



Research paper

Carbon nanostructures-modified expanded vermiculites produced by chemical vapor deposition from ethanol

Aluir D. Purceno^{b,c}, Breno R. Barrioni^b, Anderson Dias^b, Geraldo M. da Costa^b, Rochel M. Lago^a, Flávia C.C. Moura^{a,*}^a Departamento de Química, Universidade Federal de Minas Gerais, Belo Horizonte, MG, 31270-901, Brazil^b Departamento de Química, Universidade Federal de Ouro Preto, Ouro Preto, MG, 35400-000, Brazil^c Verti Ecotechnology Company, Belo Horizonte, MG Brazil

ARTICLE INFO

Article history:

Received 21 February 2010

Received in revised form 17 June 2011

Accepted 19 June 2011

Available online 15 August 2011

Keywords:

Vermiculite
Hydrophobization
Nanofibers
Oil removal

ABSTRACT

In this work, chemical vapor deposition using ethanol and FeMo catalysts at 600, 700, 800 and 900 °C was used to modify the surface of expanded vermiculite (EV). Scanning electron microscopy, Raman spectroscopy, X-ray diffraction, Mössbauer spectra, N₂-BET surface areas, and carbon elemental analyses suggested that the FeMo catalyst promoted 2–3% growth of carbon in different forms, mainly nanofibers, on the EV surface. The amount of 2–3% carbon produced by ethanol/CVD process on EV produced a 500% increase in the absorption of soybean, diesel and engine oil, with a concomitant decrease on water absorption. These results were discussed in terms of a hydrophobization of the EV surface by the carbon structures and a “sponge-like” effect due to the entangled nanofibers structure, as it was observed by microscopy, and an increase of N₂-BET surface area from 3 m² g⁻¹ for EV up to 21 m² g⁻¹ for the ethanol CVD-treated EV.

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1. Introduction

Catalytic chemical vapor deposition (CVD) synthesis of carbon nanotubes (CNT) and nanofibers using different carbon sources, e.g. CH₄, C₂ and C₃ hydrocarbons and CO with a large variety of catalysts, e.g. Fe/Mo, Ni, Co, has been extensively investigated in the last years (Chatterjee and Deopura, 2002; Dupuis, 2005; Oncel and Yurum, 2006).

The CVD process is technically simple, relatively low cost, produces high yields, and it is possible to control several features of the carbonaceous materials. Ethanol as the carbon source for catalytic CVD has not been extensively investigated. Previous work in our group has shown that ethanol in the presence of Fe catalysts produces a remarkable amount of carbon nanofibers.

Vermiculite is a clay mineral with many potential industrial and environmental applications (Calle and Suquet, 1988; Santos and Navajas, 1976). Upon sudden heating of vermiculite at temperatures higher than 700 °C, the water molecules evaporate abruptly, the vermiculite separates into packets of layers, and a highly-developed porous structure is produced. As a result, the clay volume increases up to 20 times and its density strongly decreases to ca. 0.05–0.30 g cm⁻³ (Santos, 1975; Santos and Navajas, 1976). This vermiculite floats on water (Santos and Navajas, 1976) and, due to the strong capillary

action of the slit-shaped pores, has been investigated for the removal of spilled oil from water surfaces. (Leão et al., 1996; Machado, 2000; Machado et al., 2006a; 2006b; Martins, 1990). Large water uptake and low hydrophobic organic contaminant absorption are negative properties of vermiculites due to the strongly hydrophilic clay surface. Several works and patents report different processes to hydrophobize the vermiculite surface. Some of the investigated approaches are the functionalization of the EV surface with hydrophobic molecules such as siloxanes (Martins, 2006), coating the EV surface with a hydrophobic polymer, e.g. polystyrene (Machado et al., 2006a), and even with waxes, e.g. carnauba wax (Mysore et al., 2005).

Recently, carbon deposition using methane in a catalytic CVD process was used to modify the EV surface (Moura and Lago, 2009). The CVD produced different carbon structures, such as single and multiwall nanotubes, on the EV surface, resulting in a great increase on the oil removal capacity.

In this work, we report the hydrophobization of vermiculite surface by covering the surface with a carbonaceous layer, mainly of nanofibers, by chemical vapor deposition (CVD) using ethanol as the carbon source.

2. Experimental

The vermiculite used in this work has the composition (Al_{0.30}Ti_{0.04}Fe_{0.63}Mg_{2.00})(Si_{3.21}Al_{0.79})O₁₀(OH)₂Mg_{0.13}Na_{0.02}K_{0.10}(H₂O)_n. Vermiculite was exfoliated by heating in a quartz tube at 1000 °C for 60 s. The exfoliated vermiculite (EV) was impregnated with Fe(NO₃)₃ and Mo(NH₄)₂O₂ solutions using methanol as solvent and dried at

* Corresponding author. Tel.: +55 31 34095719; fax: +55 31 34095700.
E-mail address: flaviamoura@ufmg.br (F.C.C. Moura).

80 °C for 3 h. About 1 g of the differently-prepared EVs were placed in 30 mm diameter quartz tube, heated at 10 °C min⁻¹ up to 600–900 °C, and then subjected to ethanol/CVD process with an 80 mL min⁻¹ N₂ carrier gas flow for 1 h. The reaction lasted for 60 min unless stated otherwise and afterward the system was cooled under argon flow.

The vermiculite-carbon composites were characterized by Raman spectroscopy by using a Horiba/Jobin-Yvon LABRAM-HR spectrometer. Experimental data were obtained with the 632.8 nm line of a helium-neon laser (effective power of 6 mW at the sample's surface) as excitation source, diffraction gratings of 600 and 1800 grooves/mm, Peltier-cooled CCD detector, confocal Olympus microscope (100× objective), and experimental resolution of typically 1 cm⁻¹ for 10 accumulations of 30 s.

Mössbauer spectra (MS) were collected at room temperature with a spectrometer using a constant-acceleration drive with triangular reference signal, 512 channels, and in the velocity range of -11 to +11 mm s⁻¹ (increment of ~0.09 mm s⁻¹). The velocity was calibrated from the MS of a standard α -Fe foil at room temperature. The spectra were computer-fitted either with discrete Lorentzian sextets and/or doublets or with distributions of magnetic hyperfine fields.

The powder XRD data were obtained in a Rigaku model Geigerflex using Cu K α radiation scanning from 2 to 75° at a scan rate of 4° min⁻¹. Scanning electron microscopy (SEM) analyses were carried out in a Jeol JKA 8900RL. Total carbon elemental analyses were made using a PERKIN ELMER CHN-PE-2400 and N₂-BET surface areas were measured using a Quantachrome Autosorb 1 using 22 nitrogen adsorption/desorption cycles.

Absorption experiments on simulated oil spills used 10 mL of oil (soy bean cooking oil, engine oil and diesel) in 100 mL water. The vermiculites that were hydrophobized by ethanol/CVD (100 mg) treatment were then added to the oil/water mixtures. After 5 min, the vermiculites were removed from the oil/water mixtures using a simple metal sieve and excess oil and water were allowed to drain for 3 min. Previous optimization experiments showed that the EV immediately saturates with both oil and water and contact times of 5 min are enough to reach equilibrium. Also, the drain time in the sieve has no significant influence on the amount of oil and water absorption. After absorption, the materials were weighted to determine the total amount of oil and water retained. For vegetable and engine oils the materials were dried at 80 °C overnight to remove water and weighed again to determine both the water and oil absorptions. For soybean oil, engine oil, and diesel, the vermiculite materials were initially dried at 80 °C overnight to remove any adsorbed water and weighed again after the absorption experiments to determine both water and oil absorption. For the diesel experiments, samples could not be dried at 80 °C because both water and a significant fraction of diesel would be volatilized. Therefore, the diesel vermiculite samples were weighed to determine the total amount of water and diesel absorbed. The vermiculite samples were then extracted with 20 mL of hexane to extract absorbed diesel. The hexane extracted was analyzed using a Shimadzu 17A gas chromatography equipped with FID detector and a 30 m Alltech EC-Wax capillary. From a simple calibration, the amounts of absorbed diesel were calculated from total peak areas.

3. Results and discussion

3.1. Preparation and characterization of EV/carbon composites

The vermiculite/carbon composites were prepared by impregnating EV with Fe(NO₃)₃ and Mo(NH₄)₂O₂ to obtain vermiculites with 10% Fe and 0.5% Mo. The EV samples with Fe and Mo were subjected to the ethanol/CVD process to produce carbon filaments. After CVD treatment, all samples were completely black due to carbon deposition and the vermiculite lamellar and porous structure was intact and mechanically resistant.

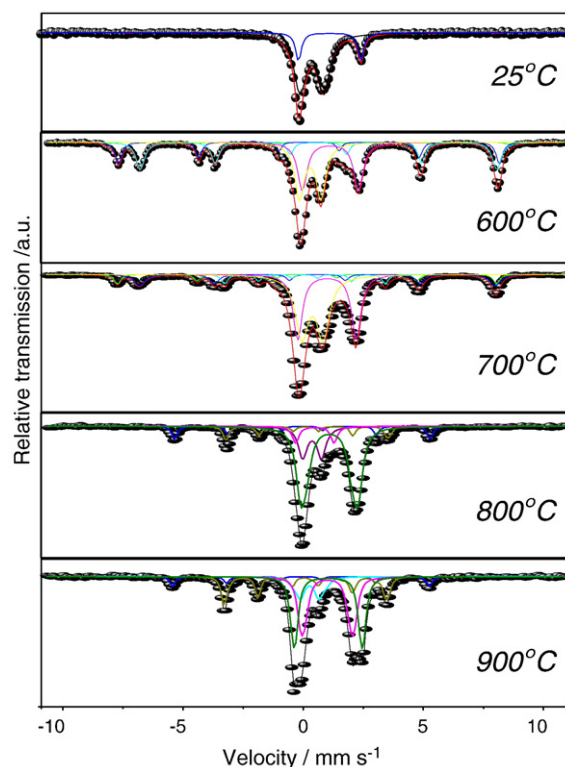


Fig. 1. Room-temperature Mössbauer spectra of EV/Fe_{10%} samples before and after ethanol/CVD treatment at different temperatures.

The EV/Fe_{10%} and EV/Fe_{10%}Mo_{0.5%} materials were characterized using Mössbauer spectroscopy (Figs. 1 and 2) after ethanol/CVD treatment.

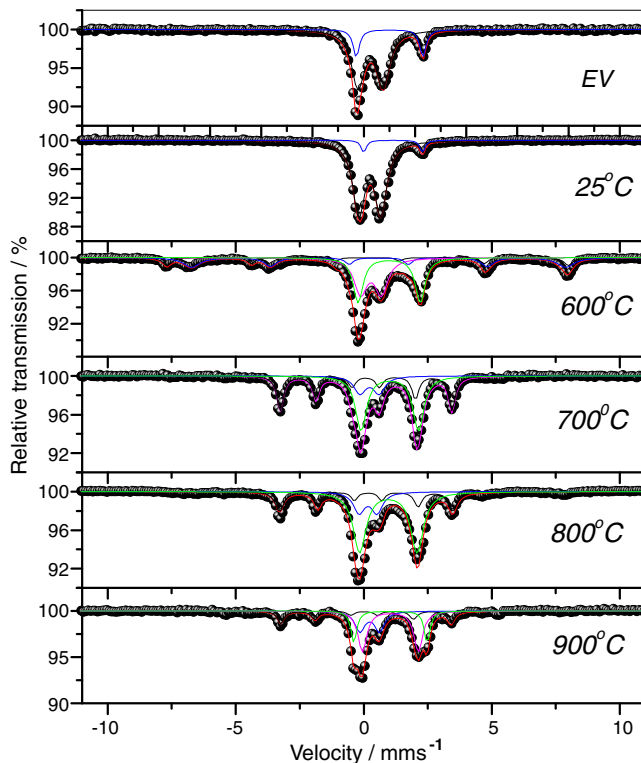


Fig. 2. Room-temperature Mössbauer spectra of EV/Fe_{10%}Mo_{0.5%} samples before and after ethanol/CVD treatment at different temperatures.

Fig. 1 shows the Mössbauer spectra for the samples EV/Fe_{10%} after CVD at different temperatures and the hyperfine parameters are shown in Supplementary material Table 1S. Mössbauer spectra of the vermiculites before ethanol/CVD treatment present a doublet due to Fe²⁺ in silicates ($\delta=1.25\text{ mm s}^{-1}$ and $\Delta E_Q = 2.30\text{ mm s}^{-1}$) with a relative area of 6%. There is also an Fe³⁺ doublet due to EV structural or Fe³⁺ impregnated on the EV surface ($\delta = 0.35\text{ mm s}^{-1}$ and $\Delta E_Q = 0.86\text{ mm s}^{-1}$) with a relative area of 94%. After ethanol/CVD at 600 °C, the Fe³⁺ was consumed and 42% magnetite (Fe₃O₄) and 2% hematite (Fe₂O₃) phases were formed on the vermiculite surface. Also, the sample shows the presence of 26% Fe²⁺ and 30% Fe³⁺ that was dispersed outside or within the clay structure. More reduced species were formed as Fe⁰ and 10% iron carbide (Fe₃C) after 800 °C treatment, and after 900 °C treatment, the carbide concentration reached 20%. For example, large amounts of Fe²⁺ were still present in vermiculite samples after ethanol/CVD at 800–900 °C. Unreduced iron species were likely protected in the EV structure or within the interlamellar space.

Mössbauer spectra are shown for EV samples with molybdenum (Fe_{10%}Mo_{0.5%}) before and after ethanol/CVD treatment at different temperatures (Fig. 2) with hyperfine parameters shown in Table 2S of Supplementary material. Mössbauer analysis identified magnetite with 34% relative area and a dispersed Fe²⁺ phase which formed in the material after ethanol/CVD treatment. At 700 °C, the magnetite phase was totally consumed and replaced with carbon deposited as iron carbide (Fe₃C) with a relative area of 37%. At higher temperatures (i.e. 800–900 °C), lower amounts of carbide were formed. It is interesting that Mo favored carbide formation in large amounts, especially at low temperatures (700 °C), but ethanol/CVD-treated EV samples without Mo favored iron reduction Fe⁰ form.

Mössbauer spectroscopy was used to determine the iron phases in EV samples with and without Mo after ethanol/CVD treatment at different temperatures (Fig. 3). It was observed by XRD (Supplementary material) that the CVD process does not significantly affect EV crystalline structure, as expected. It was not possible to observe any diffraction peaks related to Fe and Mo phases. These results suggest that these phases are highly dispersed on the surface of the material.

Scanning electron micrographs of pure expanded vermiculite (EV), and Fe/Mo-impregnated EV (EV/Fe_{10%} and EV/Fe_{10%}Mo_{0.5%}) after ethanol/CVD treatment at different temperatures are shown in Fig. 4. Pure EV has regular flat surface lamellae and a slit-type porous structure. No filaments were evident in SEM images of EV/Fe_{10%} after ethanol/CVD at low temperatures (600–700 °C). However, carbon filaments in different areas of the EV surface were observed after ethanol/CVD at 900 °C. In contrast, Mo addition and high temperatures produced large amounts of carbon filaments, which had diameters in nm and lengths of several μm all over EV surfaces.

Carbon quantities deposited on the EV samples were determined by carbon elemental analysis (Fig. 5). The ethanol/CVD treatment temperature directly affected the amount of carbon deposited. Only 0.3% was measured for EV samples with ethanol/CVD treatment at 600 °C. Deposited C increased to 2.0–2.5% for EV–Fe_{10%} samples after ethanol/CVD treatment at higher temperatures (700–900 °C). For EV samples with Mo, the amount of C deposited significantly increased to 3.0% for 700 °C treatment and 3.2% for 800 °C treatment.

Raman spectroscopy was used to characterize EV/Fe_{10%} and EV/Fe_{10%}Mo_{0.5%} samples after ethanol/CVD treatment (Fig. 6). No important Raman bands were present in pure EV. In contrast, EV/Fe_{10%} ethanol/CVD treated at 700 °C had two bands at 1319 and 1594 cm^{-1} . These bands are related to the presence of carbonaceous materials formed on the EV surface, i.e. graphitic (G band) at near 1590 cm^{-1} and defective/amorphous carbon (D band) at near 1300 cm^{-1} (Moura et al., 2008). No bands related to single wall carbon nanotubes, called RBM, were observed in the spectra.

The D band is generally more intense than the graphitic carbon G band, which suggests that defective carbon is more abundant in the ethanol/CVD treated EV samples. Raman profiles like these are typical

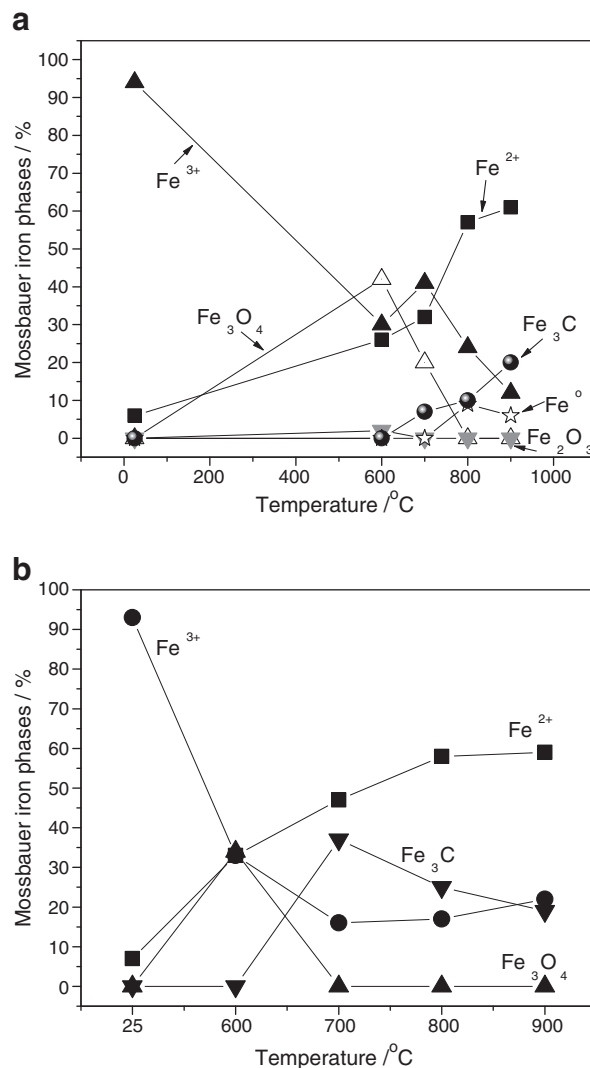


Fig. 3. Iron phase composition (%) determined from Mössbauer spectra of EV samples after ethanol/CVD treatment at different temperatures: (a) EV/Fe_{10%}, and (b) EV/Fe_{10%}Mo_{0.5%}.

for the types of irregular carbon fibers observed in the SEM micrographs in Fig. 4.

3.2. Oil removal studies

Water, soy bean oil, engine oil, and diesel absorption were measured for the EV/carbon composites prepared at different temperatures (Fig. 7). Pure EV absorbed $\sim 0.5\text{ g}_{\text{oil}}/\text{g}_{\text{EV}}$ of the oils, but relatively large ($3.5\text{ g}_{\text{H}_2\text{O}}/\text{g}_{\text{EV}}$) amounts of water. After low temperature (400–700 °C) ethanol/CVD treatment of EV/Fe_{10%}, the oil absorption capacity did not significantly increase. After ethanol/CVD treatment at higher temperatures (800–900 °C), the oil absorption capacity was slightly increased to $1.3\text{ g}_{\text{oil}}/\text{g}_{\text{EV}}$ (Fig. 7a). However, the introduction of Mo to the sample (Fig. 7b, EV/Fe_{10%}Mo_{0.5%}) increased oil absorption up to 500%. It is interesting that ethanol/CVD treatment increased oil absorption and decreased water absorption, especially for low-temperature ethanol/CVD-treated EV.

The N₂-BET surface areas increased from 3 m^2/g for EV to 16, 15, 21, and 15 for EV/Fe_{10%}Mo_{0.5%} samples that were ethanol/CVD-treated at 600, 700, 800, and 900 °C, respectively. The increased surface areas were likely due to the large areas of carbon nanofilaments grown on EV surfaces.

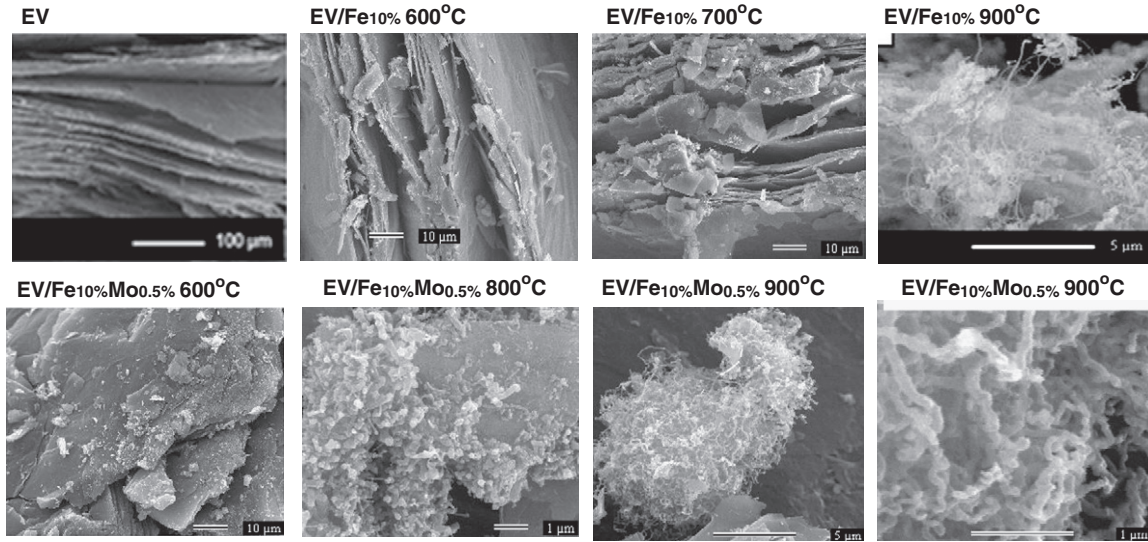


Fig. 4. Scanning electron micrographs of EV before and after ethanol/CVD for EV/Fe_{10%} and EV/Fe_{10%}Mo_{0.5%} samples at different temperatures.

Three main factors seem important to the oils and water absorption results obtained for the Fe_{10%}Mo_{0.5%}: (i) the hydrophobicity of the surface, (ii) the carbon/nanofibers sponge structure and the pore volume available for absorption. All composites were covered with a

layer composed of different forms of carbon, e.g. amorphous, graphitic and mainly nanofibers. All these carbon forms are very hydrophobic in nature and should produce a very water-repellent environment. For this reason, the water absorption by EV decreased from 3.5 to ca.

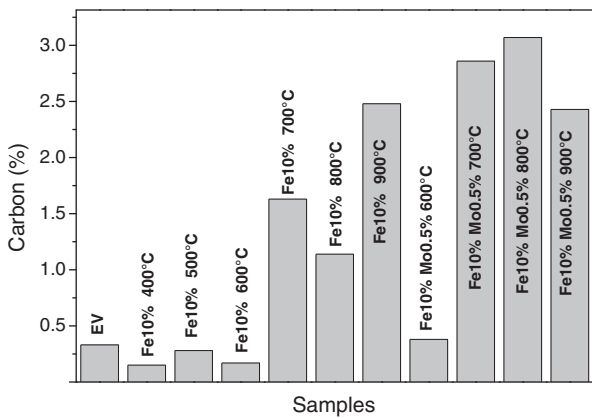


Fig. 5. Carbon elemental analyses of EV/carbon composites prepared by ethanol/CVD at different temperatures: (a) EV/Fe_{10%}, and (b) EV/Fe_{10%}Mo_{0.5%}.

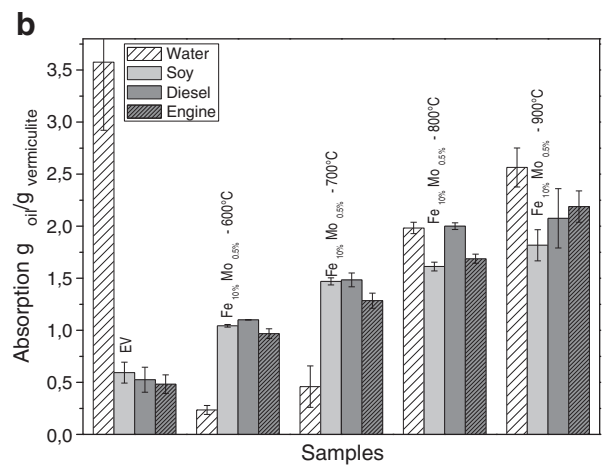
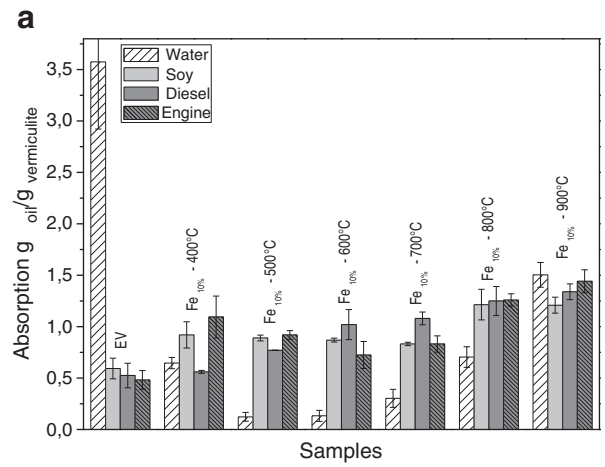


Fig. 7. Water and oil (soy bean, engine, and diesel) absorption by EV/carbon composites: (a) EV/Fe_{10%}, and (b) EV/Fe_{10%}Mo_{0.5%}.

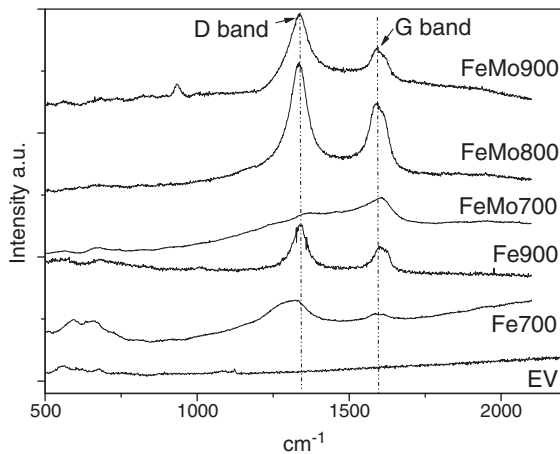


Fig. 6. Raman spectra of EV and EV/carbon composites after ethanol/CVD treatment at different temperatures.

0.3 g_{H₂O}/g_{EV} after CVD at 600–700 °C. This much lower water absorption reflects the strong hydrophobic character of the carbon deposits.

However, ethanol/CVD treatment of EV at higher temperatures significantly increased the amount of carbon filaments, which favored a sponge-like structure and increased water absorption to 2.0 and 2.5 g_{H₂O}/g_{EV} at 800 and 900 °C, respectively. Also, the more hydrophobic characteristics led to increased interactions with hydrophobic oil molecules and should lead to a general increase in oil absorption. This is especially true for the EV/Fe_{1.0%}Mo_{0.5%} carbon composites that were ethanol/CVD-treated at 800–900 °C. Although the reasons for the greater oil absorption are not clear, it might be due to the carbon nanostructures in the EV/carbon composites. The carbon nanofibers on EV lamellae should offer more surfaces for interaction with oil contaminants as indicated by the increased N₂-BET surface areas. Also, these entangled fibers produce a “sponge-like” structure which should have a strong capillary effect and favor uptake of the more viscous oils. In general, oils are more viscous (e.g. 70–80 cP for vegetable, diesel and crude oils) than water (1 cP) and penetration into the EV pore structure should be a critical step.

4. Conclusion

Expanded vermiculite (EV) can be modified by a chemical vapor deposition (CVD) process using ethanol and FeMo catalysts impregnated onto the mineral surface. The ethanol/CVD process produces large amounts of carbon nanofibers on EV, which strongly affect absorption properties. Ethanol/CVD modified EV can absorb 500% more soy bean oil, engine oil, and diesel with a concomitant decrease in water absorption. Hydrophobization of the EV surface and the sponge-like form of entangled carbon nanofibers explains the change in absorption properties.

Acknowledgments

The authors are grateful to CNPq, FAPEMIG, CAPES and Vermiculita Isolantes Térmicos e Acústicos Ltda for the support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.clay.2011.06.012.

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