO_4 (98%), HNO_3 (98%), and HCl (97%) were purchased from s. d. fine Chem. Ltd., India and were used as such.

2.2 Mechanical Activation of Fly Ash

Fly ash (FA) was washed with distilled water followed by drying at 100ºC for 24h. Dried FA was mechanically activated using high energy planetary ball mill (Retsch PM-100, Germany) in an agate grinding jar using agate balls of 5 mm ball sizes for 5, 10 and 15 hours with 250 rpm rotation speed. The ball mill was loaded with ball to powder weight ratio (BPR) of 10:1. The mechanically activated fly ash (MFA) was calcined at 800ºC for 3h for removing carbon, sulphur and other impurities before characterization. On the basis of results, MFA-15 possesses high surface area (17 m^2/g) comparatively and is chosen for further study.

2.3 Chemical Activation of Fly Ash

The chemical activation of MFA-15 was carried out in a stirred reactor by stirring 5M aqueous solutions of various mineral acids (HCl, HNO_3, H_2SO_4 and $HClO_4$) in the ratio of 1:2 (FA: Mineral acid) for 5 days at 110ºC temperature followed by washing till pH 7.0 with complete removal of soluble ionic species (Cl^-, NO_3^-, SO_4^{2-}, ClO_4^- etc.) and drying at 110ºC for 24h. The obtained solid products were calcined at 500ºC for 4h under static condition in a muffle furnace.

2.4 Characterization Techniques

The silica content of the fly ash samples after mechano-chemical activations were analyzed by X-ray fluorescence spectrometer (Philips PW1606). The BET surface area was measured by N_2 adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using Quantachrome NOVA s1000e surface area analyzer. Powder X-ray diffraction studies were carried out by using (Philips X'pert) analytical diffractometer with monochromatic CuK radiation (k = 1.54056 Å) in a 2 range of 0-80º. Crystallite size of the crystalline phase was determined from the peak of maximum intensity (2 = 26.57) by using Scherrer formula (Cullity et al., 2001) as Eq. (1) with a shape factor (K) of 0.9.

$$\text{Crystallite size = K. / W.cos} \tag{1}$$

where, W=Wb-Ws; Wb is the broadened profile width of experimental sample and Ws is the standard profile width of reference silicon sample. The FT-IR study of the samples was done using FT-IR spectrophotometer (Tensor-27, Bruker, Germany) in DRS (Diffuse Reflectance Spectroscopy) system by mixing the sample with KBr in 1:20 weight ratio. The Brönsted and Lewis acidity of the catalysts were measured by pyridine adsorbed FT-IR following the previously reported procedure (Khatri et al., 2010). The detailed imaging information about

the morphology and surface texture of the sample was provided by SEM-EDAX (Philips XL30 ESEM TMP).

3. RESULTS AND DISCUSSION

The variation in silica composition of FA with different milling time is shown in Table 1 which indicates that the silica percentage is increased marginally after milling for 5 to 15h (Paul et al., 2007; Blanco et al., 2005) but the specific surface area is increased from 9 to17 m^2/g. As compared with FA, the crystallite size is reduced from 33 to 21 nm as milling time was increase up to 15h.

Table 1. Characterization of fly ash before and after mechanical activation

Sample	Silica (wt %)	Crystallite size (nm)	Specific surface area (m^2/g)
FA	62	33	9
MFA-5	62.14	29	11
MFA-10	63.45	25	15
MFA-15	64.27	21	17

MFA-5: 5h mechanically activated fly ash; MFA-10: 10h mechanically activated fly ash; MFA-15: 15h mechanically activated fly ash

The characteristics of MFA-15 after chemical activation with various acids are given in Table 2 which indicates that the SiO$_2$ percentage of HClO$_4$ treated fly ash (PAFA) is higher (88%) compared to raw and treated with other acids.

Table 2. Characterization of MFA-15 after chemical activation with various mineral acids

Sample	Silica (wt %)	Crystallite size (nm)	Specific surface area (m^2/g)	Pore size (A)
HAFA	79	16	19	25
NAFA	84	14	21	24
SAFA	86	13	23	23
PAFA	88	11	26	21

HAFA- HCl treated FA; NAFA- HNO$_3$ treated FA; SAFA- H$_2$SO$_4$ treated FA; PAFA- HClO$_4$ treated FA

The changes in the crystalline phases in FA after ball milling have been monitored with the help of wide angle X-Ray Diffraction studies. The X-Ray diffraction patterns of the fresh as well as ball milled fly ash are given in the Fig. 1 (a-d). The peaks at 16.4º, 25.9º and 26.2º show mullite (alumino-silicate) phases while quartz (silica) exhibits strong peaks at 20.7º, 26.5º, 26.66º, 40.66º and 49.96º of 2 values. A peak at 34.856 indicates iron oxide phase (Willians et al., 2007). The ball milling of fly ash for 5 to 15h decreases the crystallite size from 33 to 21 nm resulting increasing amorphous content in it. The decrease in peak intensity of crystallite phase of quartz with ball milling hours is depicted in Fig. 1 (a-d).

XRD patterns of chemically activated MFA-15 with various acids (Fig. 2. a-d) show the presence of crystalline and amorphous phases. The characteristic peaks of quartz are more concentrated in these fractions and indicate increment in SiO$_2$ concentration. The amorphous phase of fly ash is increased more by HClO$_4$ treatment as compared with rest of three acids which results in decreased crystallite size up to 11nm.
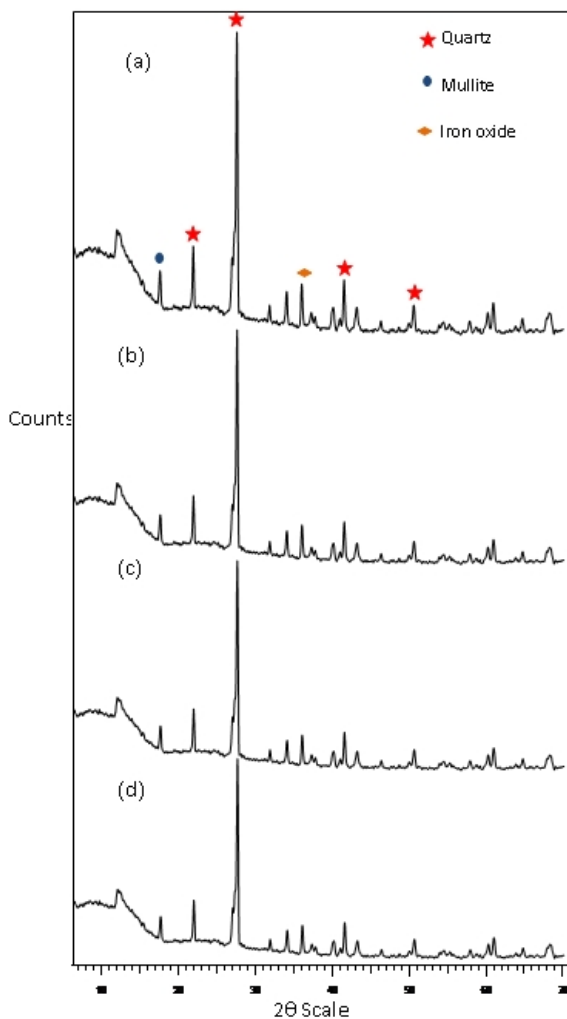
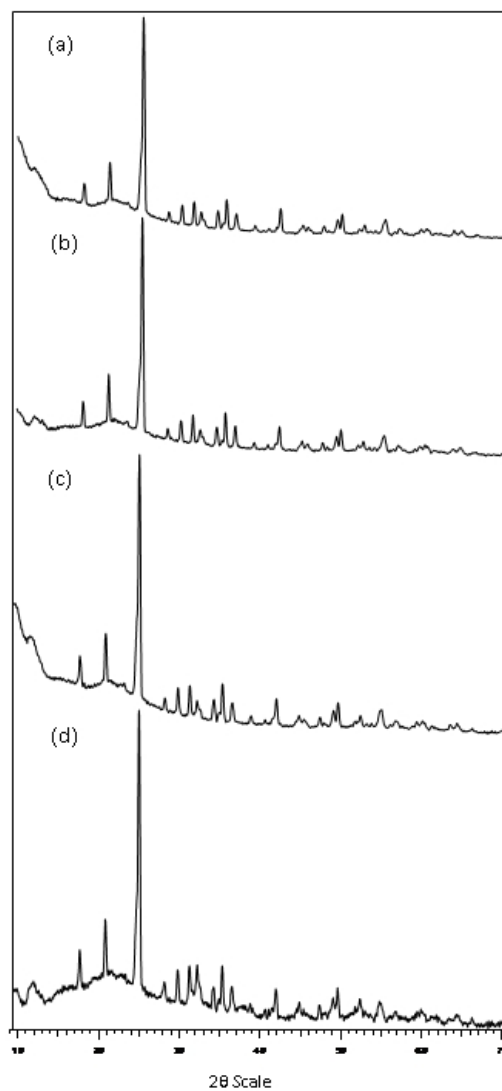**Fig. 1. XRD of (a) FA (b) MFA-5 (c) MFA-10 (d) MFA-15.**

Fig. 2. XRD of (a) HAFA (b) NAFA (c) SAFA, (d) PAFA.

The FT-IR spectra of FA and MFA-15 in Fig. 3a show broad band between 3400-3000 cm^{-1}, which is attributed to surface -OH groups of Si-OH and adsorbed water molecules on the surface. The increment in broadness after ball milling at 15h is an evidence for the breaking down of the quartz structure and formation of Si-OH groups (Patil et al., 2012). The dispersion forces increase so as the surface reactivity as the OH groups at the surface are increased (Rao et al., 2010). A peak at 1650 cm^{-1} in the spectra of fly ash is attributed to bending mode ($_{O-H}$) of water molecule. However, FT-IR studies clearly show changes in the broadening of IR peaks corresponding to Si-O-Si asymmetric stretching vibrations (1101, 1090 cm^{-1}) indicating structural rearrangement during 15h mechanical milling.

During chemical treatment, the FT-IR spectra of PAFA shows the tremendous increment in broadness at 3400-3000 cm^{-1} region as compared with SAFA, NAFA and HAFA which reflects strong hydrogen bonding between the hydroxyl groups due to increase in silica content and loss of significant amount of other components (Fig. 3b). The increased amorphous silica in the activated fly ash can be characterized by an intense band in the range 1000-1300 cm^{-1}, corresponding to the valence vibrations of the silicate oxygen skeleton. The main absorption band of the valence oscillations of the groups Si-O-Si in quartz appears with a main absorption maximum at 1160 cm^{-1} (Khatri et al., 2008).

In view of learning more about the development of the type of surface acidity after chemical activation of fly ash by different mineral acids pyridine-IR studies are performed and the FT-IR spectra obtained after pyridine adsorption of dehydrated acid activated fly ash samples are presented in Fig. 3c at the magnified range of 1600-1400 cm^{-1}. The peaks observed at 1540-1554 cm^{-1} and 1480-1490 cm^{-1} for different acid activated fly ash samples confirm the presence of sufficient Brönsted acidity on the surface due to formation of co-ordinated pyridine and hydrogen bonded pyridine respectively with surface silanol groups (Parry et al., 1963; Du et al., 2007). Small fraction of Lewis acidity (1445 cm^{-1}) also present in PAFA due to presence of $Al^{+3}/AlCl_3$ formed during digestion of fly ash with $HClO_4$. Some of the leached Al^{+3} ions from alumino-silicates skeleton forms either Al-OH bond without disturbing the mineral structure or converts into amorphous alumina phases stable at higher temperature generating Lewis acidity over surface (Jozefaciuk et al., 2002; Shaterian et al., 2008). The intensity of absorption band at 1540 cm^{-1} assign exclusively for Brönsted acidity is very low for HAFA and NAFA samples due to intense hydrogen bonding at higher concentration of HCl and HNO_3. The band at 1490 cm^{-1} almost disappeared for alumina- silicate mineral activated by 2M and higher concentration of HCl (Ravichandran et al., 1997).
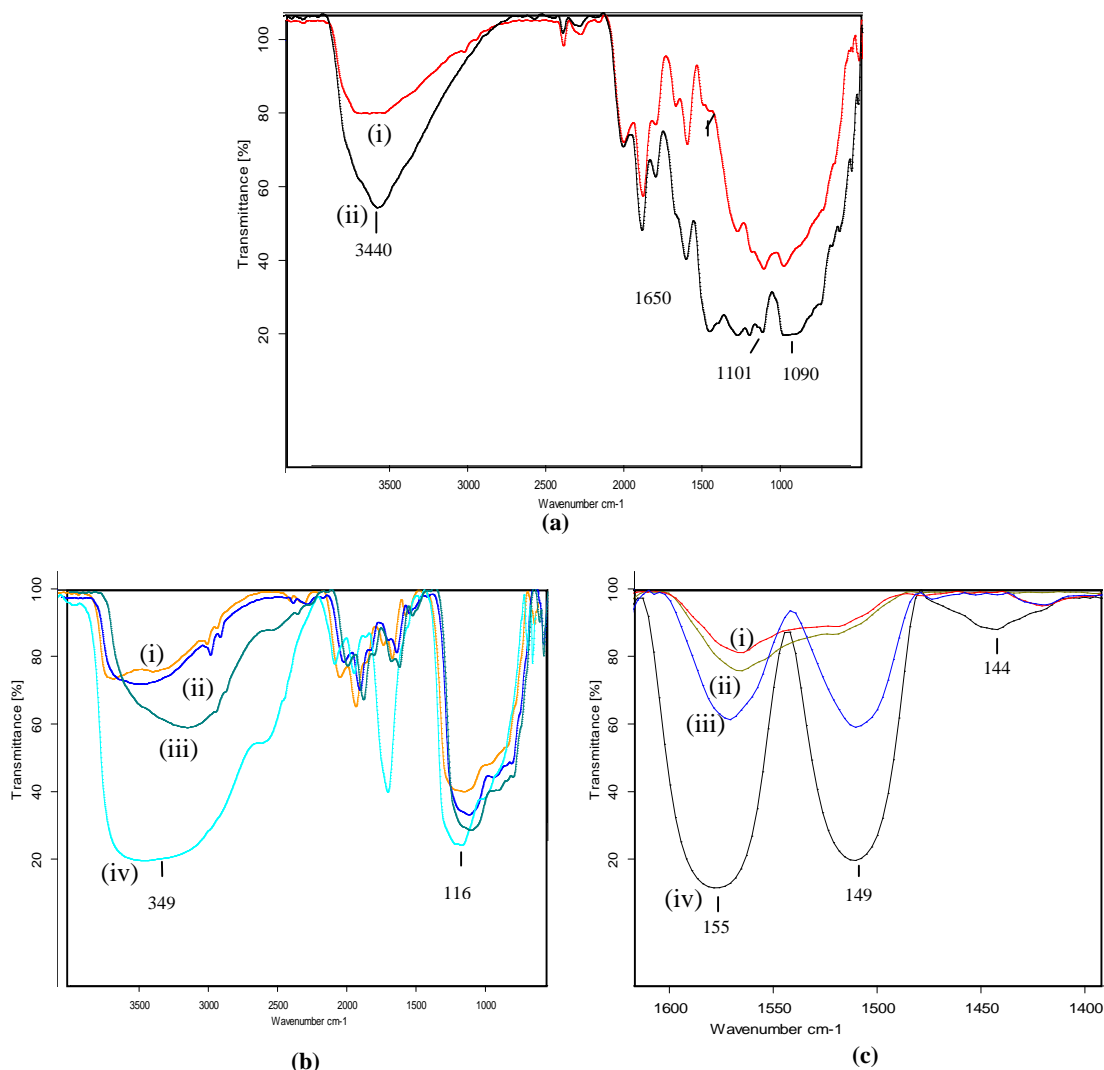
Fig. 3. (a) FT-IR spectra of (i) FA and (ii) MFA-15, (b) FT-IR spectra of (i) HAFA (ii) NAFA (iii) SAFA (iv) PAFA, (c) Magnified pyridine adsorbed FT-IR spectra of (i) HAFA (ii) NAFA (iii) SAFA (iv) PAFA

The morphology of the pure, mechanically and chemically activated fly ash is shown in Fig. 4. (a-f). The SEM photograph of pure fly ash demonstrates particles of different shapes and sizes, hollow cenospheres, irregularly shaped unburned carbon particles, mineral aggregates and agglomerated particles, whereas the typical SEM image of MFA-15 shows the structural break down of larger particles and increased surface roughness (Fig. 4b). The smooth spherical cenospheres are affected most resulting remarkable changes in morphology. After chemical activation with various acids, rough cenospheres are transformed into agglomerations of more amorphous undefined shapes with no observation of crystal formation as seen in SEM micrographs presented in Fig. 4(c-f). SEM micrograph of PAFA is seen with large gelatinous mass formed due to the breaking and dissolution of alumino-silicate phases modifying the surface morphology greatly.
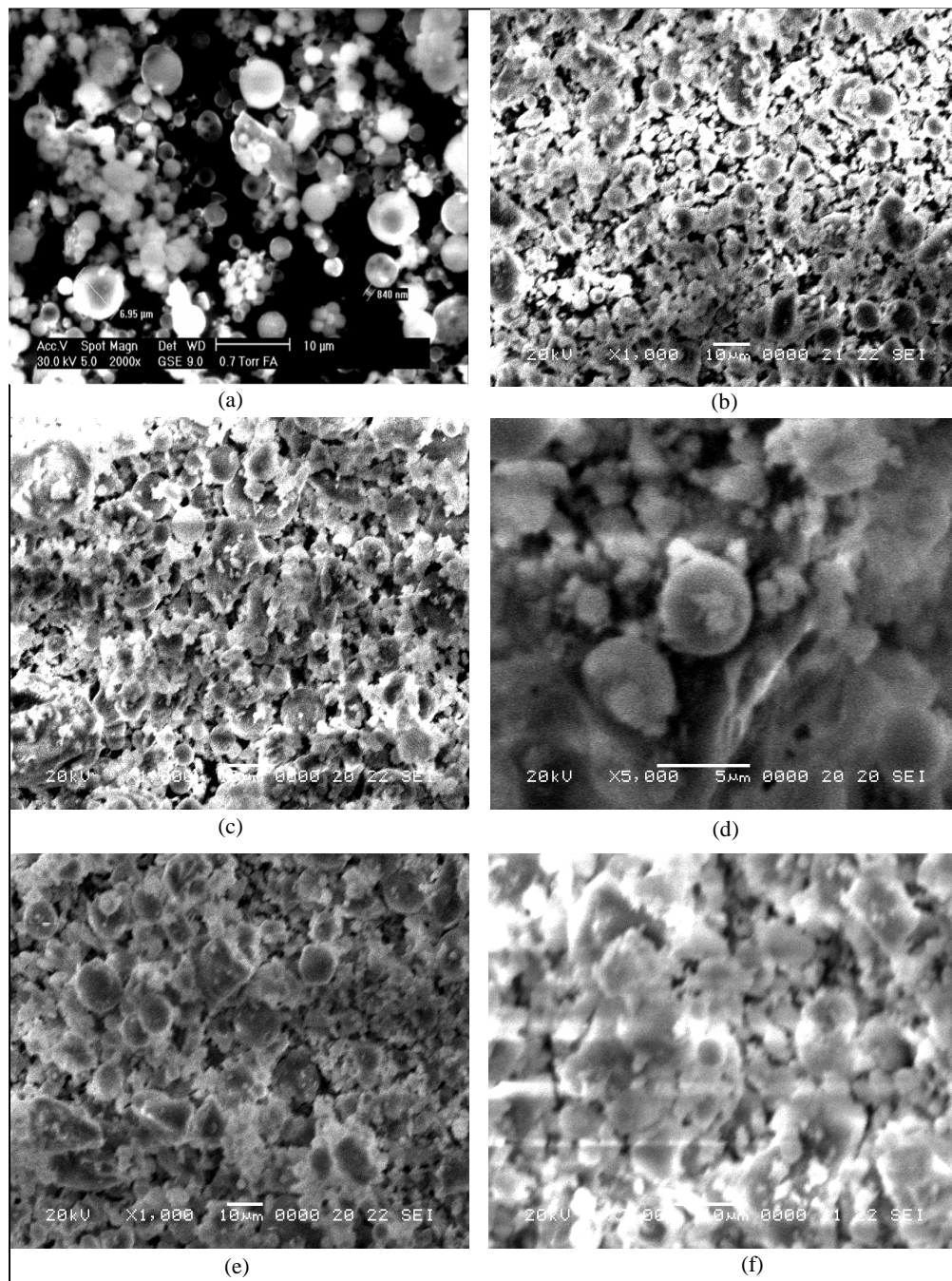
Fig. 4. SEM images of (a) FA (b) MFA-15 (c) HAFA (d) NAFA (e) SAFA (f) PAFA

4. CONCLUSION

The mechanical activation of fly ash using high energy ball mill affects the surface properties of the fly ash more than the chemical properties. With increase in milling duration from 5h to 15h silica percentage is marginally changed whereas the crystallite size of crystalline phase is reduced from 33 to 21 nm and specific surface area is increased from 9 to17 m^2/g. Chemical activation of MFA-15 with 5M concentration of different acids (HCL, HNO_3, H_2SO_4 and $HClO_4$) results in increased silica percentage and amorphous phase. The specific surface area is increased maintaining order of increment as $HClO_4 > H_2SO_4 > HNO_3 > HCl$. FT-IR studies confirmed the generation of surface silanol groups (Si-OH) with strong hydrogen bonding during acid activation. Pyridine FTIR spectra evidenced with presence of Brönsted acid sites in all acid activated samples. The intensity of peaks at 1545 and 1490 cm^{-1} assigned to protonic acidity was maximum for PAFA. Only PAFA resulted with presence of small amount of Lewis acidity due to surface Al-OH groups. It is concluded that the mechno-chemical activation can generate sufficient activity on fly ash surface rendering its potential application in heterogeneous catalysis.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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