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The Catalytic Cracking of Slack Wax with Molten Mixtures Containing Aluminum Chloride and Bromide

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The catalytic cracking of slack wax with molten mixtures of $AlCl_3$ and $AlBr_3$ was investigated in an atmospheric semi-batch reactor at low temperatures of 100—160 °C. The cracking rate was proportional to the amount of unreacted wax. The conversion at 135 °C reached 25 wt% under typical reaction conditions. About 95 wt% of the cracking products consisted of isobutane, 2-methylbutane, and methylpentanes, *ca.* 50% of these isoparaffins being isobutane. The difference in cracking activity between this catalyst and a solid acid catalyst is discussed based on the product distribution. Hardly any reaction took place without HCl, which shows that the presence of HCl is essential for this cracking. The cracking rate increased sharply with an increase in the amount of the catalyst. The rate did not depend on the composition of the $AlCl_3$–$AlBr_3$ catalyst, but the product distribution did depend on it and the content of the gasoline fraction in the products increased with an increase in the concentration of $AlBr_3$. The cracking residue was characterized by IR and NMR spectroscopy. The results show that the cracking reaction probably occurs heterogeneously at the interface between the liquid wax and the molten catalyst.

Petroleum waxes are present in all crude oils, the content depending on the source. Among imported oils, the value is high in Minas and Taching crude, reaching 15—20 wt%. In such waxy crude oils, the upgrading of the waxes may be needed in the future.

Several works on the hydrocracking or hydroisomerization of paraffin wax have been carried out for the purpose of obtaining valuable lighter products.[1,2] Since such reactions are conducted over solid acid catalysts at high temperatures, the high isoparaffin yield attainable at low temperatures is sacrificed and expensive hydrogen is consumed. The use of Lewis acid catalysts, which are very active at low temperatures and without hydrogen, may be preferable for the cracking of paraffin wax. However, little work has been published in this connection. About thirty years ago, however, Potolovsky and Spektor shortly reported the cracking of paraffin wax with the $AlCl_3$ catalyst at temperatures of 200—250 °C.[3]

We now wish to report the cracking of slack wax, the wax obtained in the process of dewaxing lubricating oils, at low temperatures of 100—160 °C. We employed molten salt mixtures containing $AlCl_3$ and $AlBr_3$ as cracking catalysts, because they had been found in preliminary experiments to have low melting points (*ca.* 90 °C) and to show a high activity toward the conversion of lower normal paraffins. In this paper, the effect of some parameters on the cracking rate and the product distribution will be investigated, and the reaction process will be discussed.

Experimental

Materials. The slack wax used in this study was supplied by Idemitsu Kosan Co., Ltd. The properties were as follows: melting point, 53.0 °C; specific gravity at 100 °C, 0.770; kinematic viscosity at 98.9 °C, 4.38×10^{-6} $m^2 s^{-1}$; oil content, 6.0 wt%; average molecular weight, 400. The weight fractions of the normal alkanes, isoalkanes, cycloalkanes and aromatics in the wax were 57.5, 30.6, 10.8, and 1.1% respectively. The carbon numbers of the normal alkanes range mainly from 26 to 30. Anhydrous aluminum chloride and bromide, and sodium chloride were of a reagent grade, and they were used as received. Helium and hydrogen chloride were of a research grade.

Apparatus. The cracking of slack wax was carried out in a semi-batch reaction system. The reactor consisted of a Pyrex test tube onto which a water-cooling jacket was glassblown. This test tube was connected to a vacuum system, a carrier gas line, and a gas-chromatographic unit through three separate metal-glass joints. The reactor was heated electrically by nichrome wire wound onto it and insulated thermally by an annular Pyrex tube. This assembly made it possible to observe the appearance of the reaction process with the naked eye. The reaction temperature was measured with a chromel-alumel thermocouple located in a well embedded in a liquid mixture of slack wax and the catalyst melt.

Procedure and Analysis. In most runs, molten salt mixtures of $AlCl_3$ and $AlBr_3$ were used as cracking catalysts. First, the catalyst was prepared in the reactor by melting a powdery mixture of the two salts at *ca.* 100 °C. The details of the preparation have been described elsewhere.[4] Care was taken throughout the preparation to avoid contact between the catalyst and moisture. After the completion of the preparation, the reactor was kept at 60 °C under flowing He. At this temperature, the catalyst was solid.

Then, a fixed amount of liquid slack wax was quickly poured onto the catalyst and the reactor was rapidly heated up to a predetermined reaction temperature. Finally, HCl diluted with the He carrier, at a total flow rate of 76 cm^3 (STP)/min, was bubbled into the mixture of slack wax and the catalyst melt, and simultaneously the mixture was stirred magnetically. This time was taken as the start of the reaction. Typical cracking conditions were as follows: amount of catalyst, 18 g; its composition, 35 mol% $AlCl_3$-65 mol% $AlBr_3$; amount of slack wax, 54 g; volume fraction of HCl, 0.21; reaction time, 3 h.

The effluent from the reactor outlet was led to a gas-chromatographic unit; all the cracking products were analyzed periodically and separated by means of a 9-m column with 30 wt% propylene carbonate on C-22.

After a constant reaction time, the flow of HCl was stopped and the reactor was cooled to room temperature. The contents of the reactor were separated into two layers by allowing it to stand. The separated materials were then analyzed by IR and NMR spectroscopy method. The IR spectra were measured by sandwiching the sample between two KBr plates. The NMR spectra were deter-

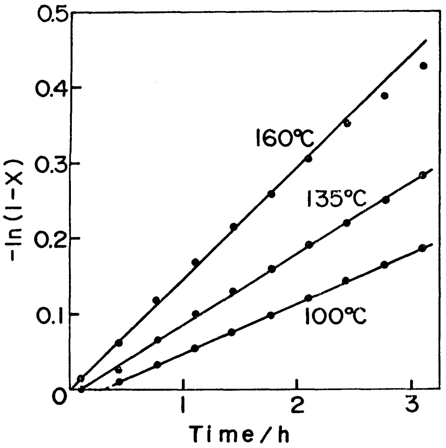

Fig. 1. First-order rate plots for the cracking of slack wax at different reaction temperatures.

mined as solutions in CCl_4 using TMS as a reference.

Results and Discussion

Cracking Rate. Figure 1 illustrates the first-order rate plots for the cracking of slack wax. The fractional conversion, X, is expressed as a weight fraction of the summation of all the cracking products in the effluent to the feed wax. In all runs, about 95 wt% of the products consisted of isobutane, 2-methylbutane, and methylpentanes. The detailed product distribution will be given later.

As is shown in the figure, a linear relationship between $-\ln(1-X)$ and time was observed at all reaction temperatures, except for the induction period at low temperatures. This result means that the cracking rate is proportional apparently to the amount of the unreacted wax. The rate constant of cracking is obtained from the slope of the straight line in Fig. 1; the values at 100, 135, and 160 °C were 1.1×10^{-3}, 1.6×10^{-3}, and $2.5\times10^{-3}\,\mathrm{min}^{-1}$ respectively. When the temperature was raised from 100 to 160 °C, the rate increased by a factor of 2.3.

The induction period was observed at low temperatures of 100 and 135 °C. The period may arise from the small contact area between wax and catalyst, because, at the beginning of the reaction, especially at 100 °C, the liquid wax and the molten catalyst were immiscible with each other, and thus there existed two separated layers. Such an incomplete mixing may be ascribed to the difference in viscosity between the two. As the cracking proceeded, the mixture apparently became homogeneous.

At high conversions at 160 °C, a little deviation from linearity was observed. The catalyst deterioration may be considered as one reason for this. It is possible that the catalyst reacts with olefinic or aromatic hydrocarbons which may be formed during the cracking, and thus loses its activity.[5]

Distribution of Cracking Products. The results are given in Table 1. The main products were isobutane, 2-methylbutane, and 2- and 3-methylpentane. The product yield increased with an increase in the cracking temperature, but the selectivity to each product depended hardly at all on the temperature. The selectivities to the above main products were 46—47, 32—33, and 14—15 wt% respectively. Thus, about 95% of the products consisted of such lower isoparaffins, which were all monomethylalkanes. The content of the gasoline fraction in the products was 51—53 wt%. No formation of olefinic and aromatic hydrocarbons was found in the products. H_2 and CH_4 were not formed, either.

Table 1. Product distribution at different reaction temperatures[a]

Temperature/°C	100	135	160
Conversion/wt%	16	24	34
Product yield/wt%			
C_3H_8	t [b]	0.2	0.6
n-C_4H_{10}	0.1	0.1	0.2
i-C_4H_{10}	7.7	11	16
n-C_5H_{12}	t	t	0.1
i-C_5H_{12}[c]	5.4	7.8	11
i-C_6H_{14}[d]	2.4	3.6	4.8
i-C_7H_{16}[e]	0.8	1.1	1.6

a) Under typical conditions. b) Trace (<0.05 wt%). c) 2-Methylbutane. d) 2-Methyl- and 3-methylpentane. e) Mixture of methylhexanes.

Table 2. Comparison of carbon-number distribution of cracking products between this molten catalyst and a solid-acid catalyst

Catalyst	$AlCl_3$-$AlBr_3$	SiO_2-ZrO_2-Al_2O_3[a]
Temperature/°C	135	500
Conversion/wt%	24	24
Selectivity/mol%		
C_1+C_2	0	5 (5)[b]
C_3	1	27 (29)
C_4	54	28 (30)
C_5	30	18 (19)
C_6	12	14 (15)
C_7	3	2 (2)
C_8^+	—	6

a) Ref. 6. b) Values in parentheses denote the selectivity calculated by excluding the C_8^+ fraction.

It is interesting to examine the difference in cracking activity between this catalyst and the solid-acid one. For this purpose we compared our carbon-number distribution of cracking products with that for the cracking of cetane over the SiO_2–ZrO_2–Al_2O_3 catalyst at 500 °C.[6] These two examples differ in feed stock, but this point is insignificant, because it has been reported that the products from centane are similar to those from paraffin wax (approximately n-$C_{24}H_{50}$) over the above solid catalyst.[7] A comparison at the same conversion is made in Table 2. The charateristics of this cracking is that the selectivity to C_3 hydrocarbons is extremely low, while the selectivity to C_4 and C_5 hydrocarbons is considerably high. Furthermore, although it is not shown in the table, another point to be noted is that the iso-to-normal ratio in total paraffins with this catalyst is significantly high,

Table 3. Effect of hydrogen chloride on cracking at 135 °C[a)]

HCl/vol%	0	10	21
$k^{b)}/10^{-3}$ min^{-1}	—	1.3	1.6
Conversion/wt%	0.1	19	24

a) Under typical conditions. b) First-order rate constant.

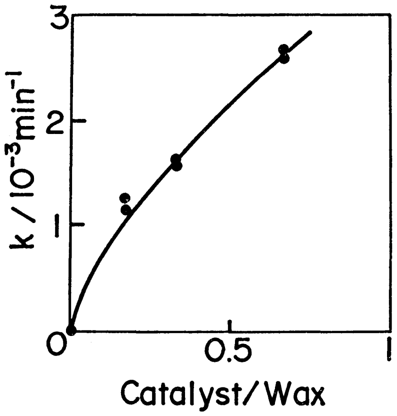

Fig. 2. Effect of amount of catalyst on the cracking of slack wax at 135 °C.

more than twenty times the ratio (*ca.* 3) with the solid-acid catalyst.[6)] The low cracking temperatures in this work are one reason for the high iso-to-normal ratio. Since the catalytic cracking of slack wax with molten salts would proceed through the same carbonium-ion mechanism as the Lewis acid-catalyzed cracking,[5)] the results shown in Table 2 may characterize this cracking as follows: normal secondary carbonium ions hardly break down into fragments of small molecules such as C_3 fragments, and such normal ions easily undergo skeletal isomerization to form tertiary carbonium ions, which then break down by β fission into fragments of C_4 or larger.

Effect of Hydrogen Chloride. As is generally accepted, hydrogen halide or an equivalent proton source is essential for the isomerization and cracking of paraffins by aluminum halide catalyst.[5)] However, such reactions also take place even in the absence of these materials at around 150 °C.[4,8)] Thus, the effect of HCl on the cracking of the slack wax was examined. The results are given in Table 3.

In the absence of HCl, a very small amount of the products was formed, and that only at the beginning of the reaction; thereafter, no appreciable cracking was observed. Consequently, the conversion was no more than 0.1 wt%. A trace amount of water present in the slack wax or catalyst probably serves as a proton source for the cracking at the initial reaction time. The addition of 10 vol% of HCl to the carrier gas increased the cracking rate considerably; the conversion reached about 20% in a reaction time of 3 h. An additional two-fold increase in the volume fraction of HCl further increased the cracking rate, but the increase in the rate seemed to level off. The presence of an optimum amount may be considered. It is evident from these results that the presence of HCl is essential for the cracking of slack wax with molten catalysts.

Table 4. Effect of catalyst composition on cracking conversion and product distribution at 135 °C[a)]

Catalyst composition[b)] (mole ratio)	$AlCl_3$-$AlBr_3$ (35:65)	$AlCl_3$-$AlBr_3$ (61:39)	$AlCl_3$-NaCl (61:39)
$k^{c)}/10^{-3}$ min^{-1}	1.6	1.6	0.50
Conversion/wt%	24	24	8.7
Selectivity/wt%			
C_3H_8	1	1	6
n-C_4H_{10}	t	1	3
i-C_4H_{10}	47	54	64
n-C_5H_{12}	t	t	1
i-C_5H_{12}	33	30	22
i-C_6H_{14}	15	10	4
i-C_7H_{16}	5	4	t

a) Under typical conditions. b) Catalyst amounts were 18, 15, and 14 g, in the order shown. c) First-order rate constant.

Effect of Amount of Catalyst. Figure 2 illustrates the effect of the catalyst amount on cracking at 135 °C. In this experiment, the weight of the molten catalyst (35 mol% $AlCl_3$–65 mol% $AlBr_3$) was varied from 9.0 to 36 g, while the weight of the wax was kept constant (54 g). In the figure, the first-order rate constants are plotted as a function of the weight ratio of the catalyst to the wax.

Without a catalyst, of course, no pyrolysis of wax was observed at temperatures of 100—160 °C. The catalyst promoted the cracking of the wax considerably, and the rate increased sharply with an increase in the amount of the catalyst. The plots of $\log k$ against log (catalyst/wax) gave a straight line, and from the slope of the line the order with respect to the amount of the catalyst was found to be about 0.6. A similar value has been reported for the liquid-phase isomerization of ethylcyclohexane in the presence of $AlCl_3$.[9)]

Such a dependence of rate on the catalyst amount suggests that a stoichiometric reaction between catalyst and wax may occur or that the extent of contact between the two may be a key factor in determining the cracking rate. If the stoichiometric reaction between AlX_3 and paraffins in the wax in the presence of HCl is predominant, the rate will not vary against the catalyst weight above an equimolar amount with paraffins. As is shown in Fig. 2, however, the rate constant increased further even against the weight ratio above 0.50, the value which corresponds to the equimolar ratio of AlX_3 to paraffins. This discussion shows that such the reaction is a minor possibility.

As is shown in Fig. 1, the induction period appears at the beginning of the reaction; it may be ascribed to the small contact area between catalyst and wax. The length of the period decreased with an increase in the amount of the catalyst, and the period disappeared at the highest amount in Fig. 2. These results also suggest that the degree of the contact between the molten catalyst and the liquid wax determines

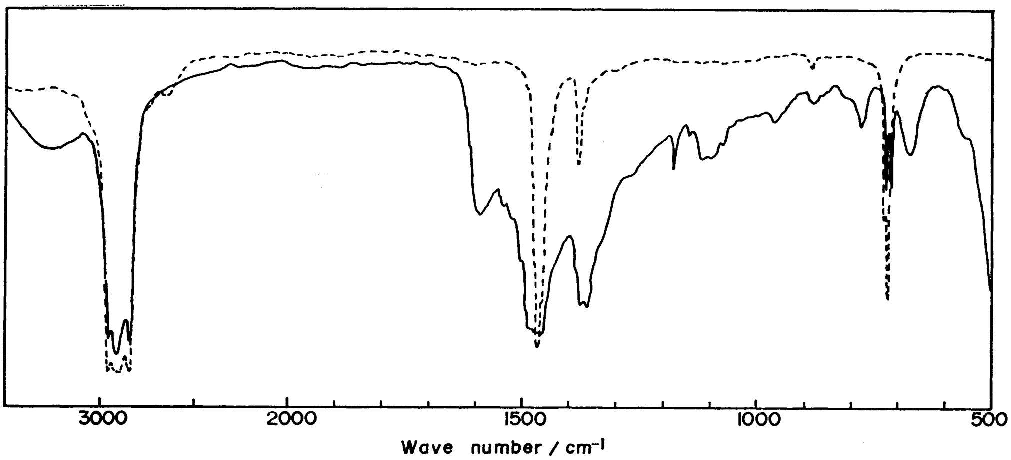

Fig. 3. IR spectra of feed wax (---) and tarry material (——).

the cracking rate to a considerable extent.

Effect of Catalyst Composition. The results are given in Table 4; three molten catalysts with different compositions were employed. The weight of each catalyst is somewhat different, as is shown in the footnote in Table 4, but the three catalysts are equal in the molar content of aluminum halide. For the $AlCl_3$–$AlBr_3$ catalyst, the cracking rate depended scarcely at all on the molar ratio of $AlCl_3$ to $AlBr_3$ within our experimental conditions, but the product distribution obviously did so depend. The selectivity to the C_4 components increased with an increase in the content of $AlCl_3$ in the catalyst, and instead the selectivity to the components above C_5 decreased. It is noteworthy that $AlCl_3$ has a higher activity to crack to lower molecules than $AlBr_3$, although the reason for this is not clear. In our unpublished work, a quite similar result was found for the catalytic conversion of lower paraffins, such as butane and pentane, on molten mixtures containing $AlCl_3$ or $AlBr_3$.

As is shown in the last two columns in the table, the substitution of NaCl for $AlBr_3$ in the $AlCl_3$–$AlBr_3$ catalyst affected both the cracking rate and the product distribution. The rate decreased by a factor of 0.3, and the selectivity to the gasoline fraction above the C_5 components decreased from 44 to 27 wt%. Therefore, the $AlCl_3$–NaCl catalyst is unsuitable for the production of a gasoline fraction by cracking slack wax. The low activity of this catalyst must be due to the decreased amount of free $AlCl_3$, which is the active species for the isomerization or cracking of lower paraffins by a molten $AlCl_3$–NaCl catalyst.[4] It is well accepted that $AlCl_3$ reacts with NaCl to form $Na^+AlCl_4^-$ in molten mixtures.[10,11] Thus, the addition of NaCl decreases the concentration of free $AlCl_3$.

Charaterization of Reaction Residue and Cracking Process. As has been described in the Experimental section, the contents remaining in the reactor after the stop of the cracking were easily separated into two layers. The upper layer consisted of a white waxy material. No ash was found to be present in it, which shows that the waxy material contains no catalyst. Its NMR and IR spectra were identical with those of feed wax, and the two were equal in the ratio of methylene-to-methyl protons obtained by the NMR spectrum. These findings indicate that the white waxy material is the feed wax itself.

The lower of the two separated layers consisted of a black tarry material including the catalyst. The IR spectrum obviously differed from that of the feed wax. Figure 3 shows this. The spectrum of the feed wax is a typical one for paraffin wax, and every peak can be attributed to aliphatic absorption bands, in which the splitting peak at 720—730 cm^{-1} is assigned to methylene chains having four or more units.

With the spectrum for the tarry material, the intensity of the peak due to the chains decreased considerably. This indicates a decrease in the chain length of paraffins upon cracking. In addition, the major aliphatic absorptions at 2840—2950 cm^{-1} and 1450—1480 cm^{-1} decreased in intensity. The increase in the intensity of the peak for methyl groups at 1370 cm^{-1} and the splitting of this peak show the presence of branched paraffins; besides, the appearance of two new peaks at 1180 and 1155 cm^{-1} enables us to assign them to isopropyl groups. Judging from the absence of any appreciable absorptions in the range of 1200—1260 cm^{-1}, *t*-butyl groups and quarternary carbons seem to be absent. The presence of isopropyl groups in the catalyst layer corresponds to the evolution of a large quantity of monomethylalkanes (shown in Table 1).

Aromatic compounds are also present in the tarry material, because the absorption bands at 1500, 1590, and 3030 cm^{-1} appeared; the former two absorptions are assigned to aromatic-ring vibrations. Thus, the peaks at 680, 780, and 880 cm^{-1} may be attributed to substituted aromatic-ring structures. Evidently the aromatization takes place concurrently with the cracking. It has been suggested that the aromatization process of a normal paraffin, such as that of *n*-dodecane by an $AlCl_3$ catalyst without HCl, takes place predominantly *via* the dehydrogenation of the cycloparaffins formed.[12] However, no evolution of H_2 in this cracking of the wax suggests a mechanism other than the above. Since carbonium ions formed in acidic systems such as $AlCl_3$–HCl are in equilibrium with the corresponding olefins,[13,14] such olefins may undergo polymerization and aromatization reactions. The aromatic compounds may react with the catalyst, which may result in catalyst deactivation.

As has been mentioned above, the catalyst layer including the cracked fragments can be easily separated from the layer of unreacted wax by allowing the reaction mixture to stand. This means that the two layers are essentially immiscible. The cracking of the wax would occur at the interface between the molten catalyst and the liquid wax in the presence of HCl. Since little formation of normal paraffins was found in the cracking products, normal paraffins in the wax may first undergo skeletal isomerization and then the cracking reaction. Part of the cracked fragments may be carried with the carrier gas to the gas phase and observed as products. The rest of the fragments may dissolve in the catalyst phase, undergo further miscellaneous reactions, and finally be converted into lower paraffins and an asphaltene-like material. In conclusion, the catalytic cracking of slack wax by molten mixtures in the presence of HCl probably occurs heterogeneously at the interface between the molten catalyst and the liquid wax.

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