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Publisher's version / Version de l'éditeur:

Proceedings of 5th International Symposium Nanoporous Materials, 2008, pp. 677-685, 2008

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SEPARATION OF HIGH SURFACE AREA MINERAL SOLIDS FROM SUNCOR COKE FLY ASH

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For the past several years, we have been involved in the development of technically and economically feasible separation techniques for the recovery of by-products from oil sands industry wastes for use as potentially marketable products. The concepts of industrial ecology and an increased societal awareness of waste management continue to provide motivation for the discovery of new applications for these materials, as well as the value-added products that may be derived. In this investigation we have applied a fractionation methodology developed previously to separate high surface area mineral solids from Suncor coke fly ash for potential commercial applications. This fraction has been characterized by EDS elemental analysis, X-ray diffraction, XPS, SEM, solid-state NMR and surface area measurements. The efficiency of separation and the characteristics of the separated mineral fraction from Suncor fly ash have been compared with the data for the mineral solids from Syncrude fly ash reported previously.

1. Introduction

The production of refinery grade oil from the Alberta oil sands deposits as currently practiced by Syncrude and Suncor, generates a substantial amount of waste including coke, fly ash, coarse sand and fine tailings [1]. Under current production conditions, a plant producing $15,900 \text{ m}^3/\text{day}$ ($100,000 \text{ bbl./day}$) of synthetic crude oil requires the processing of $100,000 \text{ m}^3/\text{day}$ ore which results in a tailings stream consisting of $100,000 \text{ m}^3$ of coarse sand, $2,000 \text{ m}^3$ of coke, 100 m^3 of fly ash and $20,000 \text{ m}^3$ of Mature Fine Tailings (30% solids) [2]. As a result, large inventories of process-affected materials are accumulating. The

major concern regarding these wastes is a question of the volumes involved. The reduction in the volume of the produced wastes by recycling would be economically and environmentally desirable.

The recognition and exploitation of the useful intrinsic properties of waste materials are becoming more important owing to increasing awareness of environmental issues. However, the commercial recycling of oil sands industry wastes is essentially non-existent because of the lack of economical technology, and the absence of compelling incentives in the form of government regulations. It is anticipated that high disposal costs and increased regulatory pressures to minimize landfill disposal options will increase the incentives for development of improved technology and economics for recycling many of the potentially useful components from oil sands mine wastes.

For the past several years, we have been developing separation techniques for the recovery of by-products from oil sands industry wastes [3-11]. The principal objective of this work has been to develop technically feasible separation techniques for potentially marketable products. Recently, we have developed a fractionation methodology for the separation of high surface area mineral solids from oil sands coke fly ash for potential use as polymer reinforcements after surface modification [11]. In this investigation we have applied this methodology to Suncor coke fly ash. The separated mineral fraction has been characterized by EDS elemental analysis, X-ray diffraction, XPS, SEM, solid-state NMR and surface area measurements. The efficiency of separation and the characteristics of the separated mineral fraction from Suncor fly ash have been compared with the data for the mineral solids from Syncrude fly ash reported previously [11].

2. Materials and Methods

2.1. Materials

A sample of Suncor fly ash originating from the burning of coke produced from Athabasca oil sands bitumen, and obtained from Alberta Research Council sample bank in 1983 was used in this investigation. This sample had been characterized previously [12]. All other reagents were obtained from Aldrich and used as received.

2.2. Measurements

^{29}Si NMR spectra were recorded at 40 MHz on a TecMag Apollo series spectrometer. Samples were spun at 4.5 kHz in zirconia rotors in a Doty 7mm

MASS probe. The 90 degree pulse length was 10 micro-seconds. A 10 second delay between pulses was found to be adequate, and spectra were accumulated overnight. ^{27}Al NMR spectra were recorded at 78 MHz on a Bruker AMX-300 spectrometer, using a Doty 5mm mass probe, a 5mm zirconia rotor and 8 to 8.5 kHz MASS. A pulse length of 1 microsecond was used, and 1000 scans were acquired, with a 0.5s delay between scans. A noticeable probe background was subtracted. The chemical shifts of aluminium and silicon were referenced against external 1 M aqueous aluminium nitrate and neat tetra-methyl silane (TMS) respectively.

XPS was performed with a Physical Electronics (Perkin Elmer, Eden Prairie, MN, USA) model 550 instrument. Monochromatic Al K α radiation was used. The dry samples were pressed into indium foil for analysis. Survey spectra were collected using pass energies of 188 eV, while high resolution spectra were recorded with a 22 eV pass energy. An electron flood gun was used to neutralize the charge during the experiment. Binding energies were referenced to the carbon-carbon bond, which was assigned a binding energy of 284.6 eV. Atomic compositions were estimated using a standard program provided with the instrument. During analysis, the pressure inside the instrument was always below 5×10^{-9} torr (<0.7 μPa).

Specific surface areas, pore volumes and pore size distributions were determined using a Micromeritics Gemini III 2375 apparatus, using nitrogen as adsorbent at 77K. The application of the BET equation was used to obtain the adsorption data [13]. The pore-size distribution of the samples was calculated from desorption isotherms, and the BJH method was used for calculations [13-15]. The density of the materials was determined by a Pycnometry measurement with helium using Micromeritics Accupyc 1330 apparatus.

X-ray powder diffraction data were collected between $2\theta = 15^\circ - 70^\circ$ with a scan rate of $2^\circ/\text{min}$ at room temperature on Scintag XDS 2000 with a theta-theta geometry and a copper X-ray tube. The diffractometer had a pyrolytic graphite monochromator in front of the detector. The samples were mounted on a zero background sample holder made of an oriented silicon wafer.

Scanning electron micrographs were recorded using a Hitachi Field Emission Scanning Electron Microscope (SEM) Model S-4800 fitted with an Oxford Inca Energy Dispersive Spectrometer (EDS) used for elemental analysis. It was operated at 1.2keV electron volts and a current of 10 μA . The working distance was 8 mm. Elemental analysis is semi-quantitative and is measured at a working distance of 15 mm with a 20 keV beam energy and 20 μA of current. An average of five determinations was carried out.

Particle size analysis. The particle size distribution of the samples were determined using highly diluted dispersions in 1% aqueous solution of Na_3PO_4 . The measurements were performed using Malvern Zetasizer Model 3000HS particle analyzer, which is based on the principle of laser ensemble light scattering. The particles are introduced to the analyzer beam in a sample presentation cell located in the optical unit. For each sample, the mean value of five replicate determinations were calculated. Values reported are the mean value for two replicate samples.

2.3. Procedures

The procedures used for the separation of mineral solids from Suncor fly ash have been reported previously [11].

3. Results and Discussion

3.1. Effectiveness of leaching process

Representative elemental analyses of the raw and treated ash samples are shown in Table 1. Compared with the Syncrude fly ash sample [11], the acid leaching of the Suncor fly ash was less effective. The treatment of the carbon free sample of fly ash from Suncor, results in only small changes, in the elemental composition of the sample. Ti, V and Ni were not amenable to leaching, which is consistent with the previous investigations [17]. Complete dissolution of sulphur moiety suggests that it may not be part of fly ash matrix. The treatment also selectively removed a smaller amount of other elements including Si and Al. However, the Si:Al ratio remained unchanged.

Table 1. The effect of acid leaching on elemental compositions of ashed fly ash samples

Sample	Elemental composition, W.W%											
	Si	Al	Fe	Mg	Ti	Ca	Na	K	S	V	Ni	Si:Al
untreated	21.0	12.2	7.5	0.7	2.0	1.2	0.7	1.1	3.1	2.7	1.2	1.7
Treated	18.4	10.8	5.9	0.4	2.1	0.5	0.3	0.8	-	2.6	1.2	1.7

Table 2 lists physico-chemical properties of the fly ash samples. The data for a Syncrude fly ash sample is from a previous investigation [11], and has been included for comparison purposes. It is obvious from this data, that the treatment of the two fly ash samples resulted in a significantly different end products. Compared with the Syncrude fly ash sample, the yield of high surface area mineral fraction from Suncor fly ash sample was essentially double. This is because of the higher ash content of Suncor fly ash and the lower leachability of

inorganic salts from the ash matrix. The density of the acid leached Suncor fly ash sample was slightly higher than the corresponding sample from Syncrude. This is because of the higher content and lower leachability of heavy metals in Suncor fly ash samples. The specific surface area of Suncor fly ash increases over 20 times on treatment. However, the surface area of treated Suncor fly ash sample was four time lower than the surface area of Syncrude fly ash sample. Relatively low cost and higher surface area of the treated fly ash samples render these materials as excellent candidates for potential applications in catalysis and/or catalyst support.

Table 2. Physico-chemical characteristics of Suncor Fly Ash samples

Sample ID	Yield	Color	Density (g cm ⁻³)	Surface Area (m ² /g)	Av. Pore Dia (nm)	Av. particle size (nm)
Untreated ashed Suncor FA	100	Black	2.7	1.7	3.4	870 ± 40
Treated ashed Suncor FA	35.6	Dark brown grey	2.8	35.6	3.4	530 ± 50
Untreated ashed Syncrude FA*	100	Black	2.3	20.6	6.3	1.1 µm
Treated ashed Syncrude FA*	18.4	Light grey	2.6	140.1	3.4	320

* Ref 11

The particle size of the separated mineral solids is significantly smaller than the original fly ash samples (~500 nm vs 5 µm). Removal of un-burnt carbon and admixed as well as surface adsorbed inorganic salts from fly ash may have resulted in the deaggregation of mineral particles. This explains the particle size reduction of the separated mineral solids. Smaller particle size in combination with large specific surface area render these mineral solids as ideal candidates for applications as inorganic fillers for clay-reinforced polymer nanocomposites [18]. The surface modification of these solids may render them compatible with the hydrophobic polymers.

3.2. X-Ray Diffraction

Figure 1 compares the XRD profiles of the Suncor fly ash samples before and after treatment. The mineral composition of the fly ash sample did not change significantly after treatment. Based on the comparison of the reported XRD patterns of similar fly ash samples [19, 20] the major phases identified included mullite, quartz and pseudobrookite. Mineral phases present in smaller amounts included: illite, albite, TiO₂, hematite and hercynite. A minor amount of

kaolinite was also identified in the untreated ashed sample. However, kaolinite was not present in the treated fly ash sample.

Figure 1 XRD patterns of Suncor Fly ash

3.3. Surface Analysis

The survey spectrum of fly ash samples showed Al, Si, Mg, Ti, V, C and O in both untreated and treated fly ash samples. Iron, potassium, calcium, sodium and sulphur were only detected in the untreated samples. XPS provides information on the top 10 nm of the surface. This suggests that these elements were selectively leached from the surface. The presence of carbon could not be confirmed by Leco combustion analyses, suggesting its presence only on the surface due to the adsorption from atmosphere.

3.4. Scanning Electron Micrography

Figure 2 show scanning electron micrograph (SEM) pictures of untreated and treated Suncor fly ash at various magnifications. Both samples show smooth spherical particles of cenospheres morphology. The diameters of these spheres range from 4-15 μm for the untreated sample and 2-10 μm for the treated sample. These spheres are interdispersed with crystalline inorganic compounds. Spheres in the untreated samples also have adsorbed inorganic matter on them that is removed by acid leaching in the treated sample. The crystalline compounds observed confirmed the presence of mullite and quartz as detected

by XRD. The admixture consists of rods, needles, platlets and porous material in the nm size range.

Figure 2. SEM photographs of: 2a-2c. Untreated Suncor fly ash; 2d-2f. Treated 1A

3.5. Solid-State NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy has been shown to be capable of providing considerable information about the structures of aluminosilicates and clay minerals [21-26]. The position of silicon resonance is affected primarily by its degree of polymerization, and by the nature of the nearest neighbor cations, whereas the aluminum resonance is sensitive primarily to the number of atoms in its immediate coordination environment, i.e. to whether the aluminum is four- or six-fold coordinated by oxygen. Solid-state NMR is particularly sensitive to amorphous phases or small crystallites many of which cannot be detected by XRD.

Figure 3 shows ^{29}Si MAS NMR spectrum of the treated sample of Suncor fly ash. The spectrum shows one major broad peak centered at -110 ppm and two shoulders at -104 and -97 ppm. The broad strong peak at the highest field

corresponds to the un-substituted $Q^4(0Al)$ units and is close to those of quartz, cristobalite and perhaps some amorphous silica [27-29]. The lines at -104 and -97 ppm can be assigned to the $Q^4(1Al)$ and $Q^4(2Al)$ units respectively in accordance with the chemical shifts in zeolite type aluminosilicates [29]. These assignments also suggest the presence of feldspars and mullite [30, 31].

Figure 3. ^{29}Si MAS NMR spectra of treated Suncor Fly Ash

The ^{27}Al -MAS spectra of raw and treated ashed Suncor fly ash samples, are shown in Fig. 4. The spectra contain two major resonances, centered at 50 and 0 ppm, which correspond to four and six coordinate aluminum species respectively [32]. The octahedral component is attributed to the aluminum in the mullite present in the ash [31]. Since ^{29}Si NMR show peaks in the range -97 to -104 attributable to $Q^4(1$ and $2Al)$, it is postulated that the Al^{IV} broad peak centered at 50 ppm arises from the Al atoms in the three dimensional silica framework [28].

Figure 4. ^{27}Al MAS NMR spectrum of treated Suncor Fly Ash

4. Conclusion

A technically feasible fractionation scheme developed previously for the separation of high surface area mineral solids from fly ash samples was successfully applied to the oil sands coke fly ash sample from Suncor. Suncor coke fly ash was found to be less amenable to acid leaching as compared to the Syncrude coke fly ash. The characteristics of the separated mineral solids such as specific surface area and morphology were also significantly different for the two fly ashes. However, compared with the untreated sample the increase in the specific surface area of the treated Suncor fly ash sample was over 20 times. SEM images for these solids show smooth spherical particles of cenospheres morphology. The particle size of the fly ash also decreased significantly after treatment as a result of leaching of the adsorbed as well as some admixed inorganic salts. Surface area and pore size determine the accessibility to active sites and this is often related to catalytic activity and selectivity in catalyzed reactions. High surface area, relatively low cost and micro-pores render these materials as excellent candidates for potential applications in heterogeneous catalysis. Other potential applications could include: adsorbent, microporous material for example for gas storage after porosity modification, as polymer reinforcements after surface modification, and flattening (mating) agent in the paint and lacquer industry.

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Nanoporous Materials

Proceedings of the 5th International Symposium

Vancouver, Canada 25 – 28 May 2008

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