Research paper

Fourier transform infrared spectroscopy analysis for hydrothermal transformation of microcrystalline cellulose on montmorillonite

Lin Mei Wu [a], Dong Shen Tong [a], Li Zhi Zhao [a], Wei Hua Yu [a], Chun Hui Zhou [a,b,*], Hao Wang [b]

[a] Research Group for Advanced Materials & Sustainable Catalysis (AMSC), Research Center for Clay Minerals, Breeding Base of State Key Laboratory of Green Chemistry Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China
[b] The Institute for Agriculture and the Environment, University of Southern Queensland, Toowoomba, Queensland 4350, Australia

ARTICLE INFO

ABSTRACT

Specifying the interactions between montmorillonite and cellulose is helpful for understanding the evolution of biomass in soil and the geological formation of fossil fuels in nature. In this work, Fourier transform infrared spectroscopy was used to investigate the hydrothermal transformation of microcrystalline cellulose on montmorillonite. A series of samples were obtained from hydrothermal treatments of microcrystalline cellulose with montmorillonite in various ratios at 200 °C for 16 h. The resulting solid samples were analyzed by using Fourier transform infrared (FTIR) spectroscopy. The subtle changes before and after hydrothermal treatments were particularly studied by using mathematical methods to generate second derivatives of absorbance spectra. It was found that there were interactions between montmorillonite and microcrystalline cellulose during the hydrothermal process. In the presence of montmorillonite, the cellulose was transformed to yield a product with aliphatic CH_x and aromatic groups. These were further confirmed by the FTIR spectra of the samples which were further treated by using an HCl/HF acid solution to remove the montmorillonite in them (demineralization). The structural parameters ('A Factor', 'C Factor' and CH_3/CH_2 ratio) were calculated. The values of the 'A Factor' and CH_3/CH_2 ratio of the resulting solid samples increased with the increase of montmorillonite. The values of 'C Factor' were little affected by the montmorillonite minerals. The findings suggested that montmorillonite-assisted hydrothermal treatment of cellulose was able to produce kerogen analogs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The past decades have witnessed a rising rate of consumption of petroleum fuel. This has led to the rapid depletion of fossil fuel resources and adverse effects on the global environment and climate because of the enormously enhanced emission of green-house gases. Cellulosic biomass, one of the most abundant renewable resources, shows great potential for sustainable production of fuels as supplements for fossil fuels (Zhou et al., 2011; Wu et al., 2014). Thermochemical conversion technologies, for example pyrolysis (Bulushev and Ross, 2011), gasification (Pereira et al., 2012) and hydrothermal liquefaction (Akhtar and Amin, 2011), are promising options for transforming cellulosic feedstocks into liquid fuels. However, these technologies have not yet met the requirements for the production of fuels on a large scale. There is still a need for seeking new routes to efficient conversion of cellulose. Besides, for the sustainable development of modern society, the scientific information on the evolution of biomass in soil is of great significance in agriculture, forestry and ecology (Jenkinson and Rayner, 1977).

In addition, biomass conversion in ancient geology is thought to the origin of petroleum and coal. Commonly, the formation of petroleum and coal from biomass is a natural geological process. Understanding this process is therefore of interest not only to oil exploration but also to the establishment of efficient catalytic processes for conversion of biomass to petroleum-like fuels. In general, naturally-occurring fossil fuels are believed to form through two stages: biomass is first converted to kerogen and then kerogen is thermally transformed to generate petroleum and natural gas (Wu et al., 2012). In particular, most hydrocarbons are thought to be generated by thermal transformation of kerogen during the burial of source rocks (Tissot et al., 1971). Earlier, kerogen has been well defined as sedimentary organic matter insoluble in the usual organic solvents. Generally, hydrogen-rich kerogen (Types I and II) is considered oil-prone, and hydrogen-poor kerogen (Type III) is considered gas-prone. Although many researchers have investigated the thermal transformation of kerogen to hydrocarbons (Van de Meent et al., 1980; Behar et al., 1992; Duan et al., 2011) and the pyrolysis of kerogen in the presence of clay minerals (Pan et al., 2007, 2009), few studies have reported the inherent roles played by co-existing inorganic minerals in the stage of biomass to kerogen.

* Corresponding author at: Research Group for Advanced Materials & Sustainable Catalysis (AMSC), Research Center for Clay Minerals, Breeding Base of State Key Laboratory of Green Chemistry Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China.
E-mail addresses: clay@zjut.edu.cn, Chun.Zhou@usq.edu.au (C.H. Zhou).

Montmorillonite (Mt) is one of the typical minerals associated with kerogen (Wu et al., 2012). Mt is a 2:1 clay mineral composed of aluminosilicate layers with exchangeable, hydrated cations in the interlayer spaces (Bergaya and Lagaly, 2013). Each aluminosilicate layer consists of two Si–O tetrahedral sheets sandwiching an Al–OH octahedral sheet by means of –Si–O–Al–O–Si– bonds, and the generic formula for Mt is $yM^+(Al_{2-y}Mg_y)(Si_4) O_{10} (OH)_2 \cdot nH_2O$ (Ruiz-Hitzky and van Meerbeek, 2006; Bergaya and Lagaly, 2013; Brigatti et al, 2013; Zhou and Keeling, 2013). It is noteworthy that the hydrothermal transformation of cellulose into coal-like materials can be used to simulate natural coalification (Bergius and Specht, 1913) and coal is a form of kerogen (Durand, 1980).

Fourier transform infrared (FTIR) spectroscopy is one of useful tools to characterize the chemical structure of inorganic minerals such as Mt and Mt-organic compounds (Madejová, 2003; Ma et al., 2010). For example, FTIR analyses have been used to classify kerogen and to probe the evolution of source rock and oil/gas generation potential of kerogen (Ganz and Kalkreuth, 1987; Chen et al., 1998). However, for the investigation of the interactions of Mt-biomass in earlier studies, the Mt-organic matter samples used for FTIR analysis were usually treated by an HF acid solution to remove silicates and clay minerals before FTIR analysis in order to avoid interferences. Such demineralization of samples enabled the dissolution of clay minerals, but the information on the structural changes of Mt was lost (Lin and Ritz, 1993a, 1993b). Thus, the early results were unable to reflect the changes of Mt and interactions between biomass and Mt. Hence, the present work attempts to reveal the interactions between Mt and microcrystalline cellulose (MCC) through the FTIR analysis of the samples produced from the hydrothermal treatment of MCC (model biomass) with Mt. The mathematical derivatives of spectral data, namely the second derivatives of the FTIR absorbance spectra (Ibarra et al., 1996), were used to disclose the subtle changes in the samples after and before hydrothermal treatment. Then the structural change of hydrothermally treated MCC in the presence of Mt was further investigated according to the FTIR spectra of the samples in which the mineral fractions were removed by using a mixed HCl/HF solution.

2. Experimental

2.1. Materials

Bentonite, obtained from a Yangyuan deposit, China, was used without further treatment. The chemical composition of bentonite determined by using an X-ray fluorescence spectrometer (XRF, ARL ADVANT'X, IntelliPowerTM 4200, ThermoFisher) was: 3.54% Na_2O, 4.63% MgO, 15.28% Al_2O_3, 71.38% SiO_2, 0.02% P_2O_5, 1.32% K_2O, 2.30% CaO, 0.03% TiO_2, 0.07% MnO_2 and 1.35% Fe_2O_3. The XRD pattern (PANalytical X'Pert PRO diffractometer with Cu Kα radiation) showed that the bentonite consists of Mt as the major mineral and minor impurities such as quartz and feldspar (Fig. 1a). Because Mt is thought to play a predominant role in mineral–organic interactions (Lagaly et al., 2006; Wu et al., 2012) and quartz and feldspars show nearly no reactivity, hereinafter the changes and the roles of Mt are concerned and discussed. Microcrystalline cellulose (MCC) was purchased from Yi Xing Shen De Li Synthetic Leather Material Co., Ltd., China and used without further treatment. The purity of microcrystalline cellulose is 99% and the particle size is around 48 μm.

2.2. Hydrothermal treatment of MCC

0.6 g, 1.0 g, 1.5 g, and 2.0 g of Mt were dispersed in deionized water (10 g) respectively. Each mixture was stirred for 30 min at room
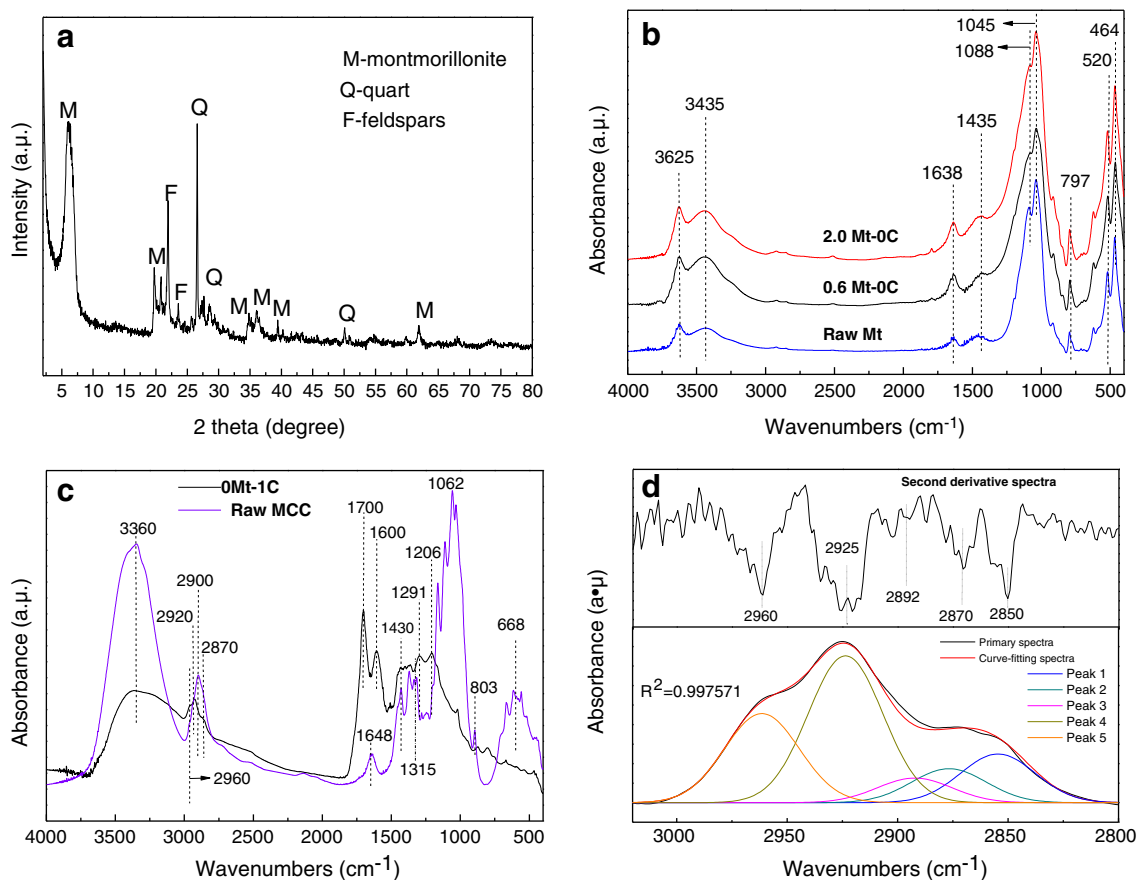
Fig. 1. (a) XRD pattern of bentonite; (b) FTIR spectra of raw and hydrothermally treated bentonite; (c) microcrystalline cellulose (MCC) before and after hydrothermal treatment; and (d) second derivative, primary and curve-fitting spectra of sample 0Mt-1C.