



## Adsorptive Desulfurization of Model Gasoline Using Attapulgite and Acid-Treated Attapulgite Adsorbents

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The objective of this work is to examine the performance of raw attapulgite and acid treated attapulgite for adsorptive desulfurization of model gasoline at room temperature. The effect of the inner structures of the adsorbent on sulfur removal efficiency was discussed. Several analytical instruments were used to analyze the adsorbents. The results indicated that the raw attapulgite had the greatest affinity for thiophene, which may be ascribed to the complicated and blocked mesoporous structure and more adsorptive activated sites on its surface.

**Keywords:** Attapulgite, Adsorbent, Desulfurization, Model gasoline.

### INTRODUCTION

It is well-known that the sulfur content is one of the index that decides the quality of transportation fuel which is either eco-friendly or detrimental to environment<sup>1,2</sup>. Many countries are enacting laws limiting the maximum sulfur emission of transportation fuels, particularly gasoline and diesel fuels. For example, America has limited the maximum sulfur concentration in highway gasoline to 10 ppm since 2009, down from 50 ppm<sup>1,3-5</sup>. Europe also envisaged EU-wide changeover to 10 ppm sulfur in gasoline for road transport. Other countries such as Japan and Canada have also issued similar regulations. It is expected that the requirements of sulfur level in fuels will become increasingly stricter in the near future for all countries due to environmental concerns. However, reducing the sulfur content of transportation fuels is a challenge to petroleum industries. The difficulty is that the cost of reduction of the sulfur level from 500 to 10 ppm using conventional technologies such as hydrodesulfurization (HDS) process is much higher than that needed in the desulfurization of crude oils to 500 ppm<sup>6,7</sup>.

The presence of "inactive sulfurs" like thiophene and its derivatives (primarily benzothiophenes and dibenzothiophenes) is refractory and they usually have to be treated under high pressure of hydrogen at elevated temperatures in the hydrodesulfurization process<sup>6,8</sup>. Oxidative desulfurization (ODS) is

an effective alternative method that has been developed for more than decades. During oxidative desulfurization process, oxidants such as organic peracids, H<sub>2</sub>O<sub>2</sub>/solid redox catalysts, *t*-butylhydroperoxide/transition metaloxides, H<sub>2</sub>O<sub>2</sub>/tungsten salts and H<sub>2</sub>O<sub>2</sub>/tungsten/ionic liquids complexes are usually selected to oxidize sulfur-containing compounds such as sulfoxide and sulfone contained in raw petroleum<sup>8-12</sup>. The oxidized products are then removed by means of solvent extraction or adsorption. The oxidants can be recovered for cyclic use in next process<sup>13-15</sup>. In this process, however, the presence of a large quantity of olefin and thiophene may disable to a great extent the fluid catalytic cracking (FCC) gasoline desulfurization to be fully carried out. The (reactive) adsorption desulfurization is a promising approach which is based on the selective attraction of the sulfur-containing compounds (or reactive products) by an adsorbent at its surface and then separation of the loaded adsorbent from oil. This technology appears particularly attractive due to its sulfur removal efficacy, lower cost and simpler operation. In the past decades, an array of researches on fuel desulfurization by adsorption strategy has been reported<sup>3,8-12,16-21</sup>. A number of adsorbents have been developed and tested with model or commercial fuel for desulfurization. Most of the adsorbents are focused on metal oxide-based adsorbents supported on zeolites, activated carbon, silica and alumina, *etc.* Natural minerals as desulfurization adsorbents were seldom reported.

Attapulgite is a hydrated magnesium aluminium silicate occurring in nature as a fibrillar silicate clay mineral that features ribbons of a 2:1 structure. It has permanent negative charges on its surface. Attapulgite particles, seen under an electronic microscope, are associated in fibrous bundles similar to those of hay<sup>22-25</sup>. Attapulgite was first utilized in 1940s and has been mainly used as an adsorbent, catalyst carrier, densifying agent, adhesive and food additive<sup>23,25</sup>. However, no systematic investigation on its adsorption desulfurization from fluid catalytic cracking (FCC) gasoline was found in literatures. In the present work, we studied the performance of attapulgite as an adsorbent before and after acid-treatment to remove thiophene in model gasoline. To examine the role played by the adsorbent, its structural analyses in each step of the absorption process were carried out.

## EXPERIMENTAL

**Adsorbent preparation:** Attapulgite was obtained from Xuyi city, Jiangsu province, China. Acidification treatment was carried out using hydrochloric acid in order to remove impurities and soluble substance prior to use. The attapulgite was put into hydrochloric acid solution (attapulgite/hydrochloric acid = 1/3, mass ratio), stirred for 24 h at 40 °C and then filtered, washed with distilled water to pH 6-7. The resultant solid was dried at 105 °C and then crushed and sieved. Those of particle size in the range of 125-180 μm (80-120 mesh) was collected for use. For comparison, raw attapulgite was also prepared by screening and classification.

**Adsorbent characterization:** All of the adsorbents before and after acid-treatment were characterized by X-ray diffraction (XRD) on a PANalytical X'Pert PRO MPD spectrometer diffractometer (CuK $\alpha$ ), XRF on a Tiger S8 Bruker, FT-IR on a Nicolet Nexus 870, TEM on a TECNAI G2 TF20 and XPS on a Thermo Fisher Scientific ESCALAB 250Xi.

**Adsorption performance studies:** To study the removal effect of thiophene on the surface of attapulgite, model oil was prepared by dissolving appropriate amount of thiophene in cyclohexane, giving rise to a S-content of 3000 ppm of oil sample. The tests of adsorptive desulfurization were performed in a 50 mL flask equipped with stirrer and condenser. In a typical run, 1 g of adsorbent, 10 mL of model oil was respectively added to the flask that was previously maintained in a water bath of 25 °C. After stirring for 0.5 h, the resulting mixture was stayed, the clear upper solution was analyzed by a Varian CP-3800 gas chromatograph with Varian CP-8410 automatic sampler, pulsed flame photometric detector (PFPD) and quartz capillary column (HP-5NS).

## RESULTS AND DISCUSSION

**Adsorbent characterization:** Elements of the natural attapulgite were analyzed in the form of oxide percentage as 5.05 % MgO, 14.74 % Al<sub>2</sub>O<sub>3</sub>, 66.05 % SiO<sub>2</sub>, 1.52 % CaO, 1.48 % Na<sub>2</sub>O, 0.068 % MnO, 1.87 % K<sub>2</sub>O, 0.300 % P<sub>2</sub>O<sub>5</sub> and 1.16 % SO<sub>3</sub>. The chemical composition of acid-treated attapulgite was as follows: 3.99 % MgO, 14.96 % Al<sub>2</sub>O<sub>3</sub>, 68.84 % SiO<sub>2</sub>, 0.412 % CaO, 1.47 % Na<sub>2</sub>O, 0.039 % MnO, 1.80 % K<sub>2</sub>O, 0.163 % P<sub>2</sub>O<sub>5</sub> and 0.245 % SO<sub>3</sub>. Fig. 1 shows the TEM images of raw and acid-treated attapulgite adsorbent. As shown clearly in Fig. 1a, the boundaries of crystal structure of raw

attapulgite are blurred. In addition, the morpha and pore channel structure is complicated and the deposit of long or short rod of attapulgite and grainy black impurities features disorderly clusters. In comparison with raw attapulgite, after acid treatment, attapulgite densely aggregate and beam are effectively separated, exhibiting a needle like crystal structure. Moreover, its specific surface area and dispersion is remarkably improved (Fig. 1b). The FT-IR spectra of raw attapulgite and acid-treated attapulgite are shown in Fig. 2(A). The bands at 3620 cm<sup>-1</sup> of raw attapulgite and 3620 cm<sup>-1</sup> for treated attapulgite are associated with the stretching vibrations of hydroxyl groups which are coordinated to the octahedral magnesium and the tetrahedral silicon. The bands at 3560 and 3580 cm<sup>-1</sup> for raw attapulgite and 3550 and 3590 cm<sup>-1</sup> for acid-treated attapulgite are attributed to the symmetric and asymmetric stretching of molecular water coordinated to the magnesium (or alternative cation for attapulgite) at the edges of the channels. The bands at 3420 and 1650 cm<sup>-1</sup> for raw attapulgite and 3420 and 1650 cm<sup>-1</sup> for treated attapulgite are attributed to the adsorbed water and zeolitic water, respectively. The bands at 1030 cm<sup>-1</sup> for raw attapulgite and 1030 cm<sup>-1</sup> for treated attapulgite are attributed to the asymmetric stretching modes of Si-O-Si<sup>26-30</sup>. To examine the structure modification of attapulgite before and after acid-treatment, the XRD analysis was performed. As shown in Fig. 2(B), for raw attapulgite, the characteristic peaks of 2θ lie at 8.32° (110), 19.80° (040), 20.84° (121) and 26.62° (311) (Fig. 2(B)a). The strong peak 2θ of 26.62° may be ascribed to the characteristic absorption peak of quartz in its internal structure. Its crystal structure hardly varied after being acid-treatment [Fig. 2(B)b], indicating that the texture of the attapulgite is almost maintained after acid treatment. These observations suggest that the chemical composition of acid-treated attapulgite has changed, but the its main surface structure did not vary apparently.

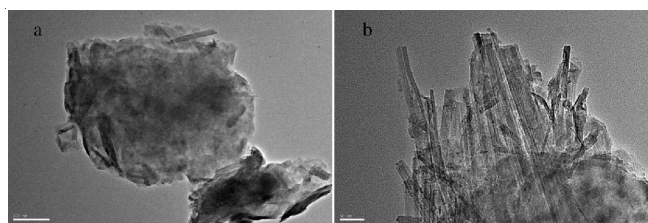


Fig. 1. TEM images of raw and acid-treated attapulgite adsorbent a: Raw attapulgite, b: Acid-treated attapulgite

**Adsorption experiment:** There are many factors such as adsorbent type, feedstock quality and process parameters can influence the degree of desulfurization of petroleum fuels. Fig. 3 shows the removal results of thiophene by natural attapulgite and acid-treated attapulgite. The data clearly indicate that natural attapulgite (Fig. 3-2) is more effective than the acid-treated attapulgite (Fig. 3-3) to remove the thiophene contained in model oil. This may be due to the complicated and blocked mesoporous structure and more active adsorption sites of natural attapulgite. In addition, the crystal structure of acid-treated attapulgite is very straightway and well-bedded, but a part of positive ions coordinated in the octahedron of attapulgite would be dissolved out when it was acid-treated<sup>23</sup>. The thiophene molecules may enter into the structure channel of

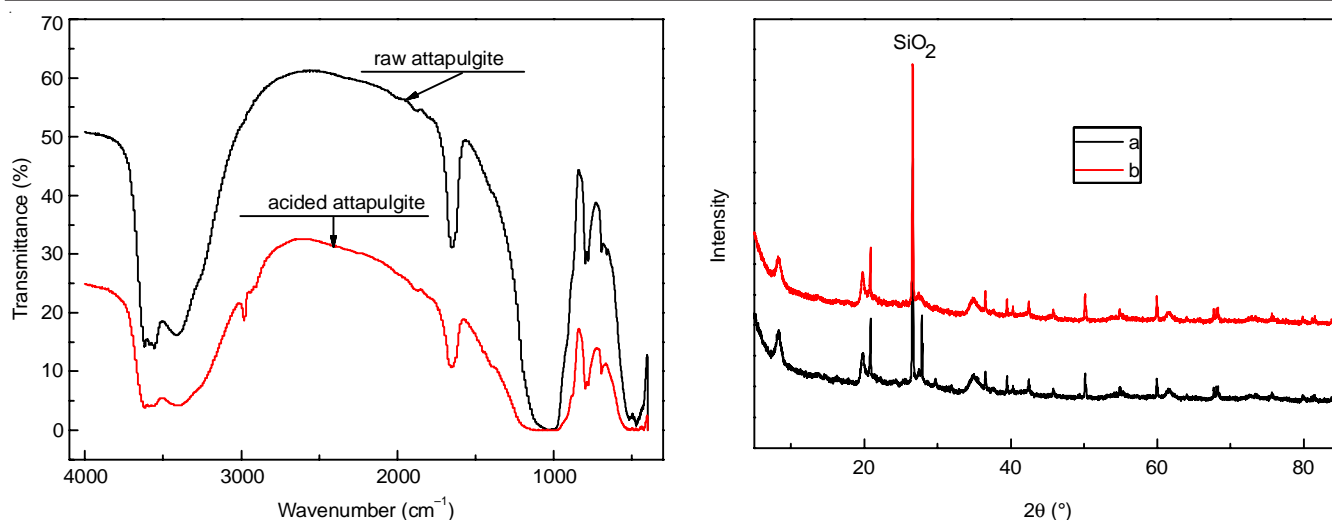


Fig. 2. FT-IR and XRD spectra of raw and acid-treated attapulgite adsorbent; a: Raw attapulgite, b: acid-treated attapulgite

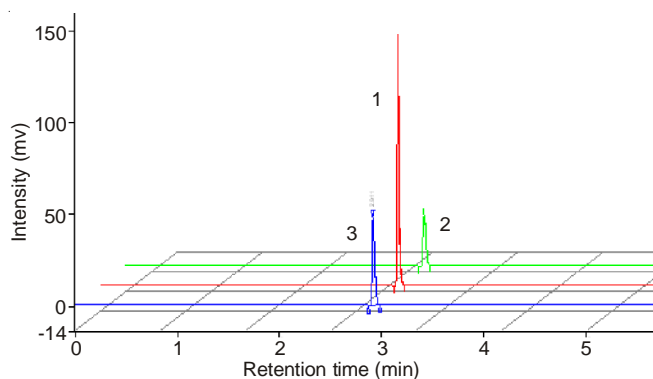


Fig. 3. Chromatograph of thiophene in model oil absorbed by raw attapulgite and acid-treated attapulgite; (1) Raw model oil with S-content of 3000 ppm, (2) Model oil absorbed by natural attapulgite; (3) Model oil absorbed by acid-treated attapulgite

acid-treated attapulgite, but the straightway, well-bedded and lack-active crystal structure led to the decrease of the adsorption efficiency. Hence, according to our preliminary results, we are convinced that the circumstances of active adsorption sites and acid activation are different at present. The acid-activated sites are coupled with thiophene more easily because of the acid-base electronic effect<sup>22-29</sup>, but the effect of the space-blocked or initial active adsorption sites are more powerful than that of the unobstructed passage ways or acid-activated sites (Table-1). In order to further examine the absorption performance of thiophene in model oil by natural attapulgite and acid-treated attapulgite, TEM images of two adsorbents after adsorption of model oil were taken. As shown in Fig. 4, the structure channel of raw attapulgite adsorbent is unblocked and unordered (Fig. 4c) and the crystal beam also becomes more obvious than before adsorption (Fig. 1a). It shows that

the impurities in raw attapulgite are washed to remove by the flowing model oil. Meanwhile, the images also exhibit that the thiophene has agglomeration to some extent due to the complicated and blocked mesoporous structure (marking as shown in Fig. 4c). In addition, as shown in Fig. 4d, the results are in accordance with previous experiments that showed the thiophene has agglomeration to some extent clearly, although the characteristic is not obvious from XRD spectra. To confirm the composition and chemical state of element on the surface of the raw and acid-treated attapulgite adsorbent after adsorption of model oil. Fig. 5(A) shows the XPS spectra of the raw and acid-treated attapulgite adsorbent after adsorption of model oil and mark the energy spectrum of C<sub>1s</sub>, O<sub>1s</sub> and S<sub>2p</sub>. Comparison energy spectrum, it can be seen that S<sub>2p</sub> appeared in the XPS spectra, which illustrates that thiophene has been introduced to the attapulgite adsorbent. Fig. 5(B) illustrates high resolution XPS spectra corresponding to C<sub>1s</sub>, O<sub>1s</sub> and S<sub>2p</sub> in the samples (e) and (f). It is noted that these binding energies are shifted slightly to higher scope, which indicates that the electronic binding energy between acid-treated attapulgite and thiophene is larger than that between raw attapulgite and

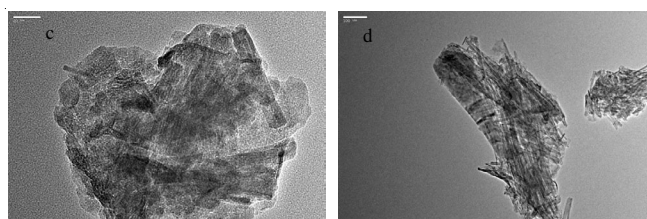


Fig. 4. TEM images of the raw and acid-treated attapulgite after adsorption of model oil; c: Raw attapulgite adsorbent after adsorption of model oil; d: Acid-treated attapulgite adsorbent after adsorption of model oil

TABLE-1  
CONCRETE CHROMATOGRAPH DATA OF THIOPHENE IN MODEL OIL

Sample	Peak no.	Ret. Time (min)	Time offset (min)	Area (counts)
1	1	2.904	0.000	175717
2	1	2.919	0.000	55154
3	1	2.911	0.000	80862

<sup>1</sup>Raw model oil with S-content of 3000 ppm; <sup>2</sup>Model oil absorbed by natural attapulgite; <sup>3</sup>Model oil absorbed by acid-treated attapulgite

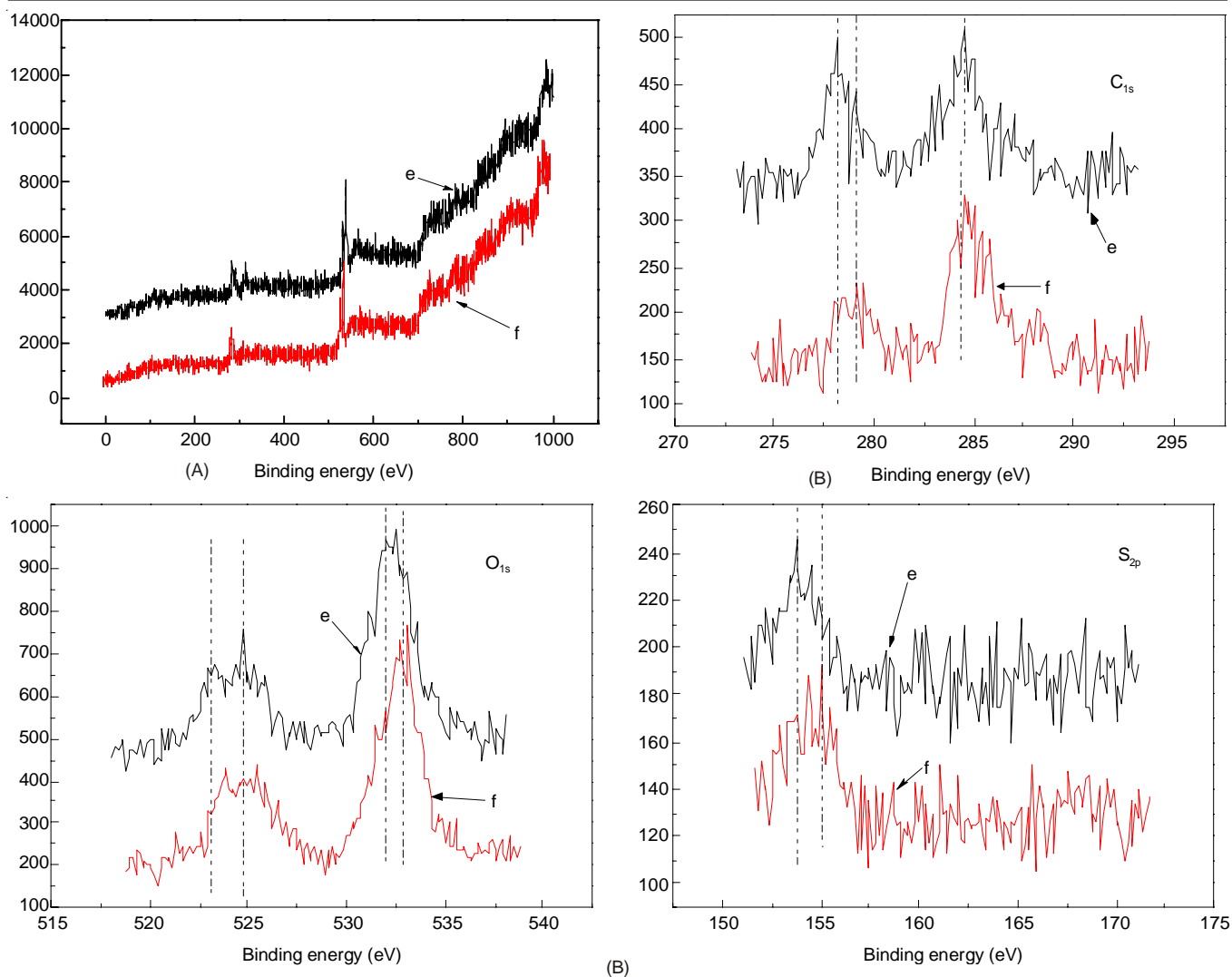


Fig. 5. (A) XPS spectra of raw and acid-treated attapulgite after adsorption of model oil; (B) Binding energy of  $C_{1s}$ ,  $O_{1s}$  and  $S_{2p}$  in the samples (e) and (f). e: Raw attapulgite after adsorption of model oil; f: Acid-treated attapulgite after adsorption of model oil

thiophene. In other words, the electrons transfer from thiophene and electron density of thiophene decreases.

### Conclusion

The performance of raw attapulgite and acid treated attapulgite for adsorptive desulfurization of model gasoline at room temperature were examined. The inner structures of adsorbent on sulfur removal efficiency were intensively discussed. Several analytical instruments were used to analyze adsorbents. According to the results of XRD and FT-IR, the attapulgite crystal structure has no apparent change interestingly. The results indicated that natural attapulgite is more effective than the acid-treated attapulgite to remove the thiophene contained in model oil due to the complicated and blocked mesoporous structure and more active adsorption sites. Although the crystal structure of acid-treated attapulgite is very straightway and well-bedded. The binding energies shifted slightly to higher energies shows that the electronic binding energy between acid-treated attapulgite adsorbent and thiophene is larger than that between raw attapulgite adsorbent and thiophene.

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### REFERENCES

1. C. Song, *Catal. Today*, **86**, 211 (2003).
2. S. Dasgupta, P. Gupta, A. Aarti, A. Nanoti, A.N. Goswami, M.O. Garg, E. Tangstad, Ø.B. Vistad, A. Karlsson and M. Stöcker, *Fuel*, **108**, 184 (2013).
3. A.S. Hussain and B.J. Tatarchuk, *Fuel*, **107**, 465 (2013).
4. B. Pawelec, R.M. Navarro, J.M. Campos-Martin and J.L.G. Fierro, *Catal. Sci. Technol.*, **1**, 23 (2011).
5. A. Stanislaus, A. Marafi and M.S. Rana, *Catal. Today*, **153**, 1 (2010).
6. Y. Zhu, Z. Hua, X. Zhou, Y. Song, Y. Gong, J. Zhou, J. Zhao and J. Shi, *RSC Adv.*, **3**, 4193 (2013).
7. M. Dougherty, R.L. Dymond, T.J. Grizzard Jr., A.N. Godrej, C.E. Zipper and J. Randolph, *Hydrocarbon Eng.*, **12**, 33 (2007).

8. J.M. Campos-Martin, M.C. Capel-Sanchez, P. Perez-Presas and J.L.G. Fierro, *J. Chem. Technol. Biotechnol.*, **85**, 879 (2010).
9. Z. Hasan, J. Jeon and S.H. Jhung, *J. Hazard. Mater.*, **205-206**, 216 (2012).
10. B. Li, W. Ma, J. Liu, C. Han, S. Zuo and X. Li, *Catal. Commun.*, **13**, 101 (2011).
11. D. Zhao, J. Wang and E. Zhou, *Green Chem.*, **9**, 1219 (2007).
12. Y. Jia, G. Li and G. Ning, *Fuel Process. Technol.*, **92**, 106 (2011).
13. L. Chen, S. Guo and D. Zhao, *Chin. J. Chem. Eng.*, **15**, 520 (2007).
14. S. Otsuki, T. Nonaka, N. Takashima, W. Qian, A. Ishihara, T. Imai and T. Kabe, *Energy Fuels*, **14**, 1232 (2000).
15. F. Al-Shahrani, T. Xiao, S. Llewellyn, S. Barri, Z. Jiang, H. Shi, G. Martinie and M.L.H. Green, *Appl. Catal. B*, **73**, 311 (2007).
16. M. Xue, R. Chitrakar, K. Sakane, T. Hirotsu, K. Ooi, Y. Yoshimura, M. Toba and Q. Feng, *J. Colloid Interface Sci.*, **298**, 535 (2006).
17. S. Hernandez, D. Fino and N. Russo, *Chem. Eng. Sci.*, **65**, 603 (2010).
18. A.J. Hernández-Maldonado, S.D. Stamatias, R.T. Yang, A.Z. He and W. Cannella, *Ind. Eng. Chem. Res.*, **43**, 769 (2004).
19. S. Kumagai, H. Ishizawa and Y. Toida, *Fuel*, **89**, 365 (2010).
20. H. Farag, *J. Colloid Interf. Sci.*, **307**, 1 (2007).
21. K. Zhang, Y. Liu, S. Tian, E. Zhao, J. Zhang and C. Liu, *Fuel*, **104**, 201 (2013).
22. E. Cao, R. Bryant and D.J. Williams, *J. Colloid Interf. Sci.*, **179**, 143 (1996).
23. J. Huang, Y. Liu, Q. Jin, X. Wang and J. Yang, *J. Hazard. Mater.*, **143**, 541 (2007).
24. E. Galan, *Clay Miner.*, **31**, 443 (1996).
25. J. Zhang, S. Xie and Y. Ho, *J. Hazard. Mater.*, **165**, 218 (2009).
26. R.L. Frost, G.A. Cash and J.T. Kloprogge, *Vib. Spectrosc.*, **16**, 173 (1998).
27. R.L. Frost, O.B. Locos, H. Ruan and J.T. Kloprogge, *Vib. Spectrosc.*, **27**, 1 (2001).
28. J. Madejova, *Vib. Spectrosc.*, **31**, 1 (2003).
29. D.M.A. Melo, J.A.C. Ruiz, M.A.F. Melo, E.V. Sobrinho and M. Schmall, *Micropor. Mesopor. Mater.*, **38**, 345 (2000).
30. D. Araujo Melo, J.A.C. Ruiz, M.A.F. Melo, E.V. Sobrinho and A.E. Martinelli, *J. Alloys Comp.*, **344**, 352 (2002).