

N°360 / OC

TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Effect of clays structure on the catalytic fast pyrolysis of biomass

AUTHORS

Roger GADIOU / IS2M CNRS, 15 RUE JEAN STARCKY, MULHOUSE

Liangyuan JIA / LRGP CNRS, 1 RUE GRANDVILLE, NANCY

Tatevik CHILINGARYAN / IS2M CNRS, 15 RUE JEAN STARCKY, MULHOUSE

Yann LE BRECHT / LRGP CNRS, 1 RUE GRANDVILLE, NANCY

Luc DELMOTTE / IS2M CNRS, 15 RUE JEAN STARCKY, MULHOUSE

Jocelyne BRENDLE / IS2M CNRS, 15 RUE JEAN STARCKY, MULHOUSE

Guillain MAUVIEL / LRGP CNRS, 1 RUE GRANDVILLE, NANCY

Anthony DUFOUR / LRGP CNRS, 1 RUE GRANDVILLE, NANCY

PURPOSE OF THE ABSTRACT

The increasing energy demand combined with the decreasing fossil fuel resources and the necessity to control greenhouse gas emissions has led to an increasing interest in biomass to energy processes. The transformation of lignocellulosic biomass to valuable molecules is a challenge. Fast pyrolysis of biomass can be used to produce bio-oil, but this liquid has to be upgraded to obtain high grade oil. Numerous catalysts have been tested to achieve this to enhance cracking, deoxygenation, cyclization, etc. Clays are an interesting alternative since they are cheap and natural materials, they exhibit Brønsted and Lewis acid sites which make them suitable for catalysis [1,2,3].

Most studies have focussed on a screening of natural clays to compare their catalytic activity. The drawback is that natural clays can exhibit a complex structures and often include elements which are not part of the clay structure. In this work, we have used synthesized clays to study their catalytic activity on the distribution of products from oak pyrolysis. Although they should be not suitable for industrial use in most cases, these materials exhibit well controlled structural and chemical properties and they have no impurities which may change the catalytic activity. We have chosen beidellite which allows to vary the aluminium/silica ratio and then to change the Lewis sites concentration.

We synthesized beidellite which have the general formula $M_x(\text{Si}_{4-x}\text{Al}_x)\text{Al}_2\text{O}_{10}(\text{OH},\text{F})_2$ with x between 0.2 and 0.8. M was Na^+ or NH_4^+ . Further treatments allowed to exchange NH_4^+ with H^+ , and to add 5 to 10 wt% of iron in the clay structure. Catalysts were characterized by XRD, XRF and solid state ^{29}Si NMR. The pyrolysis experiments were done in a double fixed bed reactor, the first one was used to generate the pyrolysis products, and the second for the catalytic cracking. A single photo-ionization mass spectrometer was used to analyse the volatile products [4].

The results showed that clay are able to undergo significant cracking of high mass molecules, the best performance was obtained with the H exchanged clay with $x=0.8$. The activity of clays with $M = \text{Na}^+$ or NH_4^+ was significantly lower whatever the aluminium/silica ratio. This shows the importance of Brønsted acid sites on clay activity. The oak/clay ratio was also a key point to achieve good performances. The doping of clays with iron leads also to an improvement of catalytic properties of the catalyst but at a far lower extend compared with H exchange.

Clays are therefore materials which may be suitable for catalytic pyrolysis, but their performances are strongly related to their chemical properties which can be tailored by simple physico-chemical treatments.

FIGURES

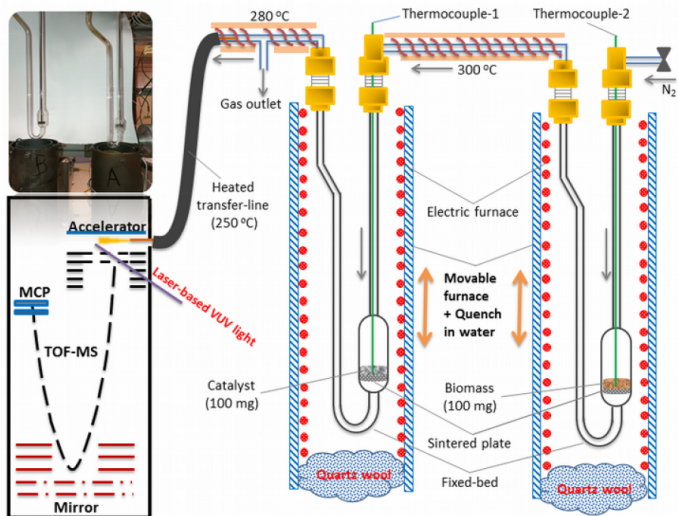


FIGURE 1

Experimental set-up

scheme of the double bed reactor with SPI-MS analysis

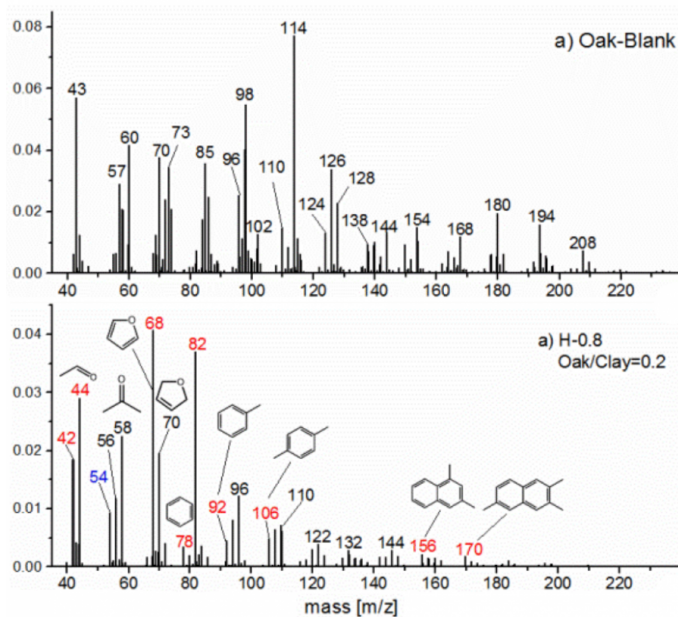


FIGURE 2

SPI-MS spectra

Example of mean SPI spectra for oak pyrolysis (top) and for oak with catalytic cracking over H exchanged beidellite (bottom)

KEYWORDS

catalysis | biomass pyrolysis | clays | mass spectrometry

BIBLIOGRAPHY

- [1] P. Rutkowski, *J. Anal. Appl. Pyrolysis*, 2012, 98, 115–122.
- [2] M. Sulman, Y. Kosivtsov, E. Sulman, V. Alfyorov, Y. Lugovoy, V. Molchanov, I. Tyamina, O. Misnikov, A. Afanasjev, N. Kumar and D. Murzin, *Chem. Eng. J.*, 2009, 154, 355–360.
- [3] A. Veses, M. Aznar, J. M. López, M. S. Callén, R. Murillo and T. García, *Fuel*, 2015, 141, 17–22.
- [4] L. Jia, Y. Le Brech, G. Mauviel, F. Qi, M. Bente-von Frowein, S. Ehlert, R. Zimmermann and A. Dufour, *Energy Fuels*, 2016, 30, 1555–1563.