Powder Technology 338 (2018) 233–242

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Surface functionalization of coal and quartz with aniline: A study on work function and frictional charge

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ARTICLE INFO

Article history:
Received 17 February 2018
Received in revised form 30 June 2018
Accepted 6 July 2018
Available online 09 July 2018

Keywords:
Tribo-electrification
Coal preparation
Work function
DFT
Surface functionalization

ABSTRACT

The present study deals with the surface functionalization of coal and quartz using aniline with an intention to achieve a higher differential charge facilitating their separation in an electric field. The Fourier Transform Infrared (FT-IR) spectroscopic studies confirm the adsorption of aniline on the coal and quartz surface after chemical conditioning. The surface work function of both coal and quartz are found to decrease after being treated with aniline. However, the work function of coal decreases to a greater extent (3.464%) in comparison to quartz which decreases by 1.016%. Thereby, the net work function difference between the coal and quartz particles increases by 129% (from 0.089 eV to 0.204 eV) after chemical treatment. The work function of the copper tribo-charging medium falls between the work function values of both the original and the aniline treated coal and quartz samples. Therefore, the charge density of the treated coal particles increases on contact with copper while there is a minor reduction in charge of the treated quartz. The charge acquisition data corroborates well with the surface work function data. Density Functional Theory (DFT) based simulation has been carried out to validate the trend of the decrease in work function after the treatment with aniline. The DFT calculations are found to be in good agreement with the experimentally measured change in the surface work function data of both coal and quartz sample after chemical treatment.

1. Introduction

Tribo-electrostatic separation is a dry method to process fine particulates. It has gained considerable attention in recent years in the field of mineral processing [1–4]. It has also application in coal preparation [5–12] and recycle industries [13–17]. There has been an ever-increasing focus on dry processes due to the increasing water scarcity and depleted grade of coal. The tribo-electrostatic process for coal preparation mainly consists of two steps: particulate tribo-charging and separation of charged particles in an electric field. The detailed separation process is described in our earlier communications [9–11]. In tribo-charging, the particles get charged on contact with another particle or with the surface of other material. The polarity and magnitude of charge acquired by the particle are based on their work function difference. Hence, the work function is the driving force for the acquisition of differential charge between the particles. The transfer of electron occurs between them until the Fermi levels equalize [7,18]. It is well documented that electron donation and acceptance are the inherent properties of the particles based on their work function. During frictional charging, the surface properties of materials control the electron transfer [7]. Two of the key factors that determine the trajectory of a particle in an electric field is its magnitude and charge polarity. The particle with higher charge magnitude travels a longer distance in an electric field [19]. Therefore, it has a better possibility of separation. It is reasonable to believe that the charge magnitude may increase by widening the work function difference between two dissimilar materials.

We have established in our research work that the surface energy of a particle changes during contact electrification [20]. There exists a correlation between the charge generated by the particles and their surface electronic state, either acceptor (acid) or donor (base). Thereby, a correlation also exists between surface energy and work function [20,21]. Consequently, an artificial modification of surface energy may also alter the work function. The adsorption of molecules on the organic and inorganic substrate is an attractive approach to control the surface and interface electronic properties [18,22,23]. It is a well-established fact that the Fermi level is modified by surface functionalization [18]. Charge transfer to and from the adsorbed species can shift the Fermi level by a significant fraction of an electron volt [24,25]. Therefore, the donor/acceptor properties of the material can also be altered by surface functionalization. The adsorption of the molecule on the substrate can modify the surface electronic properties based on two principal mechanisms [26] i.e. (1) The bonding of molecules to the surface results in the

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https://doi.org/10.1016/j.powtec.2018.07.029
0032-5910/

elimination of surface charge by quenching of gaps states, (2) The surface charge localization may occur by chemisorption with the creation of states in the substrate band gap. In addition, molecular deposition can change surface dipoles by the adsorption of a molecule containing inherent dipole moment because of the charge transfer process that supplements bond formation. Moreover, the presence of surface charge may lead to band bending. When an acceptor molecule approaches the surface, an unfilled molecular orbital shifts downward by its interaction with the substrate [27]. The broadened molecular orbital accepts an electron from the substrate and forms a Helmholtz layer on the substrate surface as per the uncertainty principle applied to electron location and energy. As a result, an electric field is established, and bands are bent upward near the substrate surface. However, the electrons transfer from the molecule to the substrate in the case of a donor molecule and a downward bending occurs [28]. Several authors suggested that both band bending and the presence of surface dipoles alter the work function of the substrate [29–31].

Our work has earlier established that, on contact with a copper tribo-charging medium, the carbonaceous matter gets a positive charge while the mineral matters such as kaolinite, quartz, and illite get charged negatively [9–11]. Zhou and Moon [32] showed that chemical treatment improves the separation of sylvite from helite minerals. Based on the contact charge measurement of these minerals, they assumed that there is a change in work function after chemical pre-treatment. However, the relevant work function values were not reported. Several authors also claimed efficient separation of coal and mineral matter after chemical pre-treatment [33–35]. Trigwell and Mazumder [7] used X-ray and UV-photo electron spectroscopy to study the effect of surface composition on the work function of tribo-charging media.

The present research work aims to enhance the differential charge between coal and quartz by surface functionalization using aniline as the dopant. In this article, we have examined the change in charge and the work function of coal and quartz before and after the surface pre-treatment with aniline. Kelvin probe is used to measure the work function while DFT based simulation is used to validate the experimental results.

2. Experimental

2.1. Materials and methods

The coal used in this study was received from JSW Ltd., Karnataka, India. Jigging process was used to reduce the ash to 7.12% while ensuring no-chemical contamination. The low ash coal was generated by using wet Alljig jigging machine. The feed size fraction of coal used for the jigging operation was −6 + 1 mm. The coal particles were stratified into different layers based on their density. The top layer with low ash content was skimmed out and used for the present studies. The high purity quartz (99%) was collected from Mayurbhanj, Odisha, India. The quartz sample was cleaned with dilute hydrochloric acid followed by a rigorous washing in distilled water to remove the contamination of iron oxides. The coal and quartz sample were ground and classified into different size fractions. The coal and quartz particles were dried in an oven for one hour at 105 °C and kept in a desiccator for various studies. The size fractions of −300 + 106 μm of both coal and quartz were utilized for charge measurement studies. The −300 + 106 μm particles were further ground to −106 μm and used for FTIR and Kelvin probe studies. The proximate and ultimate analysis of coal was carried out using the ASTM-D-3174 method using a LECO make Thermo Gravimetric Analyzer (TGA) 601 and LECO CHNS 628 analyzer. The results of proximate and ultimate analysis of coal are given in Table 1. The particle size analysis and surface area measurement were carried out using a Malvern particle size analyzer (Mastersizer 2000) and a Smart BET surface area analyzer (SORB 92/93) respectively. The densities of quartz and coal were measured using a Helium-Mercury pycnometer (Smart Pycno 30). The XRD spectra were recorded using a PAN analytical X'pert pro instrument with cobalt target.

Table 1
Proximate and ultimate analysis of coal on dry basis.

VM, %	Ash, %	F.C., %	GCV, Kcal kg^{-1}	C, %	N, %	S, %	H,%	O, %
27.30	7.12	65.58	7169	79.20	1.86	0.39	5.06	13.49

The particle size analysis of coal and quartz used for charge and work function measurement is shown in Fig. 1. The result indicates that the d_{50} and d_{80} of quartz and coal particles used for work function measurements are 63, 112 μm; and 45, 79 μm, respectively. The d_{50} and d_{80} particle size of quartz and coal particles used for charge measurement are 266 and 400 μm respectively. The densities of coal and quartz particulates were found to be 1265 and 2650 kg m^{-3}, respectively. The BET surface areas of quartz and coal particles were found to be 0.665 and 9 m^2 g^{-1}, respectively. The proximate analysis of coal indicates that it contains 7.12% ash, 27.30% of volatile matter (VM) and 65.58% of fixed carbon (FC). The ultimate analysis of coal suggests that it contains 79.20% C, 1.86% N, 0.39% S, 5.05% H and 13.49% O on a dry basis. The gross calorific value of coal was found to be 7169 Kcal/kg. The XRD spectra as depicted in Fig. 2 are showing the characteristic peaks of the quartz minerals thereby confirming its purity.

2.2. Particle tribo charging

The charge measurement of coal and quartz were carried out in a rotary cylindrical drum made up of copper as shown in Fig. 3(a). The inside length and diameter of the tribo-charging drum were 0.196 m and 0.108 m, respectively. The drum was rotated at a speed of 35 rpm. The sample was weighed and subjected to tribo-charging for a fixed interval of time such as 15, 30, 45 and 60s. After tribo-charging, the charge acquired by the particles was measured using a Faraday cup connected to a Keithley electrometer 6517 E as shown in Fig. 3(b). The Faraday cup consists of two stainless steel cups. The base of the outer cup is made up of PTFE to isolate the cups from each other. The copper drum was removed from the driving roll machine, and charged particles were poured into the inner cup. The static charge was measured with the electrometer. The sample in the cup was weighed to calculate the charge to mass ratio of the particles. Each charge measurement was repeated five times to verify the repeatability and consistency of the measurement process. The mean value of the charge was considered, and the associated errors were estimated. All the charge measurements were carried out at 20% relative humidity. The tribo-electrostatic charge measurements, separation system, and its accessories were kept in a closed room to maintain humidity level using a Bry-Air FFB 2000

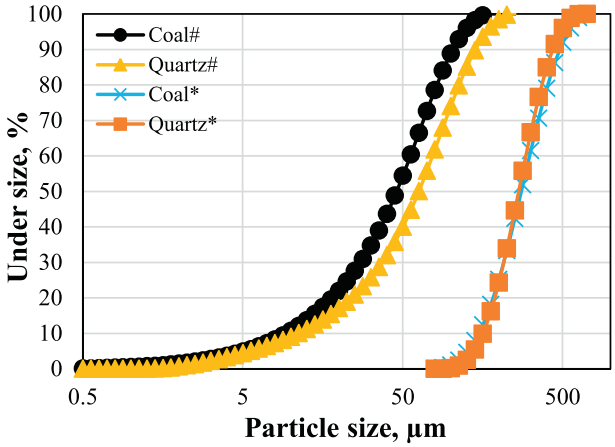

Fig. 1. Particle size distribution of coal and quartz used for Charge (*) and work function (#) measurements.