

# Effects of solid acidity of clay minerals on the thermal decomposition of 12-aminolauric acid

## A thermogravimetry study

Hongmei Liu · Peng Yuan · Dong Liu ·  
Daoyong Tan · Hongping He · Jianxi Zhu

Received: 17 August 2012 / Accepted: 11 December 2012 / Published online: 12 January 2013  
© Akadémiai Kiadó, Budapest, Hungary 2013

**Abstract** In this study, the effects of four types of clay minerals on the thermal decomposition of 12-aminolauric acid (ALA) were investigated. The decomposition temperature of ALA in ALA–clay complexes was in the range of 200–500 °C. The derivative thermogravimetry results indicated that all clay minerals exhibited catalytic activity on the decomposition of ALA. Pure ALA decomposed at approximately 464 °C, a temperature higher than the decomposition temperature of ALA in the presence of clay minerals. The decomposition temperature of ALA in different ALA–clay complexes follows the order illite (452 °C) > kaolinite (419 °C) > rectorite (417 °C) > montmorillonite (400 °C). This order is negatively correlated with the amounts of solid acid sites in the clay minerals, indicating that ALA is catalyzed by the solid acid sites in these minerals.

**Keywords** 12-aminolauric acid · Thermal decomposition · Clay minerals · Solid acidity

## Introduction

It is widely accepted that the process of petroleum formation is catalyzed by clay minerals. Simulation experiments have been conducted using mixtures of clay minerals and natural organics such as kerogen and bitumen to explore how clay minerals affect hydrocarbon generation in natural processes [1–5]. Nevertheless, due to the diversity and complexity of the chemical composition of kerogen and bitumen, the results obtained from these studies are not applicable to the investigation of the catalysis site and the corresponding catalysis mechanism related to clay minerals.

To conduct a thorough study of clay geocatalysis in hydrocarbon formation, high purity and structurally simple synthetic organics, representative of the typical organics in source rock were selected as model compounds. These compounds were mixed with clay minerals to simulate the transformation of organic matter into gas and oil [6–12]. The conversion of naturally occurring fatty acids to paraffins is considered an important reaction in petroleum genesis. Thus, fatty acids are commonly used in simulation studies. Previous investigators found that clay minerals promoted the decarboxylation of long straight-chain fatty acids to form long-chain alkanes and that the clay minerals exhibited a strong effect on the subsequent cracking of these alkanes [6, 10, 11, 13]. Organic compounds containing nitrogen are also typically found in low-rank coals, oil shales, and immature kerogens [14–16]. The discovery of porphyrin, a nitrogen-containing organic in petroleum, was one of the first indicators of the organic origin of petroleum [17]. In addition, Williams and Ferrell [18] demonstrated that a large amount of N is released in the form of  $\text{NH}_4^+$  and  $\text{NH}_3$  during the rapid degradation of kerogen. Despite the close relationship between N-related organics and petroleum's origin and maturity, few

---

**Electronic supplementary material** The online version of this article (doi:10.1007/s10973-012-2887-0) contains supplementary material, which is available to authorized users.

---

H. Liu · P. Yuan (✉) · D. Liu · D. Tan · H. He · J. Zhu  
CAS Key Laboratory of Mineralogy and Metallogeny,  
Guangzhou Institute of Geochemistry, Chinese Academy  
of Sciences, Guangzhou 510640, China  
e-mail: yuanpeng@gig.ac.cn

H. Liu · D. Tan  
University of Chinese Academy of Sciences,  
Beijing 100049, China

simulation experiments have been performed using nitrogen-containing organics as model compounds.

Goldstein stated that several model reactions involved in oil formation were difficult to perform in the laboratory using purely thermal processes, even at high temperatures, in the absence of catalysts. However, these reactions could occur under mild conditions (lower temperature and shorter reaction time) in the presence of solid acid catalysts, such as clay minerals and silica–alumina [7]. In these types of catalytic reactions, the change in thermal decomposition temperature is an effective indicator of catalytic activity.

In this study, the thermal behaviors of nitrogen-containing organics were studied in the presence of clay minerals using a thermogravimetry (TG) instrument. TG is the most commonly used thermal analysis technique in soil science [19], especially in clay mineralogy [20, 21]. The decomposition temperatures of samples can be directly obtained from the TG and derivative TG (DTG) curves. 12-aminolauric acid (ALA;  $\text{NH}_2(\text{CH}_2)_{11}\text{COOH}$ ) was selected as the model organic compound. ALA contains amino and carboxyl groups and alkyl chains with moderate numbers of carbon atoms. These groups are common in natural organics, as mentioned above, and are thus suitable for use in simulation experiments. Four types of clay minerals—montmorillonite (Mt), rectorite (Rt), kaolinite (Kt), and illite (Ilt) which are ubiquitous in source rock, were mixed with ALA in order to investigate the effect of clay minerals on the thermal decomposition of ALA. To better understand the possible reaction mechanism, the amount of solid acid sites in the clay minerals used in this study was also determined.

## Experimental

### Materials and methods

Montmorillonite (denoted as Mt, obtained from Inner Mongolia, China), rectorite (Rt, obtained from Zhongxiang, China), kaolinite (Kt, obtained from Maoming, China), and illite (Ilt, obtained from Lingshou, China) were used in this study. ALA of 98 % purity was supplied by the Tokyo Chemical Industry Co., Ltd., and was used as received.

To facilitate complete contact between the clay minerals and the ALA, 10 g of a clay mineral and 2.5 g of ALA were mixed and ground by ball milling for 20 min using a Pulverisette-6 Planetary Mill. These ALA–clay complexes were denoted as ALA–Mt, ALA–Rt, ALA–Kt, and ALA–Ilt according to the type of clay mineral used.

### X-ray diffraction characterization

The X-ray diffraction (XRD) patterns of the samples were recorded between  $1^\circ$  and  $80^\circ$  at a scan rate of  $3^\circ (2\theta) \text{ min}^{-1}$

using a Bruker D8 Advance diffractometer with a Ni filter and Cu  $K\alpha$  radiation (40 kV and 40 mA).

### Thermal analysis

The TG analysis of the samples was performed on a Netzsch 449C instrument. Approximately 20 mg of finely powdered samples was heated from 30 to  $1,000^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  under high purity  $\text{N}_2$  atmosphere ( $60 \text{ cm}^3 \text{ min}^{-1}$ ).

### Solid acidity measurements

*n*-Butylamine titration using Hammett indicators was performed to determine the amounts of inherent solid acid sites in the clay minerals [22]. Approximately 0.1 g of mineral powder was dispersed in 2 mL of dry petroleum ether in a series of capped glass bottles, and different volumes of *n*-butylamine were then added. The volume of *n*-butylamine (*V*, mL) was calculated using the following equation:  $V = NM/C$ , where *M* is the mass of the sample ( $\sim 0.1$  g), *N* is the titer of the sample ( $\text{mmol g}^{-1}$ ), and *C* is the concentration of the *n*-butylamine ( $\text{mmol mL}^{-1}$ ).

The mixture was then ultrasonically stirred for 30 min to achieve adsorption equilibrium. The dispersion was then distributed into several test tubes. The change in color of methyl red (a type of Hammett indicator,  $\text{p}K_a = 4.8$ ) in each test tube was observed. All chemicals and reagents used in this study were of analytic grade and were used as received.

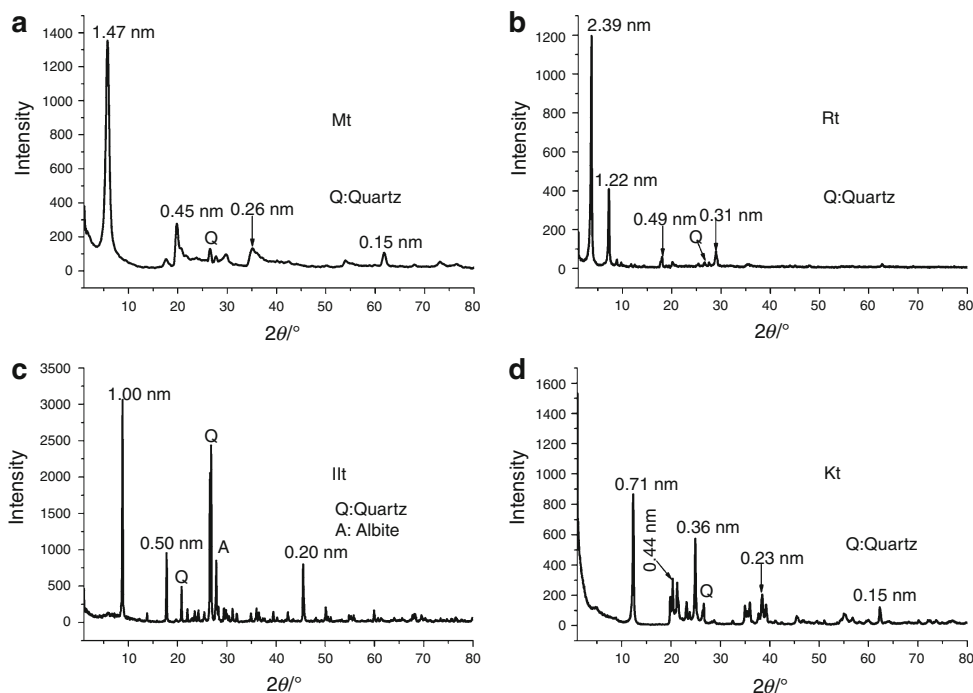
## Results and discussion

### X-ray diffraction

Figure 1 depicts the XRD patterns of Mt, Rt, Ilt, and Kt. The basal spacing of Mt is 1.47 nm (Fig. 1a). The 110 reflection corresponding to 0.45 nm is also observed. The 001 and 002 reflections of Rt appear as sharp and well-defined peaks, which can be clearly identified at 2.39 and 1.22 nm, respectively (Fig. 1b). Ilt exhibits a series of well-defined  $00l$  reflections, indicative of the highly ordered structure of Ilt (Fig. 1c). Kt has a basal spacing of 0.71 nm (Fig. 1d). XRD results of ALA–clay complexes indicate that the intercalation only occurred on Rt, rather than Mt, Ilt, and Kt during the sample preparation, based on the *d* values (see Supplementary Information Fig. S1).

### Thermal analysis

The TG and corresponding DTG results for the clay minerals are shown in Fig. 2. Mt and Rt exhibit similar thermal decomposition behaviors (Fig. 2a, b) with two degradation

**Fig. 1** XRD patterns of the clay minerals used in this study

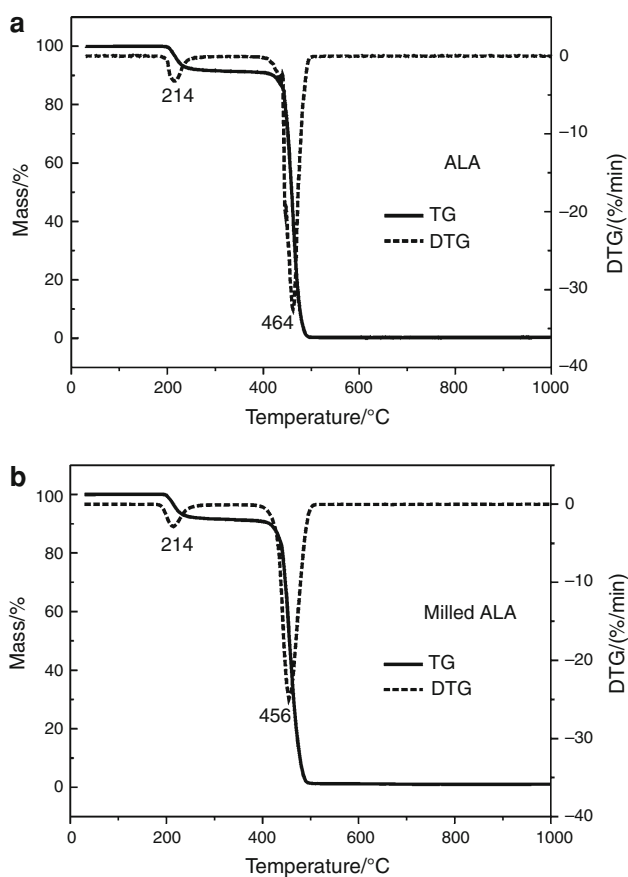
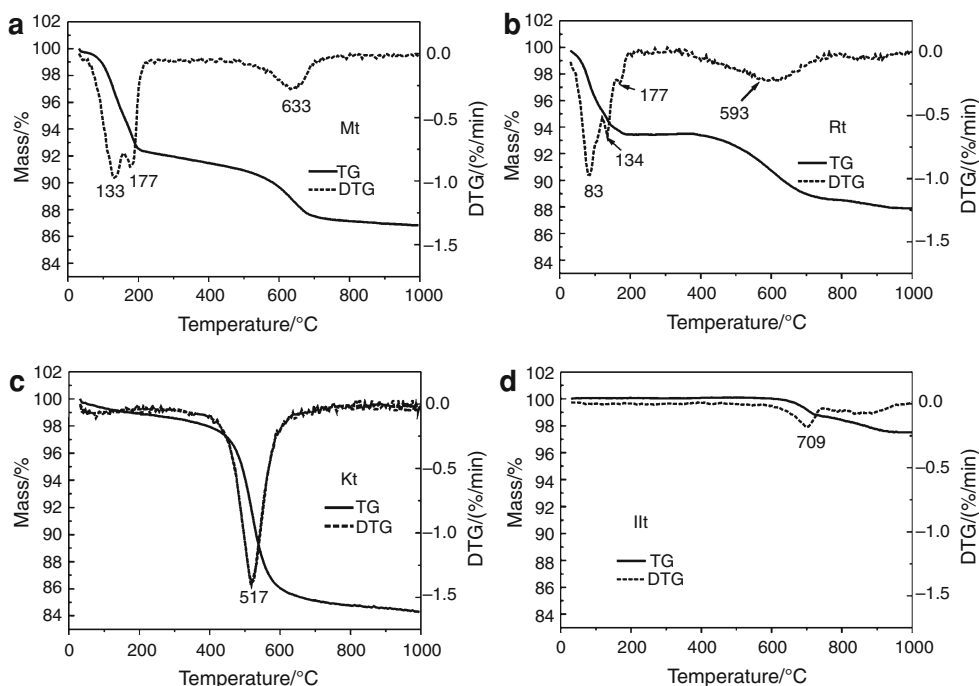
steps. In the first step (below 200 °C), free (adsorbed) water and interlayer water residing between the Mt and Rt layers is released [23]. The mass losses in this region for Mt and Rt are 7.47 and 6.31 %, respectively. Dehydroxylation occurs within the temperature range of 500–700 °C, where a broad DTG peak is resolved at 633 °C for Mt and at 593 °C for Rt. A small mass loss of approximately 2.07 % is observed for Kt below 400 °C (Fig. 2c). According to the literature, this loss is assigned to the elimination of adsorbed water molecules on the external surfaces of the Kt particles [24]. The most important thermal events for Kt occur between 400 and 700 °C with a well resolved DTG peak at 517 °C that is related to the dehydroxylation of Kt and the formation of meta-kaoline [25, 26]. In contrast to the aforementioned clay minerals, Illt exhibits a distinct thermal behavior. As noted in Fig. 2d, no mass loss is observed until 600 °C, indicating that neither adsorbed nor interlayer water is present in the Illt. The dehydroxylation of Illt occurs at a higher temperature (709 °C). The broad DTG peak at approximately 800–900 °C corresponds to the matrix destruction of the silicate lattice [27].

The thermal decomposition of pure ALA can be separated into two steps. A small mass loss is observed over the range of 200–300 °C with a small DTG peak at 214 °C (Fig. 3a). The major thermal event of pure ALA occurs within the range of 400–500 °C resulting in a sharp DTG peak at 464 °C. Considering the possible effect of milling treatment on the thermal stability of ALA, the thermal behavior of milled ALA was also studied. After milling, only a slight

decrease in the decomposition temperature of ALA (approximately 8 °C) is observed (Fig. 3b) indicating that milling has little effect on the thermal stability of ALA.

ALA–clay complexes exhibit thermal degradation characteristics that are a combination of those of pure ALA and the original clay minerals. For both ALA–Mt and ALA–Rt, the initial mass loss below 200 °C is attributed to the release of adsorbed water and interlayer water (Fig. 4a). Lower temperatures of dehydration, as defined by the DTG peaks, are observed for these two ALA–clay complexes relative to those of the original minerals (Fig. 4b). As observed for ALA (Fig. 3b), milling treatment may also slightly decrease the thermal stability of clay minerals. The most distinct difference between the original minerals and their organic-mixed products is in the temperature range of 200–500 °C, where ALA decomposed. The maximum mass loss rate for ALA–Mt occurs at 400 °C which is dramatically lower than the corresponding temperature for pure ALA (464 °C). ALA–Rt and ALA–Kt exhibit well-defined DTG peaks at 417 and 419 °C, respectively. For ALA–Illt, the maximum mass loss rate of ALA occurs at 452 °C. Thus, no obvious effect is observed on the thermal decomposition of ALA when Illt is added. The lower decomposition temperature of ALA in the presence of these clay minerals indicates that the clays used in this study accelerate the breakdown of ALA. Moreover, the small DTG peaks at approximately 220 and 450 °C (Fig. 4b) are assigned to a small amount of ALA that is unaffected by the clay minerals and decompose spontaneously. Within the temperature range of 500–1,000 °C,

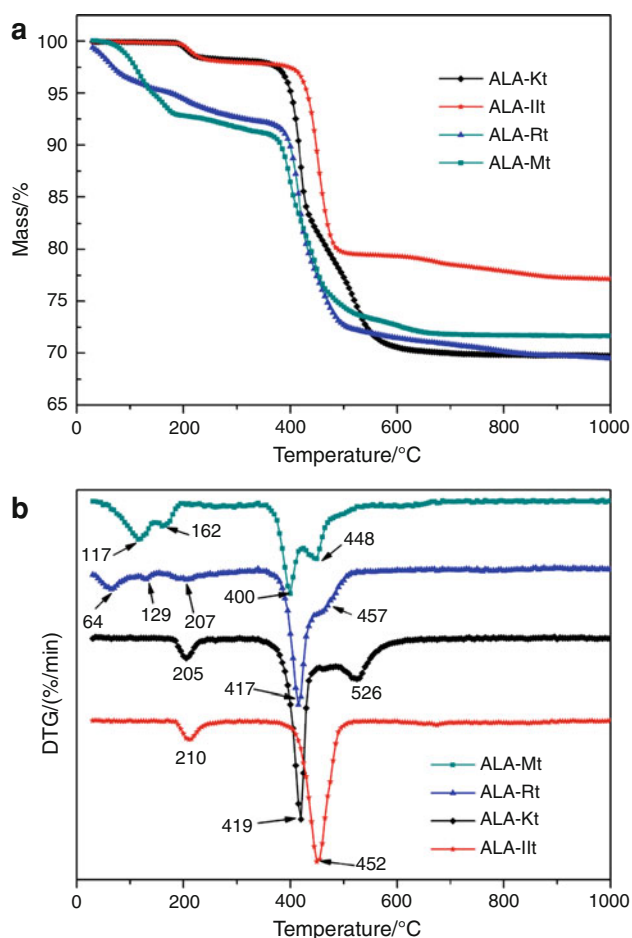
**Fig. 2** TG and DTG curves of the original clay minerals



**Fig. 3** TG and DTG curves of ALA (a) and milled ALA (b)

the DTG peaks corresponding to the dehydroxylation of the original clay minerals disappear, except that for ALA–Kt (526 °C). The amount of ALA in the ALA–clay complexes is equal to 25 % of the clay minerals by mass. This value is far greater than the percentage of hydroxyl groups in Mt, Rt, and Illt (Table 1). Thus, for ALA–clay complexes (except ALA–Kt), the dehydroxylation for clay minerals is negligible compared to the significant weight loss due to ALA decomposition.

As measured by *n*-butylamine titration, the total amount of acid sites in Mt, Rt, Kt, and Illt are 0.80, 0.25, 0.06, and 0.03 mmol g<sup>-1</sup>, respectively. Many studies have focused on the solid acidity of clay minerals. The sources of the solid acid sites in the different types of clay minerals are similar due to their similar structures. The Brønsted acidity, defined as the proton-donating capability, of Mt primarily results from the polarization of interlayer water molecules by the interlayer hydrated cations [28–30], whereas the Lewis acidity (ability of being an electron pair acceptor) generally arises from the exposed Al<sup>3+</sup> and Fe<sup>3+</sup> ions at the edge of the Mt crystallites [31, 32]. The TG data for Illt indicate the absence of interlayer water, which implies that no solid acid sites exist within this interlayer space. Thus, the trace amount of acid sites obtained in this study for Illt may be related to Lewis acid sites on its external surface. Rt is usually composed of 1:1 regular interstratification of Illt and Mt lamellars. Because the solid acidity of Illt component is weak, the main source of the solid acid sites of Rt



**Fig. 4** TG (a) and DTG (b) curves of the ALA–clay complexes

is the Mt component, which can explain why Rt has a much lower acid amount than an equal weight of Mt. In the study of Benesi [22], Kt exhibited a higher acid strength than Mt. However, the amount of acid sites of Kt is approximately one order of magnitude lower than that of Mt in our study. Kt does not contain either interlayer cations or naturally intercalated water. The small quantity of acid sites in Kt results from the coordinately unsaturated  $\text{Al}^{3+}$  ions at the edges of its external surface.

As described above, clay minerals induce the catalytic decomposition of ALA, which decreases the decomposition temperature of the ALA in ALA–clay complexes. The ALA decomposition temperatures in these complexes decrease in the following order: ALA–Ilt > ALA–Kt > ALA–Rt > ALA–Mt. Obviously, there is a negative correlation between the decomposition temperature and the amount of solid acid sites, which indicates the catalytic activity of clay minerals is primarily determined by the solid acidity. It is interesting that the main decomposition temperatures of ALA in ALA–Kt and ALA–Rt are nearly equal, even though the acid amount of Kt is only one quarter that of Rt. As mentioned above, Kt starts to

**Table 1** TG results for the dehydroxylation of the clay minerals

Clay minerals	Temperature range/°C	Mass loss/%
Mt	500–700	3.40
Rt	500–700	3.58
Ilt	500–800	1.67
Kt	400–700	12.82

dehydroxylate at 400 °C and to transform into meta-Kt. Rong and Xiao [33] noted that at a certain calcination temperature (460 °C in their article), some of the hydroxyls in Kt may break off to produce Brønsted acid sites, and the four- or five-coordinate aluminum cations, formed in the process of Kt transformation, act as Lewis acid sites. Other authors have reported similar conclusions, as summarized by Heller-Kallai [34].

The present results are comparable to the previous observation conducted on kerogen and fatty acids. Wei et al. [5] found that Mt has a significant catalytic effect on the pyrolysis of kerogen, that Kt is a less active catalyst, and that Ilt exhibits no effect. Other investigators obtained the following conclusions from their studies on fatty acids: in the transformation of fatty acids to lighter hydrocarbons, decarboxylation and C–C cleavage are the most important reactions. The former reaction is significantly promoted in the presence of clay minerals, and the related catalytic activity is ascribed to the Lewis acid sites [35]; the latter reaction is initiated by the Brønsted acid sites of clay minerals via the carbocation mechanism [36]. Because ALA has a structure similar to that of fatty acids, such a proposal may also be applicable to ALA–clay complexes. It is still unclear whether clay minerals have an effect on the decomposition of the amino group in ALA during heating and how the effect works. This research is underway and will be reported in a future publication.

## Conclusions

This study investigated the effects of clay minerals on the thermal decomposition of ALA. The presence of clay minerals promoted the catalytic degradation of ALA, resulting in a lower decomposition temperature of ALA. There was a negative correlation between the amount of solid acid sites in the clay minerals and the decomposition temperature of the ALA in the ALA–clay complexes. The amounts of acid sites of clay minerals used in this study decreased as follows: Mt > Rt > Kt > Ilt. Mt exhibited the strongest catalytic activity, with the decomposition temperature of ALA falling to 400 °C which is 64 °C lower than that of pure ALA. Rt and Kt exhibited weaker catalytic activities than Mt but are similar to each other, whereas Ilt had little effect on the thermal decomposition of ALA.

**Acknowledgments** This study was financially supported by the National Basic Research Program of China (Grant No. 2012CB214704-01), the National Natural Science Foundation of China (Grant No. 41272059), and the National S&T Major Project of China (Grant No. 2011ZX05008-002-21). This is a contribution (No. IS1592) from GIGCAS.

## References

- Huizinga BJ, Tannenbaum E, Kaplan IR. The role of minerals in the thermal alteration of organic matter—III. Generation of bitumen in laboratory experiments. *Org Geochem.* 1987;11(6): 591–604.
- Li S, Guo S, Tan X. Characteristics and kinetics of catalytic degradation of immature kerogen in the presence of mineral and salt. *Org Geochem.* 1998;29(5–7):1431–9.
- Pan C, Jiang L, Liu J, Zhang S, Zhu G. The effects of calcite and montmorillonite on oil cracking in confined pyrolysis experiments. *Org Geochem.* 2010;41(7):611–26.
- Tannenbaum E, Kaplan IR. Role of minerals in the thermal alteration of organic matter—I: generation of gases and condensates under dry condition. *Geochim Cosmochim Acta.* 1985;49(12): 2589–604.
- Wei Z, Michael Moldowan J, Dahl J, Goldstein TP, Jarvie DM. The catalytic effects of minerals on the formation of diamondoids from kerogen macromolecules. *Org Geochem.* 2006;37(11): 1421–36.
- Aizenshtat Z, Miloslavsky I, Heller-Kallai L. The effect of montmorillonite on the thermal decomposition of fatty acids under “bulk flow” conditions. *Org Geochem.* 1984;7(1):85–90.
- Goldstein TP. Geocatalytic reactions in formation and maturation of petroleum. *AAPG Bull.* 1983;67(1):152–9.
- Heller-Kallai L, Aizenshtat Z, Miloslavsky I. The effect of various clay minerals on the thermal decomposition of stearic acid under “bulk flow” conditions. *Clay Miner.* 1984;19(5):779–88.
- Johns W, McKallip TE. Burial diagenesis and specific catalytic activity of illite–smectite clays from Vienna Basin, Austria. *AAPG Bull.* 1989;73:472–82.
- Jurg J, Eisma E. Petroleum hydrocarbons: generation from fatty acid. *Science.* 1964;144(3625):1451–2.
- Shimoyama A, Johns WD. Catalytic conversion of fatty acids to petroleum-like paraffins and their maturation. *Nature.* 1971; 232(33):140–4.
- Zhang Z, Liu H, Li B, Ji Z, Lei N. Reaction of fatty acid ester catalyzed by minerals at low temperature in heavy water and water. *J China Univ Pet Ed Nat Sci.* 2008;32(5):118–20, 25.
- Johns WD, Shimoyama A. Clay minerals and petroleum-forming reactions during burial and diagenesis. *AAPG Bull.* 1972;56(11): 2160–7.
- Baxby M, Patience RL, Bartle KD. The origin and diagenesis of sedimentary of organic nitrogen. *J Pet Geol.* 1994;17(2):211–30.
- Behar F, Gillaizeau B, Derenne S, Largeau C. Nitrogen distribution in the pyrolysis products of a type II kerogen (Cenomanian, Italy). Timing of molecular nitrogen production versus other gases. *Energy Fuels.* 2000;14(2):431–40.
- Kelemen SR, Freund H, Gorbaty ML, Kwiatek PJ. Thermal chemistry of nitrogen in kerogen and low-rank coal. *Energy Fuels.* 1999;13(2):529–38.
- Treibs A. Chlorophyll- and hemin derivatives in bituminous rocks, petroleum, mineral waxes and asphalts. *Ann Chem.* 1934;510: 42–62.
- Williams LB, Ferrell R Jr. Ammonium substitution in illite during maturation of organic matter. *Clay Clay Miner.* 1991;39(4): 400–8.
- Plante AF, Fernández JM, Leifeld J. Application of thermal analysis techniques in soil science. *Geoderma.* 2009;153(1–2): 1–10.
- Frost R, Kristóf J, Horváth E. Controlled rate thermal analysis of sepiolite. *J Therm Anal Calorim.* 2009;98(2):423–8.
- Zhu J, Shen W, Ma Y, Ma L, Zhou Q, Yuan P, et al. The influence of alkyl chain length on surfactant distribution within organo-montmorillonites and their thermal stability. *J Therm Anal Calorim.* 2011;109(1):301–9.
- Benesi HA. Acidity of catalyst surfaces. II. Amine titration using Hammett indicators. *J Phys Chem.* 1957;61(7):970–3.
- Li Y, Wang X, Wang J. Cation exchange, interlayer spacing, and thermal analysis of Na/Ca-montmorillonite modified with alkaline and alkaline earth metal ion. *J Therm Anal Calorim.* 2012;11(3): 1199–206.
- Cheng H, Yang J, Liu Q, He J, Frost RL. Thermogravimetric analysis–mass spectrometry (TG–MS) of selected Chinese kaolinites. *Thermochim Acta.* 2010;507–508:106–14.
- Kakali G, Perraki T, Tsivilis S, Badogiannis E. Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity. *Appl Clay Sci.* 2001;20(1–2):73–80.
- Wang H, Li C, Peng Z, Zhang S. Characterization and thermal behavior of kaolin. *J Therm Anal Calorim.* 2011;105(1):157–60.
- Earnest C. Thermal analysis of selected illite and smectite clay minerals. Part I. Illite clay specimens. In: Smykatz-Kloss W, Warne S, editors. *Thermal analysis of selected illite and smectite clay minerals.* Lecture Notes in Earth Sciences. Berlin: Springer; 1991. p. 270–86.
- Frenkel M. Surface acidity of montmorillonites. *Clay Clay Miner.* 1974;22(5–6):435–41.
- Rupert JP, Granquist WT, Pinnavaia TJ. Catalytic properties of clay minerals. In: Newman ACD, editor. *Chemistry of clays and clay minerals.* New York: Longman Scientific and Technical; 1987. p. 275–319.
- Varma RS. Clay and clay-supported reagents in organic synthesis. *Tetrahedron.* 2002;58(7):1235–55.
- Reddy CR, Nagendrapa G, Jai Prakash BS. Surface acidity study of Mn<sup>+</sup>-montmorillonite clay catalysts by FT-IR spectroscopy: correlation with esterification activity. *Catal Commun.* 2007; 8(3):241–6.
- Tyagi B, Chudasama CD, Jasra RV. Characterization of surface acidity of an acid montmorillonite activated with hydrothermal, ultrasonic and microwave techniques. *Appl Clay Sci.* 2006;31(1–2): 16–28.
- Rong TJ, Xiao JK. The catalytic cracking activity of the kaolin-group minerals. *Mater Lett.* 2002;57(2):297–301.
- Heller-Kallai L. Thermally modified clay minerals. In: Bergaya F, Theng BKG, Lagaly G, editors. *Handbook of clay science.* Amsterdam: Elsevier; 2006. p. 289–308.
- Almon W, Johns W. Petroleum forming reactions: the mechanism and rate of clay catalyzed fatty acid decarboxylation. In: Campos R, Goni J, editors. *Advances in organic geochemistry.* 1975; Enadimsa: Madrid; 1977. p. 157–72.
- Johns WD. Clay mineral catalysis and petroleum generation. *Annu Rev Earth Planet Sci.* 1979;7:183–98.