

ACTIVE COMPONENTS IN CLAY CONDENSATES AND EXTRACTS AS POTENTIAL GEOCATALYSTS

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Abstract—Conversion of tertiary butylacetate to isobutylene and acetic acid and cracking of *n*-octane were used as model reactions to monitor the catalytic activity of a condensate and aqueous extract derived from a sample of montmorillonite. The condensate was obtained by condensing the vapor phase evolved on heating the clay and the extract was derived from the clay by prolonged water extraction. Both condensate and extract were colloidal systems, which were separated into solid and liquid fractions by distillation. Reactions carried out in a dynamic system established that the solid components acted as true acid catalysts, whereas the liquid fractions were inactive under the experimental conditions adopted. The catalytic activity per weight of the condensate exceeded that of either the parent clay or the extract.

The present results confirm that colloidal size catalysts of high activity can be generated from clays. Such materials, mobilized and transported alone or with formation fluids, may act as catalysts in places removed in space and time from their source. This finding refutes objections previously raised to the operation of bulk clays as catalysts for reactions with particulate organics and supports the concept that acid catalysts derived from clays may participate in organic geochemical reactions in an aqueous medium.

Key Words—Clay condensate, Clay extract, Geocatalyst, Octane cracking, Tertiary butylacetate decomposition.

INTRODUCTION

Clay minerals are frequently invoked as potential catalysts for diagenetic processes of organic matter in nature, in particular for the generation of petroleum hydrocarbons from kerogen and their maturation process. Objections sometimes raised against the participation of clays in such processes include the reduced catalytic effect of clay minerals in an aqueous medium and the possibility that direct physical contact between clay formations and the organic material may be very limited. Recent studies have shown that clay volatiles and condensates, that is the vapor phase evolved on heating clay minerals and the corresponding condensates, are effective catalysts for hydrocarbon cracking (Heller-Kallai et al. 1989; Miloslavski et al. 1991). Similarly extracts derived from clays by continuous washing were found to catalyze some reactions of organic matter. It seems reasonable to assume that both extracts and condensates may participate in catalytic processes at different stages of burial diagenesis. Both condensates and extracts are aqueous suspensions of varying composition, which contain some very finely divided particulate matter (Keller 1986; Heller-Kallai et al. 1988; Keller and da Costa 1989). Their reactivity is not destroyed by the aqueous environment. It has also been shown that clay condensates attack calcite (Heller-Kallai et al. 1987; Heller-Kallai and Miloslavski 1992). They may be expected to penetrate formations that are otherwise inaccessible to solid catalysts.

Because of the pervasive and circulatory nature of subsurface fluids, such condensates and extracts may travel far from their original clay source.

The present study was undertaken to confirm, beyond doubt, that clay condensates and extracts are, indeed, genuine catalysts. Previous experiments were carried out as either batch reactions or with a finite stream of clay volatiles. Catalytic activity was inferred from the nature of the products, but was not directly demonstrated in a dynamic system. An additional aim was to establish which catalysts are the reactive constituents of the aqueous suspensions and to assess their relative catalytic activity. In view of the proven ability of the suspensions to catalyze cracking of hydrocarbons, attention was focused on the activity of the components, solid and liquid, as acid catalysts. Tertiary butyl acetate (TBA) and *n*-octane were selected as model compounds. Conversion of TBA to isobutylene and acetic acid is a very facile reaction at temperatures above approximately 50 °C in the presence of an acid catalyst. Acid catalyzed cracking of *n*-octane requires more robust reaction conditions to achieve measurable conversions within a reasonable period of time.

EXPERIMENTAL

Starting Materials

TBA (99% pure) was supplied by EM Science and *n*-octane (99+% pure) by Aldrich Chemical Company. A mass spectrum of the starting *n*C₈ showed that it contained two isomers of C₈ as impurities. Gas chro-

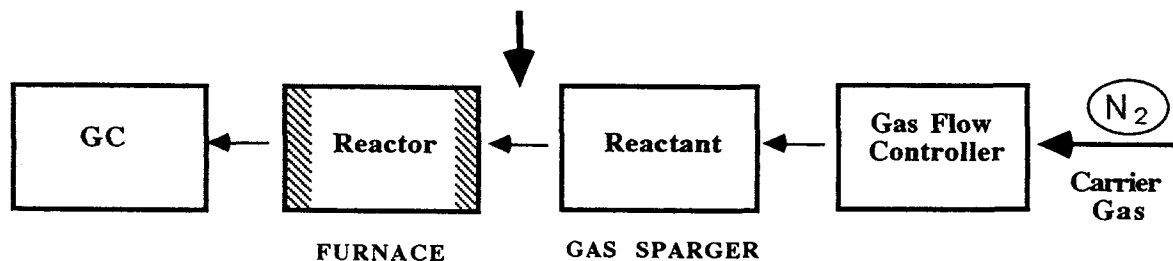


Figure 1. Reaction train. The vertical arrow marks the position of an additional sparger for reactions between octane and liquid components.

matograms demonstrated that these impurities did not exceed about 0.5%.

Ca montmorillonite from Texas (CMS Standard) was the parent clay used for all the experiments.

Condensates were obtained by the method previously described (Heller-Kallai et al. 1988), that is by heating the clay to 500 °C in a quartz reactor and condensing the vapor phase material evolved in an ice-cooled vessel.

Extracts were prepared by stirring the clay with distilled water (clay:water ratio 1:10) continuously for 10 d at room temperature. The slurry was centrifuged for 80 min at 12,000 rpm followed by 60 min at 18,000 rpm. The supernatant suspension was filtered and used for the experiments.

Both condensate and extract contained particulate matter that could not be separated by prolonged high-speed centrifuging, even with an ultracentrifuge. Complete separation of the solid from the liquid phase was achieved by a distillation process. The suspensions were placed into glass reactors at 85 °C, a stream of high purity nitrogen was bubbled through and the emerging gases were condensed in an ice-cooled receiver.

Elemental Analysis

The elemental composition of dried aliquots of the total condensate and extract and of the respective distillates was determined by microprobe analysis (EMPA), using a Jeol JXA 8600 electron microprobe in both energy (EDS) and wavelength (WDS) dispersive modes.

Reactions Between Organic Matter and Solid or Liquid Components

A schematic drawing of the reaction train is shown in Figure 1. High purity nitrogen was used as a carrier gas. Residence time of the reactant was controlled by the carrier gas flow rate. The vapor phase concentration of the reactant in the carrier gas is determined by its partial pressure at the temperature of the sparger, which can be calculated using the Antoine equation.

The sparger containing the organic matter was maintained at room temperature. The reactions with

TBA were performed at 85 °C, with either solid or liquid reagent within the furnace. Reactions with octane demanded higher temperatures, 250–300 °C. This required insertion of an additional sparger for reactions with the liquid components (Figure 1), which was kept at 85 °C. The carrier gas transferred both reagent and reactant into the empty furnace maintained at 250–300 °C. Solid or liquid components derived from 4 ml of condensate or extract were used for each experiment.

A Varian Model 3700 GC equipped with a bonded dimethylpolysiloxane capillary column, a flame ionization detector and a gas sampling valve were used for on-line analysis. The transfer line to the GC was heat traced at 80 to 90 °C to prevent condensation. Occasionally gas samples were collected from the reactor with a gas-tight syringe and injected directly into the GC, to obtain larger samples or to check for impurities.

RESULTS

The Solid and Liquid Components of the Clay Condensate and Extract

Light scattering experiments gave a mean effective diameter of about 115 nm for the particles suspended in the extract. The condensate contained some larger aggregates, which precluded measurement of particle size by the Tyndal effect. The freshly prepared distillates were completely clear and showed no light scattering when illuminated by a laser beam. The pH of distillate derived from the condensate was 3.5, that from the extract 5.0.

Microprobe analysis of dried aliquots of the distillates obtained from both condensate and extract contained Na, Ca, S and Cl. Some K was found in the extract distillate. For both distillates minor amounts of Si were detected by WDS, merely as a small increase above background response.

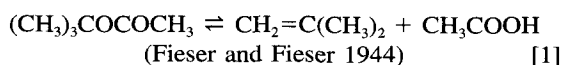
The condensate solids, 0.56 mg/ml condensate, were largely composed of silica with some Al, Mg and Fe substitution. The chemical composition of most of the particles dispersed in the extract, 1.8 mg/ml extract, was similar to that of the original clay.

Table 1. Tertiary butyl acetate decomposition catalyzed by the parent clay, the clay extract and condensate solids and an Al clay. Reaction conditions: vapor phase TBA concentration = 2×10^{-4} gm/cc; reaction period $\tau = 6 \times 10^{-2}$ h; $T = 85^\circ\text{C}$.

Catalyst	Ca clay	Extract solids	Condensate solids	Al clay
Wt. catalyst (mg)	2.2	7.6	2.2	2.1
% Conversion (observed)	1.7	<1.3	5.3	19.2
% Conversion (per mg catalyst)	0.8	<0.2	2.4	9.1

Decomposition of TBA

The decomposition of TBA to isobutylene and acetic acid is acid catalyzed. It proceeds according to Equation [1]:



By removing the products on the right side of the equation, as in our experiments, the reaction becomes essentially irreversible and its extent can be used to assay the activity of the catalyst, using standard GC technique (Goldstein 1983; Johns and McKallip 1989).

Under identical reaction conditions, the relative conversion of TBA catalyzed by the original Ca montmorillonite and the solids separated from the condensate and extract is shown in Table 1. For comparison, the relative conversion of TBA catalyzed by an Al montmorillonite, which is an effective catalyst for this reaction (Goldstein 1983), is also included. Under the same conditions, but with the liquid components of either condensate or extract in the reactor, no decomposition of TBA was detected. For control experiments, using either an empty or a quartz filled reactor, TBA did not undergo decomposition under the reaction conditions given in Table 1. This result is consistent with previous work demonstrating that non-acidic materials such as quartz or calcium carbonate do not act as catalysts for TBA decomposition under our reaction conditions (Goldstein 1983). When a dilute aqueous acid, for example 0.6 N HCl, was used as the catalyst, ester hydrolysis was the major reaction and the products were chiefly tertiary butanol and acetic acid.

Cracking of Octane

Clay condensates were previously shown to induce cracking of long-chain hydrocarbons (Heller-Kallai et al. 1989; Miloslavski et al. 1991). The present experiments were designed to compare the activity of the solid and liquid components of these condensates and of clay extracts with the parent clay. To facilitate analysis in a dynamic system, a shorter-chain hydrocarbon (C_8) was chosen.

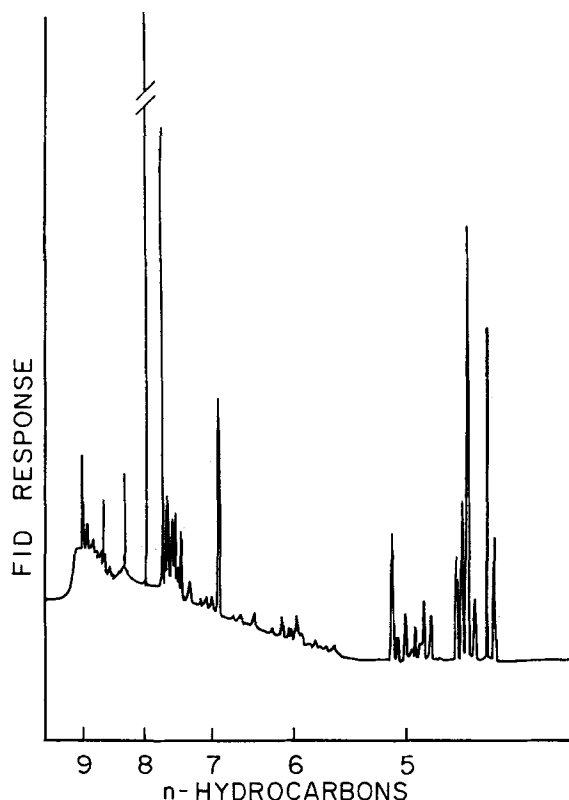


Figure 2. Typical gas chromatogram of reaction mixture obtained from clay catalyzed octane cracking.

At a temperature of 250°C even the least reactive of the three solids caused measurable conversion. Reaction to cracked products increased with increasing temperature and/or increasing residence time. Octane cracking was not observed during control experiments using either empty or quartz filled reactors under identical reaction conditions. This finding is consistent with published data (Greensfelder 1955).

Figure 2 shows a typical chromatogram of octane and its reaction products. Representative results obtained with the solid catalysts under identical reaction conditions are shown in Table 2. With time on-stream the conversion slowly decreased, as the catalysts became poisoned. The initially white solids darkened

Table 2. *n*-Octane cracking catalyzed by the parent clay and the clay extract and condensate solids. Reaction conditions: vapor phase *n*-octane concentration = 7×10^{-6} gm/cc; reaction period $\tau = 2.5 \times 10^{-1}$ h; $T = 300^\circ\text{C}$.

Catalyst	Ca clay	Extract solids	Condensate solids
Wt. catalyst (mg)	30	7.6	2.2
% Conversion (observed)	1.1	0.5	0.2
% Conversion (per mg catalyst)	0.04	0.07	0.1

progressively as coke was deposited. The cracked products are highly isomerized (Figure 2) indicative of acid catalyzed cracking (Greensfelder 1955; Corma and Wojciechowski 1985).

Reactions at 250 °C with aqueous liquids (the distillates) as potential catalysts in a flow system at atmospheric pressure necessitated some modification of the reaction train, as indicated in Figure 1. Under the conditions of these experiments, with reactor temperatures up to 300 °C, no cracking was detected.

DISCUSSION

The results show that the solid components derived from the clay condensate and from the extract act as true catalysts for the two reactions studied, whereas under the prevalent experimental conditions the liquid components did not catalyze these reactions. The relative activity of catalysts for mediating TBA decomposition is indicative of their ability to promote other acid catalyzed reactions (Goldstein 1983). For the two series of experiments, the efficiency of the solid from condensate significantly exceeded that of equal weights of either the parent clay or the solid from extract. The activity of these two solids was low, which reduced the accuracy of the results. It appears that their efficiency is similar, within the limits of the experimental errors. These observations imply that the octane cracking was, at least in part, acid catalyzed, an inference also supported by the distribution of the isomerized cracked products. It is noteworthy that for previous experiments with long-chain hydrocarbons (C₁₉ and C₂₄) and clay condensates (the aqueous suspensions) as catalysts, the dominant cracked products above C₇ were straight-chain hydrocarbons, although branched-chain ones were also present. In the lighter fraction branched-chain hydrocarbons were much more abundant (Miloslavski et al. 1991). This puzzling result requires further investigation.

Previous work demonstrated that the original condensate, which comprises both the aqueous phase and the solids, was catalytically active (Heller-Kallai et al. 1989; Miloslavski et al. 1991) as were volatiles and condensates derived from other clays. The present study suggests that the reactivity largely resides in the finely dispersed solid particles, which are mostly composed of amorphous silica substituted by Al and other cations. This material was either present within the original sample and was carried over with the evolved gases, or was derived from the parent clay within the course of evolution of the gases. Per unit weight it is a more effective acid catalyst than the parent clay.

The chemical composition of the extract solids resembles that of the parent clay. In view of the small particle size of the suspended matter (mean diameter 115 nm) these solids might be expected to be appreciably more reactive than the parent clay, both due to their larger surface area and the greater accessibility

of the clay interlayers. In fact, their reactivity does not differ substantially from that of the clay. This may, perhaps, be due to the inhibiting effect of thin surface coatings, which would escape detection by EMPA.

Implications for Geochemical Processes

It was already evident from previous work that catalytically active material can be mobilized from clay-containing formations. Moreover, this activity was observed within an aqueous medium and was known to be preserved in the finely divided solids, which are present in clay volatiles and in the corresponding condensates (Heller-Kallai et al. 1989; Miloslavski et al. 1991). The present study suggests that the acid catalytic activity resides mainly in these solids. Similarly, in extracts obtained by exhaustive water washing of the clays it is the colloiddally dispersed solid particles that are the catalytically active components.

For surface sediments the extractive process is expected to be more important, whereas at depth, catalytically reactive material may be produced by both processes, volatilization and extraction. Once formed, the highly dispersed catalyst is easily transported, either alone or with other formation fluids and can operate in places removed in space and time from the source material. In addition, since condensates can attack carbonates (Heller-Kallai et al. 1987; Heller-Kallai and Miloslavski 1992) and perhaps also silicates they are capable of altering rock porosity, thus opening new pathways for fluid transport.

The finding that finely divided, easily transportable catalysts can be derived from clays refutes the objections previously raised to a possible solid-solid interaction between organics, particularly kerogen, and bulk clay, due to their limited contact. Moreover, although the presence of water will reduce the rate (Goldstein 1983), the catalytic reactions are not completely inhibited by an aqueous medium. Clay condensates and extracts may therefore play an important role in the alteration, maturation and transport of organic matter in nature.

ACKNOWLEDGMENTS

This work was carried out while one of the authors, L. Heller-Kallai, was on sabbatical leave at Princeton University. The authors acknowledge use of the facilities and support of the Materials Institute of Princeton University. We are grateful to the Mobil Research and Development Corporation for donation of the gas chromatograph and flow and temperature controllers used in these experiments. We also thank personnel from the Hebrew University for preparing the samples (I. Miloslavski) and assistance with the microprobe analyses (D. Shafranek).

REFERENCES

- Corma A, Wojciechowski BW. 1985. The chemistry of catalytic cracking. *Catal Rev Sci Eng* 27:29-150.
- Fieser L, Fieser M. 1944. *Organic chemistry*. Boston: D.H. Heath & Co. p 178-179.

- Goldstein TP. 1983. Geocatalytic reactions in the formation and maturation of petroleum. AAPG Bull 67:152–159.
- Greensfelder BS. 1955. The chemistry of petroleum hydrocarbons. Brooks BT, editor. Reinhold Pub. Co. 2:137–164.
- Heller-Kallai L, Miloslavski I, Aizenshtat Z. 1987. Volatile products of clay mineral pyrolysis revealed by their effect on calcite. Clay Miner 22:339–348.
- Heller-Kallai L, Miloslavski I, Halicz L, Aizenshtat Z. 1988. Chemical and mass spectrometric analysis of volatiles derived from clays. Am Miner 73:376–382.
- Heller-Kallai L, Miloslavski I, Aizenshtat Z. 1989. Reactions of clay volatiles with n-alkanes. Clays & Clay Miner 37:446–450.
- Heller-Kallai L, Miloslavski I. 1992. Reactions between clay volatiles and calcite reinvestigated. Clays & Clay Miner 40:522–530.
- Johns WD, McKallip TE. 1989. Burial diagenesis and specific catalytic activity of illite-smectite clays from Vienna Basin, Austria. AAPG Bull 73:472–478.
- Keller WD. 1986. Composition of condensates from heated clay minerals and shales. Am Mineral 71:1420–1425.
- Keller WD, da Costa LM. 1989. Comparative chemical compositions of aqueous extracts from representative clays. Am Mineral 74:1142–1146.
- Miloslavski I, Heller-Kallai L, Aizenstat Z. 1991. Reactions of clay condensates with n-alkanes: Comparison between clay volatiles and clay condensates. Chem Geol 91:287–296.

(Received 15 February 1995; accepted 4 August 1995; Ms. 2623)