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CLAY MINERAL ACTIVATORS AND HYDROCARBON GENERATION DURING EXPERIMENTAL KEROGEN PYROLYSIS

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Abstract: Pyrolysis-Gas Chromatography and Pyrolysis-Gas Chromatography-Mass Spectrometric studies were carried out on smectite/kerogen and illite/kerogen mixtures. Using homoionic cation-exchanged clays, the catalyzed production of hydrocarbons depends on the ionic potential (ionic radius/ionic charge) of the exchange cation, and decreases in the order $Mg^{++} > Ca^{++} > Na^{+} > K^{+}$. This effect is related to the Bronsted acidity developed as the exchangeable cations cause dissociation of solvating water molecules in the interlayers of smectite and on external surfaces of illite crystallites.

GC-MS characterization of the hydrocarbon pyrolysates indicates increasing isoalkane/n-alkane ratios (branching ratios), suggesting the importance of carbonium ion mechanisms induced by the Bronsted acidity.

Key words: clay/kerogen pyrolysis, clay catalysis, smectite, illite catalysis.

Introduction

Numerous workers have studied the pyrolysis of oil shales and kerogens isolated from oil shales and other petroleum source rocks, and in recent years the importance of shale matrix mineralogy in determining product distributions in natural and experimental pyrolysis has become apparent (Johns 1981). Espitalie et al. (1980) and Horsfield & Douglas (1980) continuously pyrolyzed clay-kerogen mixtures and noted a catalytic effect on the production of light hydrocarbons from these mixtures. In the case of illite-kerogen mixtures, almost all of the hydrocarbons produced were light hydrocarbons. This was attributed to the retention of the heavier hydrocarbons by the illite matrix. In the case of smectites, the greater amount of light hydrocarbons produced, relative to kerogen alone was explained as due to catalytic cracking of thermally-produced hydrocarbons rather than as the result of directly catalyzed kerogen decomposition. Tannenbaum & Kaplan (1985) found, however, that under static pyrolysis condition (200 - 300 °C, 2 - 2000 hours, sealed tubes) the decomposition of kerogen was catalyzed directly by smectites, with little or no catalysis by illite. In none of these experiments were the clay mineral catalysts fully structure-chemically characterized, that is, with respect to internal ionic substitutions or to exchange capacities and composition.

The likely source of this catalytic activity has been attributed (Johns 1981) to the dissociation of water molecules closely associated with the exchangeable cations in the interlayer spaces of these clays, as suggested even earlier by Mortland & Raman (1968). This process makes smectites relatively strong Bronsted acids, with their acidity depending on the nature and number of exchange cations present in the layer-silicate interlayers. It has been noted also that greater water dissociation occurs when the exchangeable counter-ions neutralize layer charges arising from tetrahedral substitution of Al^{3+} for Si^{4+}, analogous to Al-Si zeolite catalysts.

This formation of Bronsted acidity can be summarized by the following reaction:

$$nM^{+z}(H_2O)_x \rightarrow nM[(H_2O)_{x-1}OH]^{z-1} + nH^+$$

where n equals the number of exchangeable cations of charge z, and x the number of cation-solvating water molecules. The greater the cation exchange capacity and cationic charge, and the greater the tetrahedrally-derived charge, the greater the proton-generating capacity and Bronsted acidity of the potential clay catalyst. It is to be emphasized that this reaction takes place within the interlayers of the readily expanding smectite clay structure, as well as on the external planar surfaces of non-expanding illite packets.

Recent work by Johns & McKallip (1989) confirms this effect. They studied the catalytic effect of different ion-exchanged clays on the acid-catalyzed decomposition of t-butyl acetate, which had been used by Goldstein (1983) as a means of measuring catalytic activity of clays. Their results showed that the specific catalytic activity of the clays was strongly dependent on the charge/size ratio (the ionic potential) of the exchange cation for this acid-catalyzed reaction.

To date no one has studied systematically the effect of varying the exchangeable cation on a given clay on kerogen reactivity in pyrolysis. The results of a study of this kind could reinforce the role played by Bronsted acid sites also in the case of kerogen pyrolysis, and could signal the importance of formation-water chemistry to the formation of petroleum from kerogen, if indeed clay minerals act as natural catalysts as has been suggested.

The purpose of this study is to ascertain whether the same acid sites noted by Johns & McKallip (1989) are effective in catalyzing the breakdown of kerogen during pyrolysis, as inferred by Tannenbaum & Kaplan (1985) from product distribution ratios. To that end we have studied the pyrolysis of clay-kerogen mixtures, utilizing well-characterized smectites and illites, ion-exchanged with K, Na, Ca, and Mg ions, and kerogen isolated from Green River oil shale. Pyrolyses were conducted mainly in a rapid-pulsed, stepped-temperature mode in an attempt to minimize dehydration of the clay during the process.

Experimental

The clays used in this study were obtained from the Clay Mineral Society-Univ. of Missouri Source Clays Repository. They were prepared for catalytic studies by standard fractionation techniques (Jackson 1969). The raw clay was separated by wet sedimentation into coarse (2.0 - 0.2 μm) and fine (<2 μm) clay fractions. After treatment with 30 % H_2O_2 to oxidize any adsorbed organic matter, the samples were rinsed with distilled-deionized water, dried in vacuo, and ion-exchanged with 1M solutions of K, Na, Ca, and Mg chlorides at 45 °C for 24 hours. The resulting ion-exchanged clays were rinsed repeatedly to remove excess electrolyte, as evidenced by a negative chloride test. Chemical analyses of these clays showed them to be homoionic with respect to exchange ions and gave the following calculated (Marshall 1949) structural compositions:

SAz-1 smectite

$(\text{exch.cat.})_{.90}(\text{Ca}_{.03}\text{Na}_{.05}\text{K}_{.11})(\text{Al}_{2.68}\text{Fe}_{.14}\text{Mg}_{1.12})(\text{Si}_{8.02})\text{O}_{20}(\text{OH})_4$, with a corresponding NH_4^+-exchange capacity of 120 meq./100 gr.

STx-1 smectite

$(\text{exch. cat.})_{.82}(\text{Al}_{3.06}\text{Fe}_{.14}\text{Mg}_{.82})(\text{Si}_{8.00})\text{O}_{20}(\text{OH})_4$, with a corresponding NH_4^+-exchange capacity of 97 meq./100 gr.

IMt-1 illite

$(\text{exch.cat.})_{.11}(\text{K}_{1.50}\text{Na}_{.05}\text{Ca}_{.02})(\text{Al}_{2.72}\text{Fe}_{.80}\text{Mg}_{.45})(\text{Si}_{6.87}\text{Al}_{1.13})\text{O}_{20}(\text{OH})_4$, with a corresponding NH_4^+-exchange capacity of 14 meq./100 gr.

Kerogen from the Green River shale was isolated by the method of Siskin (1985). This method, which minimizes chemical alterations of the kerogen structure, involves grinding the raw oil shale to 80 - 200 mesh, Soxhlet extracting the resulting powder with CCl_3 for 24 fours to remove bitumen, and refluxing the bitumen-free shale in a 50 : 50 mixture of toluene and 1M $(NH_4)_2SO_4$ under N_2 for 72 hours. The kerogen concentrate was decanted along with the toluene layer, concentrated by sink/float methods, and reextracted with CCl_3 before drying in vacuo.

Chemical analysis of the resulting kerogen concentrate yielded the following results:

C	H	N	total S	Fe_2O_3	ash	SO_3 on ash
43%	5.2%	1.6%	2.4%	3.2%	37.5%	4.4%

The high atomic H/C ratio (1.45) indicates this kerogen to be an immature type I variety. The high ash content is not a hindrance to this work. This method of kerogen concentration was used, since it results in less alteration than do the more conventional methods.

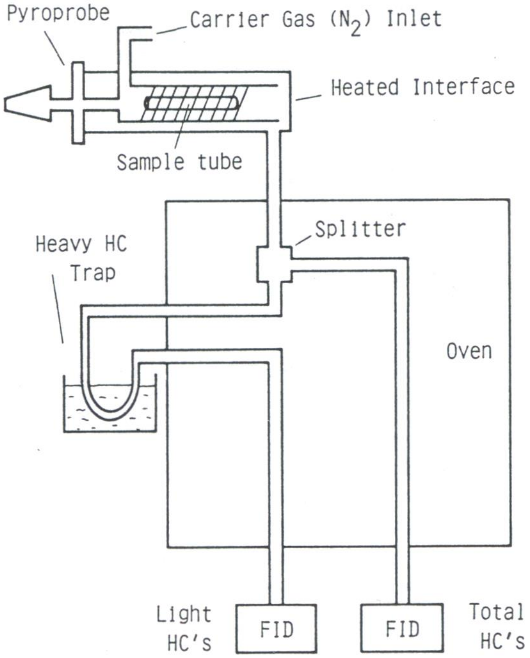

Fig. 1. Schematic diagram of Pyroprobe-Gas Chromatographic instrument for determining light-HC and total-HC effluents from pyrolysis of clay/kerogen mixtures.

Clay-kerogen mixtures were produced by grinding approximately 100 mg samples under H_2 in an agate mortar. The most reproducable pyrolysis results were obtained at clay/kerogen ratios of 50 : 1 and with sample sizes of 5 to 10 mg.

Pyrolyses were carried out using a Chemical Data Systems Model 122 Pyroprobe, equipped with a large coil probe. Samples were weighed to within 0.10 mg directly into 12 mm by 3 mm i.d. open-ended quartz sample tubes. The sample was held within the quartz tube by two plugs of quartz wool, and the sample tube placed in the Pt heating coil of the pyroprobe. This sample probe was inserted into an interface heated to 225 °C, which was connected directly to the inlet of a Bendix 2500 Gas

Table 1: Light-HC/total-HC ratios clay/kerogen pyrolysates continuous pyrolysis, 200 - 600 °C (duplicate runs).

	Exchange cation					
	K^+	Na^+	Ca^{++}	Mg^{++}	Aver.	Kerogen
SAz-1 mectite	0.80	0.68	0.80	0.79	0.78	0.60
	0.78	0.71	0.79	0.82	0.78	
IMt-1 illite	0.54	0.60	0.58	0.59	0.58	0.60
	0.56	0.59	0.59	0.61	0.61	

Table 2: Heavy-HC/total-HC ratios for clay/kerogen pyrolysates continuous pyrolysis, 200 - 600 °C (duplicate runs).

	Exchange cation					
	K^+	Na^+	Ca^{++}	Mg^{++}	Aver.	Kerogen
SAz-1 smectite	0.20	0.32	0.20	0.21	0.23	0.41
	0.22	0.29	0.21	018	0.23	
IMt-1 illite	0.46	0.39	0.42	0.41	0.42	0.41
	0.44	0.41	0.41	0.40	0.42	

Chromatograph. Pyrolyses were conducted in two modes. Preliminary runs used continuous heating from 200 - 600 °C, following the mode of Espitalie et al. (1980). Most of the data were obtained subsequently by a second mode, using pulsed heating, with pulse times of 20 seconds. Evolved hydrocarbons were swept from the sample by the preheated, water-saturated, 60 ml/min N_2 carrier gas stream. This effluent stream was routed directly in to a 400 °C GC oven where it was split in a 50 : 50 ratio, one fraction going directly to a FID detector as a measure of total hydrocarbons produced. The other half of the effluent stream was routed out of the oven into a cooled heavy-hydrocarbon trap, then back into the oven to a second FID as a measure of light-hydrocarbons produced (Fig. 1). The external heavy-hydrocarbon trap was maintained at ambient temperature and condensed hydrocarbons less volatile than n-undecane. The FID response was recorded, and the temperature was increased at 50 °C intervals as soon as the FID response had dropped to 5 % of its maximum for that pulse. Reproducibility was good for carefully packed samples.

Sample pyrolysis temperatures were calibrated using two different methods. The first method involved the use of standards of known melting point, which were placed in thin-walled capillaries and inserted into the center of a clay-packed quartz sample tube. These were then heated under pyrolysis conditions and the samples observed for evidence that melting had occurred. The other method of exact temperature determination, the "molecular thermometer" method of Levy (1965), involves pyrolysis of a small quantity of Kraton 1107 (obtained from Shell Chemical Campany). The ratio of several of the pyrolysis products is indicative of the pyrolysis temperature. Both of the methods agreed well over the range that they overlapped, and gave evidence that the temperature the sample experienced was often significantly lower than that set on the Pyroprobe. It is to be emphasized that the temperatures thus measured do not represent equilibrium temperatures because of the short duration of successive heating pulses.

Pyrolysis/gas chromatography was accompanied utilizing a Hewlett Packard Model 5830A recording gas chromatograph interfaced to the CDS Pyroprobe. The chromatographic column was a Supelco WCOT wide-bore capillary column, 30 meters x 0.75 mm i.d. The stationary phase was SPB-1. Helium was employed as a carrier gas, with a 30 ml/min flow, maintained through the

Table 3: Light-HC/heavy-HC ratios for clay/kerogen pyrolysates continuous pyrolysis, 200 - 600 °C (duplicate runs).

	Exchange cation				
	K^+	Na^+	Ca^{++}	Mg^{++}	Kerogen
SAz-1 smectite	4.00	2.13	4.00	3.85	1.45
	3.57	2.44	3.85	4.54	
Aver.	3.78	2.28	3.92	4.19	
IMt-1 illite	1.18	1.52	1.39	1.43	1.45
	1.28	1.45	1.43	1.54	
Aver.	1.23	1.48	1.41	1.48	

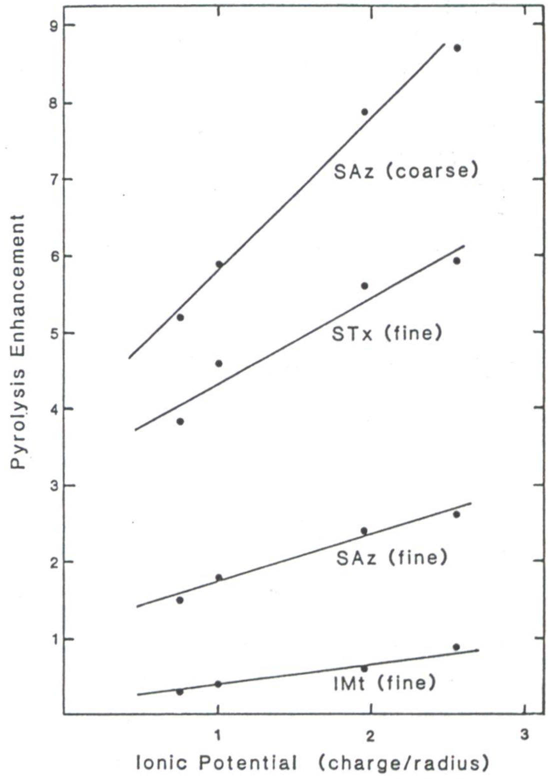

Fig. 2. Relationship between ionic potential (charge/ionic radius) of clay exchange cations and pyrolysis enhancement for some clay/kerogen mixtures, normalized to HC yield of pure kerogen.

Table 4: Total hydrocarbons from clay/kerogen pyrolysates pulsed mode, 250 - 500 °C (normalized to kerogen HC yield = 1, pyrolysis enhancement).

		Exchange cation			
	size/fraction	K^+	Na^+	Ca^{++}	Mg^{++}
STx-1 smectite	fine	3.8	4.6	5.6	5.9
SAz-1 smectite	coarse	5.2	5.9	7.9	8.7
	fine	1.5	1.8	2.4	2.6
IMt-1 illite	coarse	1.5	1.6	2.7	6.4
	fine	0.3	0.4	0.6	0.9

Table 5: Light-HC/total-HC ratios for clay/kerogen pyrolysates pulsed mode, 250 - 500 °C (ratio for kerogen alone = 0.13).

		Exchange cation			
	size/fraction	K^+	Na^+	Ca^{++}	Mg^{++}
STx-1 smectite	fine	0.32	0.34	0.36	0.36
SAz-1 smectite	coarse	0.32	0.34	0.42	0.43
	fine	0.25	0.27	0.30	0.32
IMt-1 illite	coarse	0.23	0.26	0.32	0.32
	fine	0.17	0.20	0.26	0.28

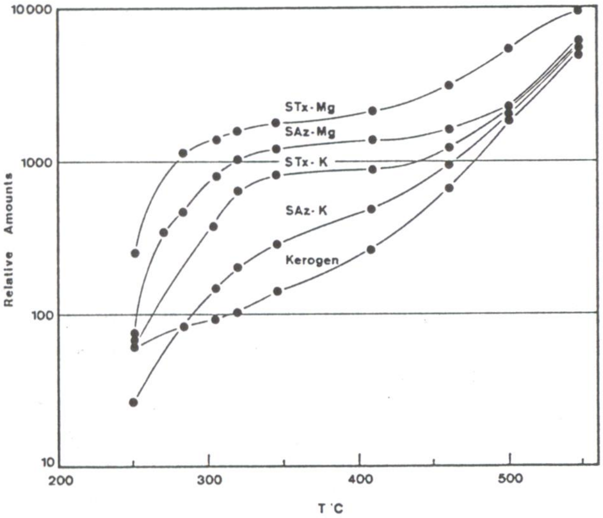

Fig. 3. Cumulative total-HC/temperature plot for pulsed mode pyrolysis of clay/kerogen mixtures.

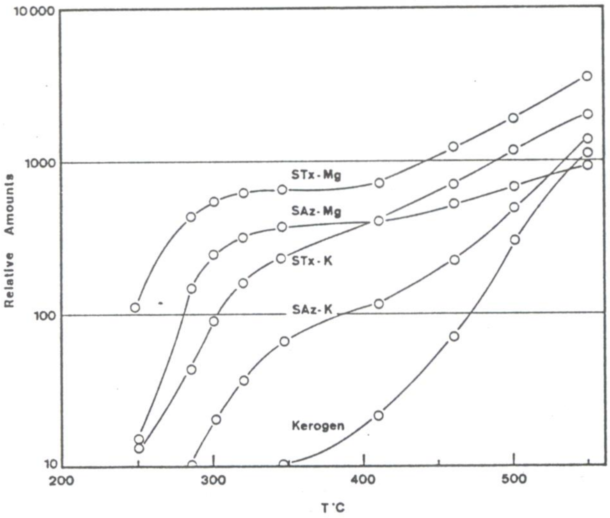

Fig. 4. Cumulative light-HC/temperature plot for pulsed mode pyrolysis of clay/kerogen mixtures.

Pyroprobe interface. This effluent was split at a 5 : 1 ratio, resulting in a flow rate of 5 ml/min through the column.

Pyrolysis/GS/ mass spectrometry was used to identify components of the gas chromatograms. The columns and conditions used were the same as utilized in the pyrolysis/GS. The instrument employed was a Carlo Erba system Model 4160 Gas Chromatograph, equipped with a Kratos data system.

Results and discussion

There were several clear objectives for the present study: *1* - to confirm the findings of other workers regarding catalytic effects of clays on kerogen reactivity, *2* - to examine the effects of exchange cations on the amount and distribution of products from clay/kerogen pyrolysis, and *3* - to seek evidence for carbonium ion reactions that would confirm the role played by Bronsted acidity of the clay catalysts.

Our preliminary experiments involved continuous pyrolysis of homoionic (<0.2 μm fraction) SAz-1 smectite/ and IMt-1 illite/kerogen mixtures over the temperature range 200 - 600 °C, following the heating mode of Espitalie et al. (1980). Both total HC and light HC pyrolysis products were monitored as described earlier. Tabs. 1 - 3 summarize the light-HC/total-HC ratios, heavy-HC/total-HC ratios, and light-HC/heavy-HC ratios, produced from each homoionic-clay/kerogen mixture. These data, representing duplicate runs in each case, show the excellent reproducibility of our FID monitoring procedure. When each of these sets of data is compared to respective ratios for kerogen pyrolysis alone, it is clear that the illite/kerogen mixtures reveal no significant differences under this continuous heating mode. On the other hand the smectite/kerogen mixtures show appreciable increase in light-HC at the expense of heavy-HC products (approximately 20 % more light-HC in the total-HC, a 2 - 3 fold increase in light-HC/heavy-HC ratios). No significant cationic effect was revealed in this series of experiments, except perhaps in the case of light-HC/heavy-HC ratios for the divalent Ca- and Mg-smectite. The FID monitoring in these runs indicated that pyrolysis had gone to completion, but did not allow resolution of product distribution at any intervening temperature.

Table 6: Hydrocarbon composition. Pyrolysis-GS-Mass spectrometry major components C_9-C_{14} range (n-alkane retention times) (pyrolysis to 315 °C, 20 sec).

	Percentages				
	n-alkanes	isoalkanes	alkenes	aromatics	a.b.r.*
Kerogen	45	13	32	10	3.5
SAz-1 - K^+	61	18	7	14	3.4
Na^+	54	25	4	17	2.2
Ca^{++}	52	25	5	18	2.1
Mg^{++}	48	28	3	20	1.7
STx-1 - K^+	59	27	9	9	2.2
Na^+	50	30	8	12	1.7
Ca^{++}	41	42	3	14	1.0
Mg^{++}	42	38	5	15	1.1

* alkane branch. ratios n-alkane/isoalkane

Table 7: Hydrocarbon compositions. Pyrolysis-GC-Mass spectroscopy major components C_9-C_{14} (n-alkane retention times) (pyrolysis to 700 °C, 20 sec).

	Percentages				
	n-alkanes	isoalkanes	alkenes	aromatics	a.b.r.*
Kerogen	32	11	44	12	2.9
Smectite (coarse)					
SAz-1 - K^+	20	15	38	27	1.3
Na^+	11	29	30	30	0.38
Ca^{++}	5	63	6	26	0.08
Mg^{++}	tr.	68	4	29	
Illite (coarse)					
IMt-1 - K^+	14	14	40	32	1.0
Na^+	18	13	38	31	1.4
Ca^{++}	16	21	25	38	0.76
Mg^{++}	16	17	23	43	0.94

Therefore, we turned to the pulsed-heating mode, monitoring the light-HC and total-HC product distributions at each 50 °C interval over the range 200 - 500 °C. In this case we utilized again SAz-1 smectite/ and IMt-1 illite/kerogen mixtures, and also STx-1 smectite, with composition very similar to SAz-1. Also we repeated runs, using in addition the coarse (2.0 - 0.2 μm) SAz-1 smectite and IMt-1 illite. Tab. 4 summarizes the relative amounts of total-HC produced over the entire heating range, normalized to total kerogen-HC = 1 (pyrolysis enhancement). A significant cation effect is noted in each clay sample tested. Mg-exchanged clays produced in all cases the greatest amount of HC over this temperature range with lesser amounts being produced from clays in the order $Mg^{++} > Ca^{++} > Na^+ > K^+$. This order is as expected from size/charge ratios, if these cations are acting as a source of Bronsted acidity, as suggested by Mortland & Raman (1968) and Johns & McKallip (1989). This effect can be seen more clearly in Fig. 2, wherein the pyrolysis enhancement ratio is plotted for several clays versus ionic potential of exchange cations.

Even in the case of coarse Mg-illite (Tab. 4, not shown in Fig. 2), more HC were produced than from kerogen alone and from this illite/kerogen mixture the initial rate of HC production is higher for the illite/kerogen mixture than for kerogen alone. This would seem to indicate that the coarse illite is acting both as a catalyst in the initial cracking of kerogen and is retaining or disproportionating the thermally produced HC. Espitalie et al. (1980) did not observe a catalytic effect for illite, nor did we in the continuous-heating mode, and they ascribed reductions in total HC and changes in product distribution to a retention effect.

Because the amount of HC produced at any given temperature in the pulsed-pyrolysis mode is probably a function of previous heating episodes, a cumulative HC-temperature plot best shows the catalytic effect on the rate of reaction as in Fig. 3 for Mg- and K-exchanged clays and for kerogen alone.

The absolute quantities of HC produced were difficult to determine. Thus we are reporting these results only in relative quantities, using kerogen as a standard for comparison. That this pulsed, stepped-temperature pyrolysis was not an equilibrium process was evident from the continued production of HC at temperatures greater than 600 °C, a point at which HC production has ceased during slower continuous pyrolysis.

The product distribution (light-HC/total-HC) is recorded in Tab. 5 and for selected clays the total light-HC are shown graphically in Fig. 4 (note log scale). Again one notes a strong cation effect, with the light-HC/total-HC ratio for any given clay decreasing in the order $Mg^{++} > Ca^{++} > Na^+ > K^+$. In all cases the artio is substantially higher than for kerogen alone.

There also appears to be a clay particle size effect on both the amount of HC produced and on the light-HC/total-HC ratio (Tabs. 4 and 5). The fine clays in all cases produced less total HC than the coarse clays, as well as lower light-HC/total-HC ratio. We can only surmise that under these experimental conditions the coarse clay crystallites, with their broader lateral dimensions, are able to retain more readilly the adsorbed water responsible for the catalytic activity. This effect remains to be investigated further.

We see also that the nature of the clay mineral has an effect on both total yields and ratios. Smectites of a given size fraction produce higher total yields and higher light-HC/total-HC ratios than does illite. The STx-1 smectite appears to be a better catalyst than SAz-1 smectite. Although we cannot explain this difference, this may be also a particle-size effect.

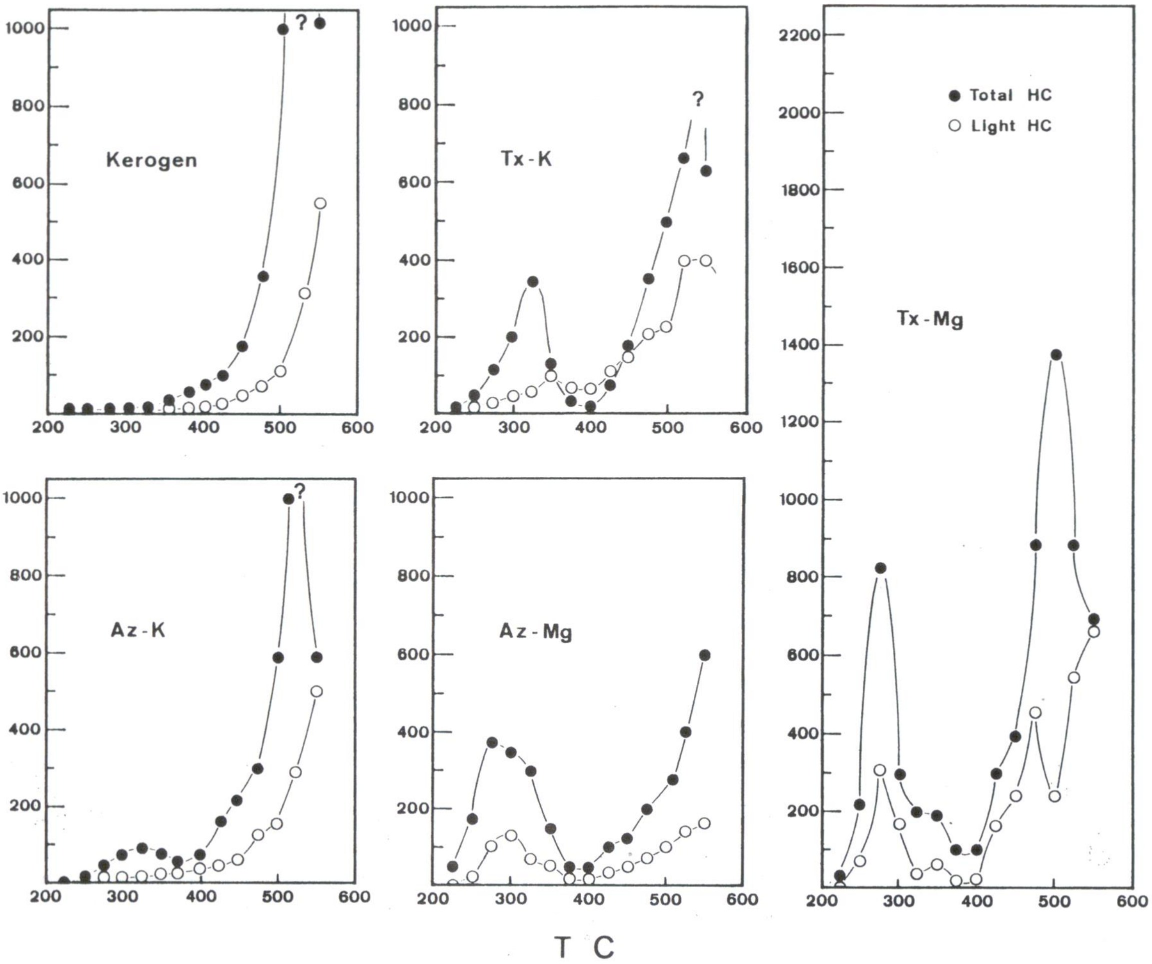

Fig. 5. Differential plots of HC yield per each 25 °C (based on Figs. 3 and 4) for pulsed mode pyrolysis of kerogen and clay kerogen mixtures. Black circles - total-HC; open circles - light-HC.

From Figs. 3 and 4 it can be seen that under these dynamic heating conditions kerogen pyrolysis is initiated at about 350 °C, and becomes rapid at about 450 °C. On the other hand the smectite/kerogen mixtures commence pyrolysis at about 250 °C with rapidly increasing rate by 300 °C. Thus there are two episodes of pyrolysis, a low and high temperature production of HC. This can be seen best by differentiating the cummulative curves (Figs. 3 and 4) through temperature increase as shown in Fig. 5. Here intermediate 25 °C intervals are interpolated from each smoothed cumulative curve. The two episodes of HC formation are seen clearly, peaking at about 300 °C and 500 °C respectively, the latter maximum corresponding to that of kerogen alone. It is apparent that the low temperature HC production (total-HC, filled circles; light-HC, open circles) represents a significant proportion of the total produced over the entire temperature range, especially in the case of the STx-1 smectite. The enhanced effect of Mg- over K-exchange cation is evident also.

It is apparent from these results that clays catalyze the decomposition of kerogen at reduced temperature during pyrolysis and effect also the product distribution. The cation effect noted would seem to have no other explanation than that the exchange cation is acting in promoting Bronsted acidity in these clay minerals, and that catalytic activity is related to that acidity.

Product distribution as revealed by pyrolysis-GS and pyrolysis-GS-Mass Spectroscopy also leads to similar conclusions (Tabs. 6 and 7; Fig. 6). While the most abundant components of the pyrolyzate of kerogens are n-alkanes and n-alkenes, in smectite/kerogen mixtures the relative abundance of n-alkanes decreases and branched alkanes increases (alkane branching ratios n-alkane/isoalkane), as the size/charge ratio of the exchange cation decreases. This indicates that a carbonium ion mechanism is controlling product distribution. This cation effect is evident in both the low and high temperature regimes (Tabs. 6 and 7 respectively). Since during the higher temperature regime (700 °C) the coarser clay fractions were used, the lower branching ratios, indicative of more active catalysis, confirm the earlier suggestion of greater water retention in the interlayers of coarser particles.

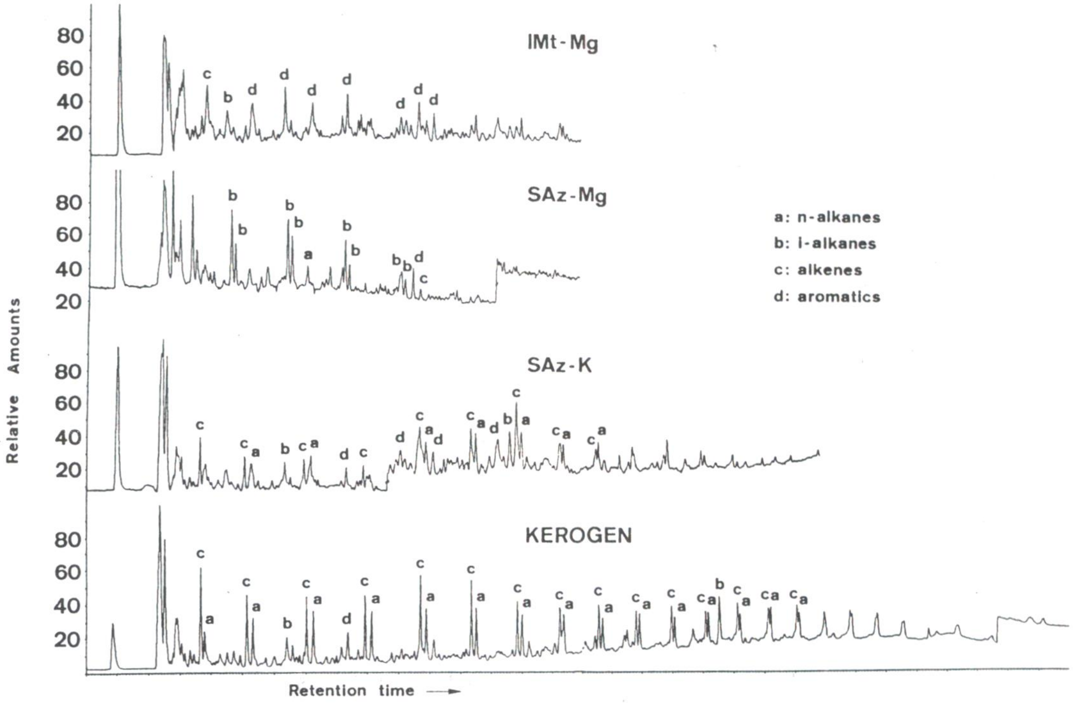

Fig. 6. GC traces of HC produced by pyrolysis (315 °C, 20 sec) from kerogen and 50 : 1 clay/kerogen mixtures. Compounds identified using coupled Mass Spectrometer.

It is interesting that illite exhibits significant catalytic activity, despite its non-expanding structure. Although illite does not offer as catalytic sites the greater interlamellar surface that smectites do, the high external-surface charge of illite, and the tetrahedral substitution associated with this charge, produces a larger density of more accessible external sulfure catalytic sites. As a corollary, it is apparent that the interlamellar spaces in smectites are important sites, regardless of the problems involved in bringing bulky kerogen particles into intimate contact with these sites.

The retention of HC on illite surfaces apparently becomes more important at higher temperatures, as evidenced by the pyrolysis enhancement ratios less than 1. Several explanations can be advanced for this. One is a catalyst-fouling mechanism; while the clay/kerogen ratios employed are quite high, the kerogen and clay particles are immobile, and the illite surfaces in the immediative vicinity of a kerogen particle might experiencee fouling. Another possibility is that the illite external surfaces dehydrate more readily at these higher temperatures, resulting in both lowered Bronsted acidity and lowered catalytic activity.

The particle size effect of illite is difficult to explain. The standard assumption of greater surface area providing greater specific catalytic activity does not seem to apply here. To explain the lower HC yields requires the assumption that any retention effect increases faster with decreasing particle size than does the catalytic activity. Also the exposed surfaces of a clay platelet are of two distinct types, basal and edge surfaces. The relative areas of these surfaces probably change with a change in particle size and there is no *a priori* reason to believe they would have the same catalytic properties.

Summary

Smectite clays can act as strong acid catalysts in the pyrolysis of kerogen, that is, they can catalyze directly the decomposition of kerogen, in addition to the cracking of hydrocarbons released by thermal decomposition of kerogen. This catalysis proceeds by a carbonium ion mechanism and has its origin in the Bronsted acidity of the clay. The catalytic activity is controlled for a given clay by the exchangeable cations, and is related also to the source of interlayer charge, neutralized by these counter ions.

A previously unnoticed effect of clay particle size was observed, affecting the amount and product distribution from pyrolysis of clay/kerogen mixtures. In these experiments coarser fractions of clays appear more catalytically active than the corresponding finer fractions. Investigations into the causes of this effect are contininug.

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