TABLE III

In situ X-RAY DIFFRACTION STUDY OF ALUMINA-SUPPORTED MOLYBDENUM TRIOXIDE[a]

Reaction	Reaction conditions				Type of operation[b]	Substances identified[c]	No. of X-ray patterns
	Hours	T, °C.	P., atm.	Flow rate, ml./hr.			
I. Reduction with H_2	0–59	421	1.34	1.6	I	MoO_3, MoO_2, γ-Al_2O_3, Be[d]	23
	59–318	421–596	1.48	1.8–2.6	C	MoO_2, γ-Al_2O_3, Be[e]	26
II. Oxidation with air	0–216	24–366	1.34	1.6–3.6	C	MoO_2, γ-Al_2O_3, Be	14
	216–505	410–471	1.34	1.2–2.0	C	MoO_3, MoO_2, γ-Al_2O_3, Be[f]	18
	505–550	510	1.34	1.2	C	MoO_3, γ-Al_2O_3, Be[g]	4
III. Reduction with H_2	0–23	374	1.27	1.7	C	MoO_3, γ-Al_2O_3, Be	3
	23–40	430	1.27	1.4	C	MoO_3, MoO_2, γ-Al_2O_3, Be[h]	4
	40–86	430	1.27	1.6	C	MoO_2, γ-Al_2O_3, Be[i]	5

[a] 20% MoO_3 on γ-Al_2O_3 (Aluminum Co. of America H-40 Grade alumina). [b] C, continuous; I, intermittent. [c] Diffraction patterns obtained with MoKα X-radiation. [d] MoO_2 observed after hr. 11; MoO_3 absent after hr. 50. [e] Reduction terminated. [f] Very weak MoO_2 reflections. [g] Oxidation terminated. [h] MoO_2 observed after hr. 26. [i] Reduction terminated.

to note that Griffith, Chapman and Lindars[12] report the formation of small quantities of molybdenum metal on reduction with hydrogen at 450° of MoO_3–SiO_2 preparations in which the Si atoms/100 Mo atoms ratio varied from 4.4 to 9.4. Although the Al_2O_3-supported MoO_3 preparation employed in this work contained sufficient SiO_2 to yield a Si atoms/100 Mo atoms ratio of the order of 50 and although a temperature level of 596° was investigated, reduction below the +4 oxidation state was not observed.

The effect of a single reduction–oxidation cycle on the ease of subsequent reduction was also investigated in the case of the regenerated, alumina-supported MoO_3. Contrary to the results experienced with regenerated bulk MoO_3, the reduction–oxidation cycle was ineffective in increasing the susceptibility of the reoxidized, supported material to reduction. During a period of 23 hours at 374°, the diffraction patterns showed no indication of reduction; however, at 430° (approximately the same temperature required for reduction of the original material) reduction was evident after 3 hours of operation and was essentially complete 14 hours later. Based on these observations, "surface clean-up" apparently is not too important a factor where highly specific portions of a surface, rather than the total surface, are involved.

Although the foregoing data and discussion have been restricted to the chemical reactions observed between the gas and the solid, it is obvious that the microreactor apparatus possesses great utility for the study of heterogeneous catalysis *per se;* however, such application is beyond the scope of the present paper.

Acknowledgment.—The author wishes to express his appreciation to Humble Oil and Refining Company for permission to publish this research. He is indebted to Professor W. O. Milligan for helpful discussions and suggestions during the course of these investigations. The contributions of R. W. Terry and H. W. Oliver of the Company's Instrument Department, who fabricated the special apparatus required, and of Mrs. C. E. W. Souby and Miss V. Harleston, who carried out the experimental work, are gratefully acknowledged.

BAYTOWN, TEXAS RECEIVED APRIL 27, 1951

[12] R. H. Griffith, P. R. Chapman and P. R. Lindars, *Discussions Faraday Soc.*, No. 8, 258 (1950).

[CONTRIBUTION FROM THE UNIVERSITY OF PITTSBURGH AND MELLON INSTITUTE]

The Adsorption of Normal Paraffins on Cracking Catalysts[1]

BY ROBERT C. ZABOR AND PAUL H. EMMETT

Adsorption measurements have been made for *n*-butane, *n*-heptane and *n*-octane on a Houdry S-46 cracking catalyst in the temperature range from room temperature up to and above the lowest temperature at which decomposition occurs. The adsorption appears to be physical in nature up to about 150°. Above this temperature, and even at cracking temperatures, the adsorption is very small, being equal to or less than 0.005 millimole (~0.1 cc.) per gram of catalyst.

Numerous papers[2–6] have been presented in recent years which postulate that the decomposition of hydrocarbons over cracking catalysts results from the combination of the hydrocarbon molecule with the hydrogen ion on the surface of the catalyst to form carbonium ions[7] or polarized complexes. However, since no adsorption data for paraffins on cracking catalysts have been published, it has been impossible to judge the extent to which carbonium ions or chemisorbed hydrocarbons are actually present on a catalyst during cracking. The present paper reports the results of an experimental study of the adsorption of *n*-butane, *n*-heptane and *n*-octane on a Houdry S-46, silica–

[1] Contribution from the Multiple Fellowship of Gulf Research & Development Company, Mellon Institute, and the University of Pittsburgh, Pittsburgh, Penna.

[2] C. L. Thomas, J. Hickey and G. Stecker, *Ind. Eng. Chem.*, **42**, 866 (1950).

[3] C. L. Thomas, *ibid.*, **41**, 2564 (1949).

[4] B. S. Greensfelder, H. H. Voge and G. M. Good, *ibid.*, **41**, 2573 (1949).

[5] R. C. Hansford, *ibid.*, **39**, 849 (1947).

[6] B. S. Greensfelder and H. H. Voge, *ibid.*, **37**, 514, 983, 1038 (1945).

[7] F. C. Whitmore, THIS JOURNAL, **54**, 3274 (1932).

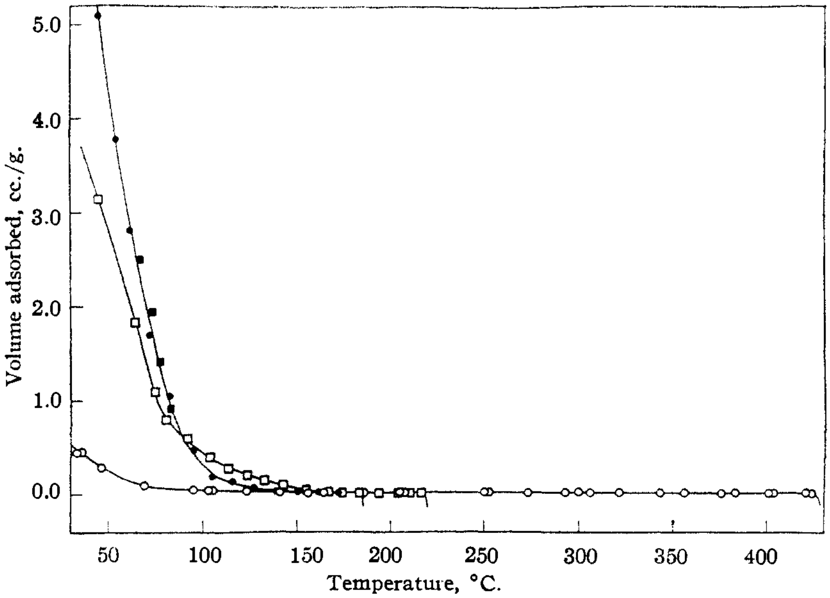

Fig. 1.—Volumetric measurements of the adsorption isobars for *n*-butane, ○; *n*-heptane, □; and *n*-octane, ● at a pressure of 4 mm. on a standard silica-alumina cracking catalyst. The adsorption of *n*-octane after the chemisorption of 1.8 cc. of water vapor per g. of catalyst is shown by the solid squares, ■.

alumina cracking catalyst over the temperature range 40 to 530°. These saturated hydrocarbons were chosen because they are convenient ones with which to work and because they should be typical of the remaining members of the homologous series of normal paraffins.

Experimental

Two sets of adsorption apparatus were used. The first was similar to the conventional volumetric gas adsorption system,[8] except that it was modified to operate at moderately low pressures (4 to 30 mm.), where complications due to extensive physical adsorption would be lessened, and that it made use of mercury cutoffs instead of stopcocks. In this low pressure range, absolute pressures were determined by means of a large bore mercury manometer read to 0.05 mm. with the aid of a traveling microscope.

The volumetric system itself was separated into two portions by one of the mercury cutoffs. One portion of the system, containing the calibrated burets, was used for determining the volume of charge; the other portion was a small circulating system in which gases were circulated over the catalyst bed by a magnetic glass pump.[9] The dead space in the entire system was calibrated with helium in the usual way. Although this apparatus was used predominantly for low pressure measurements, it was also possible to use it at somewhat higher pressure. For example, it was possible to employ this same apparatus for measuring the surface areas of the catalyst samples by the B.E.T. method,[10] using nitrogen as adsorbate at −195°.

The furnace for heating the catalyst sample had a stainless steel core of 1.5 inch inside diameter wound with nichrome wire. The temperature of this unit was controlled with an accuracy of ±0.25° by the change in resistance with temperature of an auxiliary winding, the controller circuit being similar to that of Benedict.[11] Temperatures were measured to an estimated accuracy of ±0.5° by means of a calibrated chromel-alumel thermocouple inserted in the well of the sample tube, readings being taken in millivolts on the Leeds and Northrup precision portable potentiometer.

In this apparatus, after the catalyst had been given the desired pretreatment, it was evacuated to 10^{-4} mm. at 500° and then cooled to the lowest temperature to be used in the adsorption run (usually a temperature in the range 25 to 50°). Gaseous hydrocarbon was then condensed at −195° in the trap, pumped to eliminate volatile impurities, vaporized, measured and allowed to expand to a pressure of about 4 mm. into the circulating system containing the sample tube. Adsorption measurements were then made in a similar fashion at successively higher temperatures.

For measurements at higher pressures and temperatures, a system was used in which adsorption was measured gravimetrically instead of volumetrically. This system was a flow-type apparatus in which the hydrocarbon was passed over the heated catalyst at any desired partial pressure, prepurified nitrogen being used as a diluent if the desired partial pressure of the hydrocarbon was less than 1 atmosphere. This gravimetric apparatus contained also a circulating system, permitting circulatory adsorption runs to be made to check the flow experiments.

The course of adsorption for runs made in the flow system was followed quantitatively by periodic weighing of the sample tube attached to the system by ground glass joints. Blank runs indicated that it was possible to remove the grease from the slip joints and weigh the adsorption tube to ±0.5 mg. Accordingly, at the beginning and at the end of each run, the adsorption bulb was weighed to the nearest milligram. The sample tube was always cooled quickly to room temperature in an atmosphere of nitrogen at the end of an adsorption experiment, so that all weighings were made with the adsorption bulb filled to atmospheric pressure with dry nitrogen.[12] Approximately 10 g. of catalyst was used in each gravimetric run; the adsorption bulb had a dead space of about 30 cc.

In the gravimetric setup, calcium sulfate or magnesium perchlorate and ascarite traps were placed in the exit flow line to permit the measurement of water vapor and carbon dioxide in the exit gases. The ascarite tube, of course, increased in weight only during the time in which the catalyst was being regenerated by the combustion of any coke or chemisorbed hydrocarbon that might remain on the catalyst at the end of an experiment.

The *n*-butane, *n*-octane and *n*-heptane were all pure grade hydrocarbons obtained from either the Phillips Petroleum Co. or Humphrey-Wilkinson, Inc. The catalyst was a standard silica-alumina cracking catalyst designated as Houdry S-46.

Results

Experimental results can, perhaps, most conveniently be discussed by considering each adsorbate separately.

***n*-Butane.**—The isobar for *n*-butane, as measured at 4 mm. pressure in the volumetric adsorption system, is a

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[8] W. E. Barr and V. J. Anhorn, *Instruments*, **20**, 454, 542 and 716 (1947).

[9] F. Porter, D. C. Bardwell and S. C. Lind, *Ind. Eng. Chem.*, **18**, 1086 (1926).

[10] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 310 (1938).

[11] M. Benedict, *Rev. Sci. Instruments*, **8**, 252 (1937).

[12] Since it was found that butane adsorption was instantaneous on the cracking catalyst, it was safe to assume that any butane left in the gas phase at the end of the run would be completely equilibrated with respect to adsorption by the time the tube was cooled in nitrogen to room temperature. Since the adsorption of butane at room temperature (32° in these runs) was 1.0 cc. at 10 mm. pressure and 3.0 cc. at 50 mm. pressure, it can be shown that for runs made with a partial pressure of 1 atmosphere of butane, this simplifying assumption leads to values that are too high by amounts ranging from 0.08 cc. per gram for a run made at 200° to 0.03 cc. for one made at 531°, provided the actual adsorption at 200 to 530° and 1 atm. pressure is only a few tenths of a cc. per gram. However, in view of the fact that 1 milligram increase in the weight of the adsorption bulb is equivalent to 0.04 cc. per gram and that the tube was weighed only to the closest milligram, no correction was made for the trace of hydrocarbon left in the gas phase even in runs at 1 atmosphere partial pressure of butane.

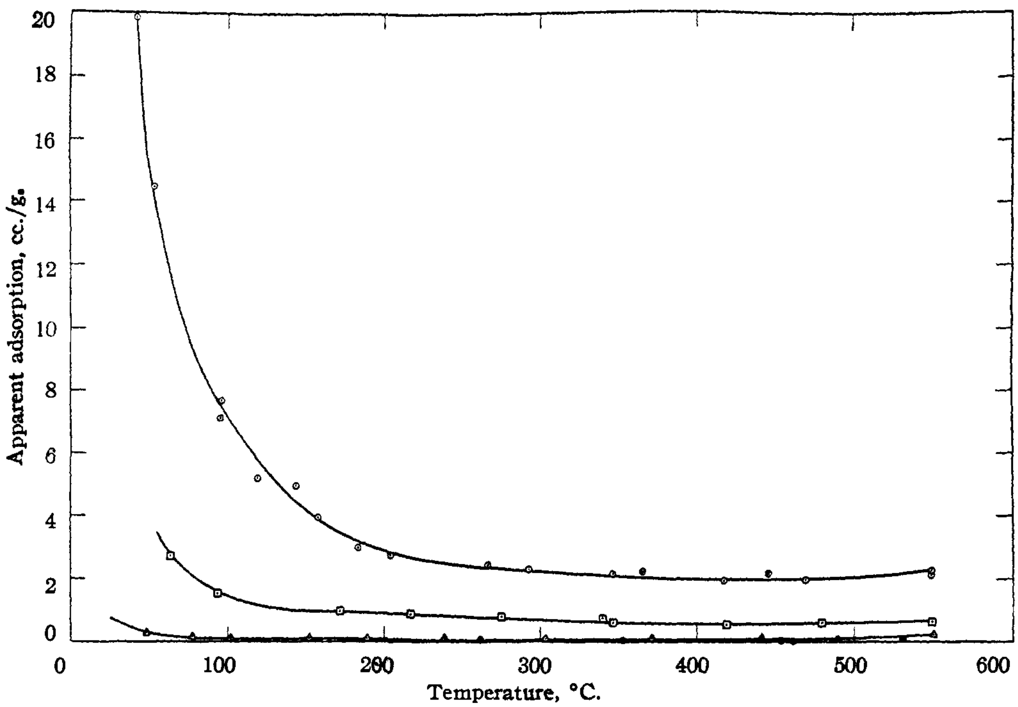

Fig. 2.—Gravimetric measurements of the adsorption isobars for *n*-butane on a Houdry S-46 cracking catalyst. The open circles, squares and triangles represent preliminary results in a flow system on tank butane at 760, 100 and 5 mm. partial pressure of butane. The solid circles represent the adsorption of butane at about 1 atm. pressure on a sample of butane freed from O_2 and other volatile impurities by repeated evaporation and condensation.

smooth curve (see Fig. 1), showing an initial adsorption of about 0.5 cc. per gram at 37°. The adsorption falls off rapidly with increasing temperature; from 150 to 424° (beginning of incipient decomposition), it is nearly constant at a value of about 0.002 cc. per gram. This is equivalent to a coverage of only 0.01% of the surface. The adsorption of butane in these volumetric measurements under all conditions is quite reversible. Furthermore, it is found not to be affected by the amount of chemisorbed water present on the catalyst. For these reasons the adsorption at temperatures at which it is appreciable is believed to be purely physical in nature.

Preliminary adsorption measurements for *n*-butane on this catalyst in the flow system at 5 mm., 100 mm., and 1 atmosphere partial pressures yielded surprisingly large adsorption values. These results are shown in Fig. 2. At 5 mm. pressure, the isobar was quite similar to that determined in the volumetric system, although the flat portion of the curve was somewhat higher, corresponding to about 0.1 cc. per gram. The higher pressure isobars are also smooth curves, indicating chemisorption to be occurring in the temperature range 150 to 450° to the extent of about 0.8 and 1.6 cc. per gram at 100 and at 760 mm., respectively.

Since these apparent chemisorption values were considerably higher than those obtained in the static runs at 4 mm. pressure, it was decided that some impurity in the butane might possibly be affecting the results in the flow measurements. Accordingly, the circulatory part of the flow-type apparatus was used for a series of runs in which the butane was first freed of any possible trace of oxygen or other volatile impurities by being carefully pumped during several successive condensations at −195°. This circulatory technique was then used to make spot adsorption determinations at a pressure of 1 atmosphere at 262, 353, 461, 454, 490 and 531°. A typical curve showing these results is also plotted in Fig. 2. It is evident that these precautions to remove impurities from the butane, the resulting adsorption values fall to a limit of less than 0.1 cc. per gram even at a pressure of 1 atmosphere, the actual readings for the above-mentioned temperatures being 0.10, 0.05, 0.05, 0.05, 0.10 and 0.10 cc. per gram, respectively.[13] Each of these experimental points constituted a complete run, the duration of which was one hour. To confirm the fact that the apparent adsorption of butane in the first flow experiments was actually due to an oxygen impurity in the butane, several runs were made in which air or oxygen was added back to carefully purified butane. Invariably the adsorption values increased approximately to those that had been noted in the early flow experiments.

The quantitative results obtained in the flow system, as compared with those obtained in the circulatory system, could also be confirmed by qualitative observations. In the flow experiments, the catalyst always became colored a light yellow at about 150°. This coloring deepened to a violet color at about 450°. In contrast with this, in the experiments in the circulatory system after removal of oxygen impurities, the catalyst showed no coloration at 150° and just the faintest detectable violet color at 450°. Accordingly, these qualitative as well as the more quantitative measurements, combine to indicate that the chemisorption of butane, at temperatures just below those at which cracking begins, is actually very small, being no more than 0.1 cc. per gram at one atmosphere pressure and 450°. This is sufficient butane to cover no more than 0.5% of the surface of the cracking catalyst (B.E.T. area of 265 sq. m. per gram). Even at 490 and 531°, at which rapid cracking occurs, there is no sudden build-up of chemisorbed hydrocarbon, though, of course, a coke deposit slowly accumulates.

Good evidence that the adsorption of butane was purely physical in nature, in the lower temperature region, was obtained from a mass spectrographic analysis of gases desorbed in a typical butane isobar. The gases desorbed between 50 and 250° contained 97.2% *n*-butane, 1.9% isobutane, 0.8% propane and 0.1% butene. The absence of appreciable amounts of decomposition and isomerization products in these samples suggested that no carbonium ion complex with the hydrogen ion of the catalyst surface had been formed up to 250°. It was also noted that, although no water was evolved in this lower temperature range, at temperatures at which cracking of *n*-butane occurred, some water was evolved (approximately 1 mg./g. of catalyst at 531°).

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(13) *It is interesting to note that if one applies the slight corrections mentioned in footnote 12 for the weight increment due to the small but finite residual partial pressure of hydrocarbon present in the sealed adsorption bulb at the end of a run, then these six adsorption values become 0.03, −0.006, 0.007, 0.007, 0.015 and 0.02 cc. per gram, respectively.*

n-**Heptane.**—The isobar of *n*-heptane on Houdry S-46 at 4 mm. pressure, as shown in Fig. 1, is also a smooth curve with high initial adsorption which falls off asymptotically with increasing temperature. At 40°, the adsorption is about 3.5 cc. per gram; at 175° it has fallen to about 0.015 cc. per gram. The adsorption is then essentially constant up to a temperature of 215°, at which incipient cracking begins. This adsorption corresponds to a surface coverage of about 0.1%. An adsorption isotherm run at 45° at pressures up to 20 mm. showed the adsorption to be physical in nature; the adsorption was almost instantaneous and was readily reversible.

n-**Octane.**—Also shown in Fig. 1 is the isobar of *n*-octane at 4 mm. pressure on Houdry S-46. It has the same general shape as that for the two previous saturated hydrocarbons described above. The initial adsorption at 45° is about 5.1 cc. per gram. This value is greater than that for *n*-heptane which, in turn, was greater than that for *n*-butane. The adsorption isobars are thus in the order that one would expect, except for the fact that for some unexplained reason the adsorption of heptane between 100 and 150° appears to be slightly larger than the adsorption of octane. However, the evidence seems to be conclusive for all three of these saturated hydrocarbons that only physical adsorption occurs to any appreciable extent up to the temperature of cracking, and that this adsorption becomes negligible above 150°.

Discussion

The adsorption measurements reported here for the saturated hydrocarbons show clearly that any chemisorption of the C_4, C_7 or C_8 normal paraffins that may exist on a standard cracking catalyst, at temperatures from room temperature up to and into the range in which considerable decomposition occurs, is no greater than 0.1 cc. per gram. To appreciate properly the significance of this value, one has only to realize that it is equivalent to 0.005 millimole per gram. This is one-tenth as many moles of saturated hydrocarbon as the 0.05 millimole of quinoline found by Mills, Boedeker and Oblad[14] to be chemisorbed by a cracking catalyst and one one-hundredth as large as the number of milliequivalents of H^+ generally believed to be present on the surface of a cracking catalyst.

As pointed out previously, no data have been published up to the present time reporting the adsorption of normal paraffins on silica–alumina cracking catalysts. However, there are several reasons for believing that the experience of other workers in the field is probably similar to our own in indicating only slight or negligible chemisorption for normal paraffins on cracking catalysts under these conditions.

Adsorption isobars in Fig. 1 are in agreement with conclusions mentioned by Greensfelder in one of the AAAS conferences at Gibson Island about six or seven years ago. He reported that the measurement of the volume of a saturated hydrocarbon adsorbed as the temperature was slowly increased yielded a smooth isobar that approached zero adsorption as the temperature was raised and at no point indicated detectable amounts of chemisorption.

Further indication of the extent of adsorption of paraffin hydrocarbons can be drawn from data given by Hansford, Waldo, Drake and Honig[15] in a recent paper in which they studied the rate of exchange between adsorbed deuterium oxide and hydrocarbon gases. In Table I of their paper are presented data that enable one to obtain some estimate as to the amount of paraffin hydrocarbons adsorbed. Specifically, from the amount of charge admitted to the reaction system and from the resultant pressure built up in the reaction system, we estimate an approximate adsorption value of 0.19 cc. of *n*-butane per gram of cracking catalyst at 280° at a pressure of about 0.5 atm. This is to be compared with a value of 0.1 cc. per gram obtained in our circulatory experiments at a pressure of 1 atm. A similarly estimated value of 1 cc. per gram for *n*-heptane at a partial pressure of 40 mm. at a temperature of about 200° in their experiments is to be compared with a value of 0.1 cc. per gram that we obtained at a pressure of about 5 mm. of heptane. Although their adsorption values are several-fold greater than those that we obtained, and might perhaps have been due to traces of oxygen or other impurities in their hydrocarbons, they still indicate that the total adsorption on a cracking catalyst corresponds to a coverage of, at the most, only a few per cent. of the catalyst surface for either butane or heptane.

Thus, there seems to be agreement on the fact that up to temperatures of decomposition, only a very small fraction of the catalytic surface is covered with adsorbed saturated hydrocarbon. It should further be emphasized that according to our gravimetric adsorption measurements on purified butane, even in the temperature range of catalytic decomposition, there is no extensive accumulation of adsorbed molecules on the catalyst surface.

The only positive evidence for the chemisorption of a saturated hydrocarbon by a cracking catalyst has been obtained by tracer experiments. Thus, although Taylor and his students[16] were not able to detect the chemisorption of methane on a standard cracking catalyst by the usual means, they did find that CH_4 and CD_4 interacted to form the partially deuterated methanes at 350°. This was taken to be an indication that, at least on a few active points, methane was capable of being dissociatively adsorbed by the cracking catalyst. Similarly, the exchange of the hydrogen of saturated hydrocarbons with adsorbed D_2O and surface deuterium ions at and above 60°, as noted by Hansford and his co-workers[14] and by Hindin, Mills and Oblad,[17] suggests the existence of chemisorption on at least a few active points on the catalyst surface.

The absence of any appreciable chemisorption of the saturated hydrocarbons even at cracking temperatures suggests that if the carbonium ion theory is to explain the cracking, then the slow step in the process must be the formation of the carbonium ion on the surface. This seems to be reasonable since the formation of a carbonium ion from a surface H^+ and a saturated hydrocarbon presumably entails the breaking of a C–C or C–H bond. Very likely, at the temperature at which this slow step can occur at a reasonable rate, the carbonium ions decompose instantaneously into volatile reaction products and hence do not result

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[14] G. A. Mills, E. R. Boedeker and A. G. Oblad, This Journal, **72**, 1554 (1950).

[15] R. C. Hansford, P. G. Waldo, L. C. Drake and R. E. Honig, A. C. S. Meeting, Chicago, Ill., September, 1950.

[16] G. Parravano, E. F. Hammel and H. S. Taylor, This Journal, **70**, 2269 (1948).

[17] S. G. Hindin, G. A. Mills and A. G. Oblad, *ibid.*, **73**, 278 (1951).

in chemisorption to a large extent even at cracking temperatures.

It might be pointed out in connection with these results that physical adsorption of normal paraffins could be important in the decomposition of much higher hydrocarbons in this series. At temperatures of 450°, paraffins from C_{16} to C_{20} have a relative pressure of about 0.01 to 0.05, at which upwards of a monolayer of physical adsorption might be expected to form.

Acknowledgment.—We wish to thank Dr. N. D. Coggeshall and Mr. N. F. Kerr of the Gulf Research & Development Company for obtaining mass spectrographic data referred to in this work.

PITTSBURGH, PENNSYLVANIA RECEIVED MAY 23, 1951

[CONTRIBUTIONS FROM THE UNIVERSITY OF MISSOURI, SCHOOL OF MINES AND METALLURGY, DEPARTMENT OF METALLURGY]

Precision Determination of Lattice Parameter, Coefficient of Thermal Expansion and Atomic Weight of Carbon in Diamond[1]

BY M. E. STRAUMANIS AND E. Z. AKA

Four diamond samples from the Belgian Congo were used for the investigation. Spectrographic analysis revealed the presence of traces of fifteen elements in the samples. The lattice parameter determinations were carried out by means of the asymmetric method, with a 64 mm. precision camera in a thermostat at five constant temperatures (10, 20, 30, 40 and 50°). The powder mounts, 0.12 mm. in diameter, were translated and rotated during the exposure in order to assure uniformity of the lines. Only the (331)-Co$K\beta_1$ line was used for the determinations. The three clear white diamond samples showed the same lattice parameter: 3.55960 ± 0.000016kX. (3.56679 Å.) at 20°, corrected for refraction. The accuracy of determination was better than 1:200,000. The parameter of gray boart was 3.55968 ± 0.00003kX. at 20°. The thermal lattice expansion coefficient, as determined from all samples, was $(1.38 \pm 0.12) \times 10^{-6}$. The atomic weight of carbon in the clear diamond samples was 12.0096 (the average value of the densities obtained by Bearden and Tu being used for the calculations). This weight is 0.003% lower than the chemical atomic weight, but is well within the error limit of the method. Therefore, the diamond lattice is sound and the method of lattice constant determination applied is an absolute one. Comparison with the work of other authors shows that clear white diamonds usually have the same lattice constants as noted above. Thus, the impurities are included mechanically. However, a very limited formation of a solid solution with silicon or other elements is not excluded (gray boart).

Introduction

The greatest accuracy previously attained in the determination of the lattice parameters of diamond (±0.00005 Å.), was achieved by Lonsdale[2] and Tu.[19] As the asymmetric method[3a,b] allows still greater precision, the determinations were repeated with four kinds of diamond (white boart, gray boart, and two diamond stones of gem quality—No. 1 and No. 2, all from the Belgian Congo) at closely controlled temperature intervals. The thermal lattice expansion coefficient thus determined, together with the computed atomic weight of carbon in diamond, provide data for the discussion of the soundness of diamond crystals,[4] the solubility of solids in diamonds frequently found in these stones,[5] and the applicability of diamond powder as a standard substance for Debye–Scherrer photographs.[6]

Spectroscopic Analysis and Experimental Procedure

Diamonds No. 1 and 2 were irregular octahedrons, containing microscopic inclusions and weighing 0.118 and 0.17 g., respectively. After the stones had been crushed in a steel mortar, the powder was treated with hot hydrochloric acid in order to remove any iron.

Semi-quantitative analyses of three diamond samples based on emission spectra (arc method),[7,8] were carried out with an Abney grating spectrograph having a range capable of detecting the elements usually found in diamonds.[5] All precautions were taken to detect all of the trace elements and to introduce no new ones. Only a visual examination of the relative line intensities was made (Table I).

TABLE I

IMPURITIES IN THE DIAMOND SAMPLES

Abbreviations: xxxx—major contamination; xxx—strong trace; xx—trace; x—faint trace; ?—questionable

Impurity	Gray boart	Diam. No. 1	Diam. No. 2[a]
Al	xxx	xxx	xxx
B	x	x	. .
Ca	xxx	x	xxxx
Co	. .	xx	. .
Hf	xxx	. .	x
Fe	xxx	?	x
Pb	. .	?	?
Mg	xxxx	xxxx	xx
Mn	x	. .	?
Pt	. .	. .	x
Si	xxx	xxxx	xx
Ag	xx	. .	xx
Sn	xx	. .	. .
Ti	x	xx	xxx
Zn	. .	xx	. .

[a] The sample was treated with HF for 12 hours in a Pt crucible.

Among the 15 elements found, magnesium, aluminum, silicon, calcium, and titanium constitute a persistent group which appeared in all three diamond samples. The relative concentrations of silicon and aluminum agreed with the ob-

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(1) Based on a thesis submitted by E. Z. Aka to the Graduate School of the University of Missouri, School of Mines and Metallurgy, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented at the 1950 Spring Meeting of the American Crystallographic Association in Penn. State College.

(2) K. Lonsdale, *Phil. Trans. Roy. Soc. (London)*, **A240**, 219 (1946).

(3) (a) M. E. Straumanis, *J. Appl. Phys.*, **20**, 726 (1949); (b) M. Straumanis and A. Ievins, "Die Präzisionsbestimmung von Gitterkonstanten nach der asymmetrischen Methode," J. Springer, Berlin, 1940; reprinted by Edwards Brothers, Inc., Ann Arbor, Michigan, 1948.

(4) M. E. Straumanis, *Acta Crystallogr.*, **2**, 82 (1949).

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(6) W. Trzebiatowski, *Roczniki Chem.*, **17**, 73 (1937).

(7) R. A. Sawyer, "Experimental Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1944, p. 298.

(8) G. R. Harrison, R. C. Lord and J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1948, p. 426.