[Contribution from the Houdry Laboratory, Houdry Process Corporation]

Chemical Characterization of Catalysts. I. Poisoning of Cracking Catalysts by Nitrogen Compounds and Potassium Ion*

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During recent years the detailed information on catalysts given in the literature is largely concerned with the physical properties of catalysts. However, the real insight obtained from this information into the nature of catalytic action has proved to be disappointingly small. On the other hand, one is struck with the lack of specific information on the significant chemical properties of the catalysts themselves. The great specificity of catalysts can only mean that specific chemical properties of catalysts are involved in catalytic action.

In this laboratory a fundamental study has been undertaken to establish the essential chemical properties or active principles of a number of catalysts. The basic philosophy of this work is that very significant information about catalysts can be obtained from a study of the type and amount of various substances which react readily with catalysts. This paper describes a portion of the results of this study and more specifically, is concerned with the reactions of nitrogen compounds and potassium ion with siliceous cracking catalysts and the effect of these substances on the activity of these catalysts.

Materials able to inactivate catalysts were studied in order to develop information on both the chemical nature and amount of the catalytically active principles. In this connection the use of nitrogen compounds as poisons proved most efficacious because: (1) their interaction with catalysts can be measured by adsorption techniques at or near temperatures at which the catalysts function, (2) there exist nitrogen compounds with a variety of properties, and (3) this type of poison can be added from the gas phase with minimum change in the catalyst. Poisons added from an aqueous medium suffer from uncertainties since concomitant alterations occur due to the action of water on oxide catalysts.

Experimental

Catalysts.—Catalysts IA, IIA, IIIA, IVA and VA were pelleted synthetic silica—12.5 wt. % alumina materials manufactured by the Houdry Process Corporation.[1] These had been calcined at about 750° in the presence of steam. Catalyst VIA contained 1% alumina and was prepared by dipping silica gel chunks (adsorbent VIIS) in aluminum nitrate solution followed by drying and calcining the resultant mass in air at 565°. Adsorbent VIIS was a silica gel prepared from Philadelphia Quartz Company N-Brand sodium silicate and sulfuric acid at a *p*H of less than 1.0. It was dried, washed free of sulfate ion, dried again and finally calcined at 760° in dry air. Catalyst VIIIZ was a pelleted synthetic silica—9.5 wt. % zirconia material prepared by a coprecipitation method. The dried catalyst mass was calcined at 760° in the presence of 5 mole % steam at 1 atmosphere. Catalyst IXM was a pelleted synthetic silica—32 wt. % magnesia material calcined at 735° in steam at atmospheric pressure. Catalyst XC was prepared from acid activated bentonite clay, manufactured by the Filtrol Corporation for use in Thermofor Catalytic Cracking. This was further processed by washing free of sulfate ion, then pelleting, drying and finally calcining in dry flowing air for two hours at 845°. The properties of these catalysts are summarized in Table I.

Catalysts containing potassium were prepared by addition of potassium by ion exchange. For the uncalcined silica–alumina, the exchange of potassium for ammonium ions was accomplished by repeatedly dipping the catalyst (Houdry synthetic pellets, 12.5 wt. % alumina) in 15 wt. % potassium nitrate solution. The catalyst mass was then washed until free of soluble salts. Calcined catalyst IA was packed into a glass column and a buffer solution containing potassium acetate and acetic acid was passed over the catalyst at a constant rate. This treatment was continued until the *p*H of the effluent solution was the same as that of the solution being charged to the column. The catalyst mass was washed free of excess solution with alcohol (rather than water) to prevent hydrolysis of the potassium exchanged catalysts.

Measurement of Catalytic Activity for Cracking.—As a measure of activity the cracking of Light East Texas Gas Oil and cumene, respectively, was studied. In the case of the gas oil the secondary reactions following cracking are very prominent. In the case of the cracking of cumene, the primary cracking reaction is preponderant. For the cracking of the gas oil the catalytic Activity Test-A procedure and apparatus[2] were used. Cracking of cumene (dealkylation) was studied in the same apparatus at 425°, 2.0 liquid hourly space velocity (LHSV). The duration of the runs was thirty minutes. The gaseous products from this reaction were analyzed by means of a Consolidated Engineering Company mass spectrometer. The results were similar to those described in the literature.[3]

Measurement of Quinoline and Pyridine Adsorption.—A sensitive direct weighing technique was developed for determining the amount of quinoline or pyridine adsorbed by the catalysts. The apparatus is shown in Fig. 1. The adsorbent was suspended in a perforated glass basket by a thin glass rod attached to one end of the beam of an analytical balance. Quinoline was maintained at a constant pressure, *p*, in a flowing stream of nitrogen (99.98%) by passage of the nitrogen through two saturators containing liquid quinoline. The saturators were connected in series and were maintained at constant temperature by a jacket containing a boiling liquid. To insure saturation, the first saturator was held above the temperature of the second by suitable choice of boiling liquids. For example, ethylene glycol and cumene were frequently used in, respectively, the first and second saturator jackets for this purpose. That saturation was achieved, was substantiated experimentally by collecting and weighing the quinoline for a known period of time without catalyst

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* Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, San Francisco, March, 1949.

(1) H. A. Shabaker, see specification U. S. Patent 2,433,869 (1948).

(2) J. Alexander and H. G. Shimp, *Natl. Petroleum News*, **36**, (31), R-537 (1944); J. Alexander, *Proc. Am. Petroleum Inst.*, **27**, (III) 51, Nov. (1947).

(3) B. S. Greensfelder, H. H. Voge and G. M. Good, *Ind. Eng. Chem.*, **37**, 1168 (1945); C. L. Thomas, J. Hoekstra and J. T. Pinkston, This Journal, **66**, 1694 (1944).

TABLE I

CATALYST PROPERTIES

		Physical properties		Catalytic properties CAT-A				Catalytic properties Cumene cracking				
Catalyst number	Description	Area, sq. m./g.	Bulk dens., g./cc.	Gaso. vol. %	Coke, wt. %	Gas, wt. %	Gas grav. (air = 1.0)	Benzene, wt. %	Coke, wt. %	Gas, wt. %	Gas grav. (air = 1.0)	Ability to chemisorb quinoline at 315° me./g.
IA	Houdry type S, SiO_2–12.5% Al_2O_3	273	0.61	45.1	3.2	10.1	1.58	39.7	0.62	17.2	1.41	0.06
IIA	Same	196	.60	35.6	1.7	6.1	1.55	40.7	0.39	15.9	1.40	.044
IIIA	Same	...	.62	32.1	1.6	6.2	1.57	..	..	..	..	.027
IVA	Same	111	.67	28.2	1.0	3.1	1.50	27.3	0.1	10.1	1.40	.021
VA	Same	44	.96	16.2	0.5	1.2	1.23	19.5	.05	6.9	1.37	.009
VIA	SiO_2–1% Al_2O_3	390	.73	27.2	1.3	4.3	1.49	..	..	..	..	.020
VIIS	SiO_2	330	.74	7.0	0.3	..	..	1.7	..	..	..	.001
VIIIZ	SiO_2–9.5% ZrO_2	251	.63	35.7	2.0	4.2	1.41	26.3	.16	8.9	1.33	.033
IXM	SiO_2–32% MgO	426	.65	47.0	3.7	5.5	1.49	..	..	..	..	.09
XC	Filtrol Clay	41	.91	25.9	1.4	2.7	1.13	..	..	..	.	.018
None	Empty reactor	...	..	5.0	0.1	0.6	1.1	..	0.1	0.7	1.0	...

present. The vapor transfer lines were heated to prevent condensation of the quinoline vapor. After passing over the catalyst sample, the vapor was removed by withdrawing it at a side exit as indicated in the diagram. A second stream of nitrogen was preheated and part of this flowed out past the glass rod and part was withdrawn with the quinoline–nitrogen stream as shown. Using the flow rates indicated, no quinoline was observed to escape around the glass rod. At these rates of gas and vapor flow, only a small buoyancy effect was introduced during weighings and since the weighings were always taken at constant flow conditions, no inaccuracy in the amount of quinoline adsorbed was introduced on this account. In order to determine the amount of quinoline chemisorbed, the saturated catalyst or adsorbent was flushed with nitrogen (100 cc./minute) to remove the physically adsorbed quinoline. The ability to obtain continuous measurements was of a distinct advantage. Using this technique and with a 10-g. sample of the catalyst the addition of 1 mg. was accurately determinable.

Another procedure, used originally, was to pass 2.0 cc. (in some cases 5.0 cc.) of liquid quinoline through a quartz preheater and over a 200-cc. bed of catalyst maintained at 425° in a CAT-A apparatus[2] which had been flushed with nitrogen for three minutes at 300 cc./minute. Quinoline vapors and the physically adsorbed quinoline were removed by flushing with nitrogen (300 cc./minute) for ten or more minutes. The catalyst was then regenerated at 480–540° with oxygen and the amount of quinoline chemisorbed was calculated from the carbon dioxide formed. The amount of quinoline chemisorbed by a sample of catalyst was found to be the same by the two procedures.

The vapor pressure of quinoline, p_0, as a function of temperature was measured by placing quinoline in a stainless steel bomb, increasing the temperature, and measuring, meanwhile, the pressure on a calibrated gage. For the range 240–315° the vapor pressure of quinoline in mm. was found to be expressed by the following equation, where T is in degrees Kelvin: $\log p_0 = (0.5223)(-48{,}080)/T + 7.797$. Synthetic quinoline and pyridine obtained from the Eastman Kodak Company were used without further purification. Temperature measurements in all cases are believed to be accurate to ±2°.

Results and Discussion

Sorption of Basic Nitrogen Compounds.—The chemisorption of ammonia was studied. However, it was found that organic nitrogen compounds gave results more directly interpretable since they are more strongly chemisorbed at cracking temperatures. Quinoline was selected for more detailed study because it was found to be quite stable in the presence of silica–alumina catalyst at elevated temperature, and because it is representative of large organic molecules having basic properties. The results with quinoline are also of interest because its homologs occur in petroleum.[4]

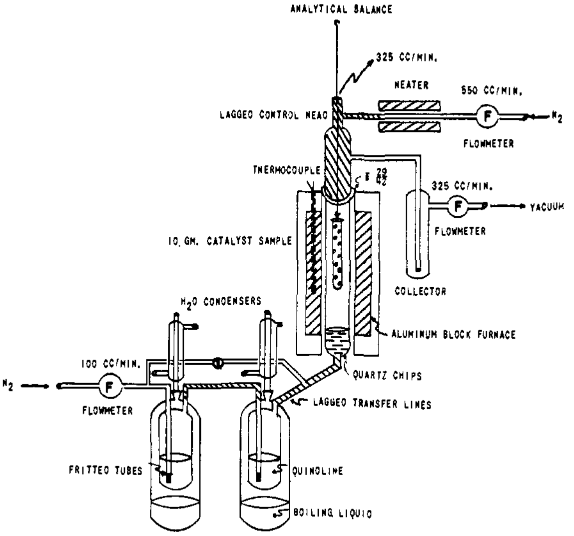

Fig. 1.—Apparatus for measurement of quinoline adsorption.

The sorption of quinoline from a stream of nitrogen having a constant quinoline partial pressure was measured as a function of time for a silica gel and for an active silica–alumina catalyst. Typical results for this measurement are shown in Fig. 2. Although the physical properties of these two adsorbents are similar, an important difference is observed in that the quinoline is, within experimental accuracy, completely desorbed from the catalytically inactive silica gel whereas, under the conditions used only a part of the quinoline is desorbed from the active catalyst. In the case of silica–alumina, a fraction of the quinoline sorbed is held physically and the balance by chemisorption.

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[4] A. C. Bratton and J. R. Bailey, THIS JOURNAL, 59, 175 (1937).

As is illustrated in Fig. 2 the physically adsorbed portion can be easily added and removed whereas the chemisorbed portion is not readily desorbed. This phenomenon is similar to the behavior of carbon monoxide sorbed on an iron catalyst.[5]

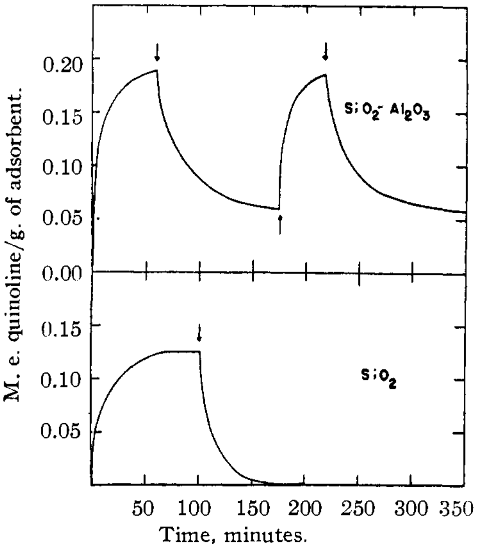

Fig. 2.—Sorption and desorption of quinoline at 315° on calcined silica gel VIIA or on catalyst IA (SiO_2–12.5% Al_2O_3). Quinoline partial pressure in flowing nitrogen stream was 73 mm. Arrows indicate start of sorption or desorption.

Catalyst on which quinoline has been adsorbed at 425° has a pale green color. This is in marked contrast to the black appearance of a catalyst which has been inactivated by the deposition of a hydrocarbonaceous residue during cracking. On boiling a quinoline-treated catalyst with aqueous hydrochloric acid solution an extract was obtained which was shown to contain quinoline. These observations substantiate the premise that the quinoline is held as such by the catalyst rather than as its decomposed or polymerized product.

As was expected, at constant temperature, the amount of physical adsorption was found to vary with the partial pressure of quinoline in the nitrogen stream. On the contrary, the amount of chemisorption remained constant. Results illustrating this are given in Table II and Fig. 3.

Table II

Adsorption of Quinoline on Catalyst VIA, 99% Silica–1% Alumina at 315°

Quinoline pressure Mm.	p/p_0	Quinoline adsorbed, me./g. catalyst Chemical	Physical
8.5	0.0025	0.014	0.016
73	.022	.021	.065
281	.083	.019	.31

The effect of temperature on chemisorption of quinoline or pyridine on a catalyst was investigated for the range 175–482°. The results are given in Table III.

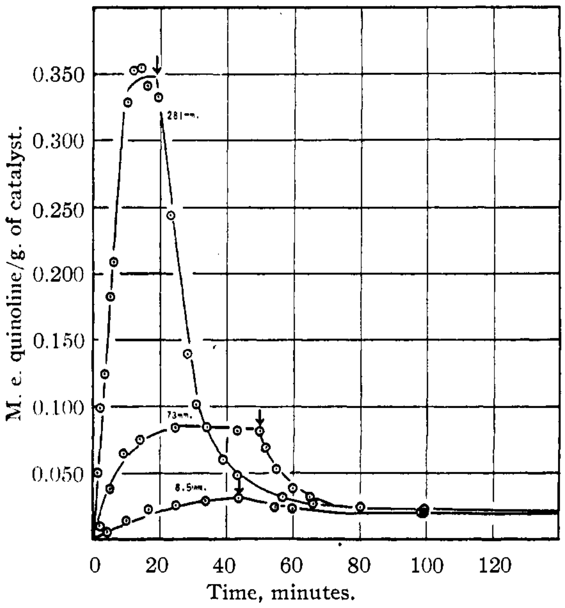

Fig. 3.—Sorption and desorption of quinoline at 315°: calcined SiO_2–1% Al_2O_3 catalyst VIA. Partial pressure of quinoline in flowing nitrogen stream given on graph in mm. Arrows indicate start of desorption.

Table III

Effect of Temperature on Sorption by Catalyst IA Using Nitrogen Saturated at 152° with Quinoline or 65° for Pyridine

Temp., °C.	Adsorbate	Total	Sorption, me./g. Chemical	Physical
482	Quinoline	0.035	0.015	0.020
427		.047	.022	.025
371		.078	.039	.039
316		.104	.055	.049
260		.132	.067	.065
475	Pyridine	.080	.047	.033
375		.121	.055	.066
275		.207	.064	.143
175		.632	.135	.497

It should be pointed out that the division reported here between chemisorbed and physically adsorbed quinoline is somewhat arbitrary. Undoubtedly, there is an overlapping of the chemical forces and physical forces involved in the adsorption of the nitrogen compounds. There is an apparent distribution of affinities amongst the active sites responsible for chemisorption. As a catalyst sample becomes saturated with the nitrogen compound, the final amounts chemisorbed are less strongly held than those adsorbed at first. The forces holding the final amounts, therefore, approach the physical forces in strength. As a further effect of the distribution of active sites, the amount of nitrogen compound chemisorbed becomes a function of temperature. At a given temperature the bulk of the chemisorbed

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(5) P. H. Emmett and S. Brunauer, This Journal, **59**, 1553 (1937).

nitrogen compound nevertheless is held by chemical forces much greater in strength than the van der Waals forces. Thus, the desorption of chemisorbed nitrogen compound occurs only slowly. On the other hand, the desorption of physically held nitrogen compound is rapid. It is thus possible to distinguish between the two types of sorption. These facts should be kept in mind when considering the absolute amounts of chemical and physical adsorption.

Pyridine was found to be chemisorbed in a manner similar to that of quinoline. The amount of pyridine chemisorbed is greater than that of quinoline at the higher temperatures. At the lower temperatures, however, they are approximately equivalent in amount. The difference between pyridine and quinoline, in the amounts adsorbed, and in the effect of temperature on the amounts adsorbed is probably a measure of the difference in the strength of the two substances as bases.

It was found most convenient to make measurements at a temperature of 300° or somewhat higher. At temperatures of 425° or above, it was found that when the sorption time was extended to several hours the catalyst gradually picked up more quinoline. At the same time, the catalyst turned black. Under these circumstances there is apparently a slow decomposition of quinoline upon the catalyst surface. On the other hand, at temperatures below 260°, for example at 200°, the rate of desorption is slow. Even at 315° with an adsorbent of very large area and small pores, such as silica gel manufactured by the Davison Chemical Company, desorption proceeded slowly, although eventually all the quinoline was removed.

Poisoning of Cracking Catalysts by Nitrogen Compounds.—It is well known that gas oils containing nitrogen compounds give low gasoline yields when catalytically cracked. It has been found in this laboratory as well as in others[6] that the gasoline yield is much improved by removal of these nitrogen compounds. The effect of nitrogen compounds on the activity of a catalyst is more pronounced upon pretreating a catalyst with a basic nitrogen compound, flushing out the excess and then proceeding with the cracking test using a nitrogen-free oil, than when cracking a stock containing nitrogen compounds. The results given in Table IV compare the effect of nitrogen compound poisoning on the cracking of cumene when quinoline is added before or dissolved in the cumene.

The interpretation is that pretreatment with a nitrogen base inactivates all the active centers so that none are available for subsequent cracking. However, when a stock containing a nitrogen base in amounts sufficient to poison a catalyst completely is cracked, some reaction is obtained due to the fact that in the initial stages of the run the catalyst is only partially poisoned. The intermediate yield of benzene given in Table IV under these conditions is in accord with this.

TABLE IV

COMPARISON OF QUINOLINE CHARGED BEFORE OR WITH CUMENE OVER CATALYST

Catalyst IIIA (200 cc.), cracking cond.: CAT-A (425°, 1.5 LHSV, 10 min.)

	Benzene, wt. %	Coke, wt. %	Gas, wt. %	Gas grav. (air = 1.)
Cumene	27.6	2.3	12.5	1.42
Cumene + 1.8 vol. % quinoline	10.9	2.7	4.4	1.33
2.0 cc. quinoline passed over catalyst flushed with nitrogen, then cumene charged	1.9	2.8	1.2	(0.9)

It was found that upon regeneration by air oxidation of a catalyst poisoned by nitrogen bases, the activity was regained completely.

The effect of quinoline pretreatment was also determined on a more active catalyst when cracking either cumene or Light East Texas Gas Oil. Less complete poisoning was obtained in the case of the gas oil, Table V.

TABLE V

EFFECT OF QUINOLINE POISONING OF A CATALYST FOR CRACKING LIGHT EAST TEXAS GAS OIL OR CUMENE

425°, 1.5 liquid hourly space velocity

Catalyst condition	Charge	Gaso. (vol. %) or benzene (wt. %)	Coke, wt. %	Gas, wt. %	Gas grav. (air = 1.0)
Catalyst IA.	LETGO	45.1	3.2	10.1	1.54
No catalyst	LETGO	(5)			
Catalyst IA poisoned with quinoline	LETGO	15.3	[a]	1.1	0.9
Catalyst IA	Cumene	42.1	1.6	20.0	1.57
No catalyst	Cumene	0	0.1	0.7	1.0
Catalyst IA poisoned with quinoline	Cumene	6.3	[a]	1.7	1.25

[a] "Coke" value included chemisorbed quinoline.

Because of the size of the quinoline molecule, it may not be able to get to some active areas located in very small pores. What seems more likely, however, is that some adsorbent groups for reasons already given may not retain quinoline under these conditions. A small amount of cracking is observed on this account.

Pretreatment of a catalyst with ammonia also is effective in diminishing its cracking activity (Table VI). Unpublished studies in this laboratory have shown that ammonia is chemisorbed at this temperature, the amount of chemisorption being governed by the vapor pressure of ammonia. Desorption of ammonia from the catalyst was found to be slow.

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(6) C. L. Thomas, U. S. Patent 2,352,236 (1944).

Table VI

Effect of Ammonia on Cracking of Cumene

Ammonia passed over catalyst at 425° at about 500 cc./min. over 200 cc. catalyst. Case purged with 900 cc. nitrogen and cumene cracked 425°, 1.5 liquid hourly space velocity, ten minutes on stream

G. NH_3 passed[a]	Wt. % benzene	Wt. % gas	Wt. % coke	Gas gravity
0	27.6	12.5	2.3	1.42
1.6	18.7	8.4	1.4	1.39
2.9	16.1	6.6	1.1	1.37
7.5	12.8	5.0	1.3	1.35

[a] This value was determined after passage over catalyst and does not include that adsorbed by the catalyst.

Partial poisoning was investigated by determining the effect on the cracking of cumene after pretreatment of a catalyst with various amounts of quinoline or various other organic nitrogen compounds. The data from this study are shown in Fig. 4. It appears that the relationship between the amount of poison on the catalyst and its activity for dealkylation of cumene is not linear but of an exponential form.

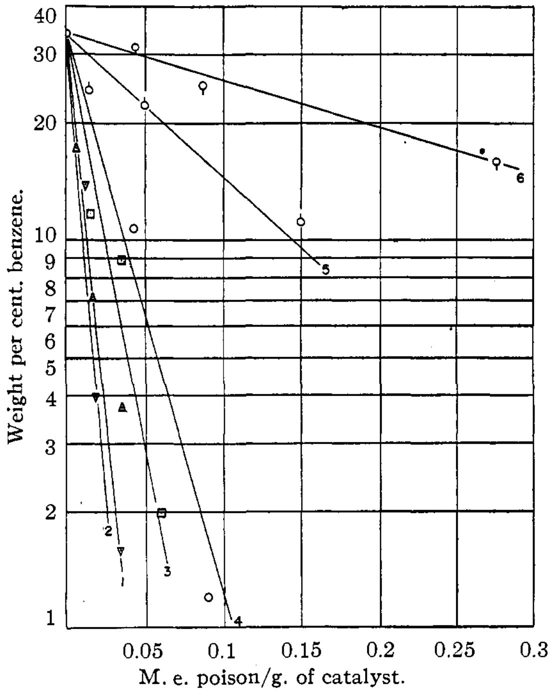

Fig. 4.—Poisoning effect of organic nitrogen compounds on the catalytic dealkylation of cumene catalyst IIIA: 1, quinoline; 2, quinaldine; 3, pyrrole; 4, piperidine; 5, decylamine; 6, aniline.

The various basic nitrogen compounds inactivate the catalyst to varying degrees. For the nitrogen compounds under consideration, the effectiveness as poisons can be listed in the following order: quinaldine > quinoline > pyrrole > piperidine > decylamine > aniline. When considered strictly from the standpoint of basicity, piperidine should be the most effective poison in the list given above. Piperidine, however, is decomposed to the extent of about 54% under the experimental conditions employed. Quinoline and quinaldine undergo no decomposition under these conditions and both are effective poisons. The comparatively high poisoning effect of pyrrole may be due to the deposition of polymer on the catalyst since pyrrole is known to be easily polymerized in the presence of acids. Moreover, van der Waals forces, for reasons already given, should be modifying factors influencing the chemisorption of the nitrogen bases. The extent of this influence must be taken into account as molecular size and structure of the adsorbate changes.[7] Under the conditions used (Table VII) heterocyclic nitrogen compounds with the exception of piperidine and possibly its analogs are ordinarily affected only slightly by the catalyst.

Table VII

Cracking of Nitrogen Compounds

CAT-A Conditions: 425°, 1.5 LHSV, 10 min. on stream 50 ml. liquid charged; catalyst IIIA

Compound cracked	Vol. in ml. of liq. recovered BP below charge	BP of charge	BP above charge	Coke, wt. %	Gas, wt. %	Gas, grav.[b]
Piperidine	None	23.2	18.1	2.7	3.1	0.5
Pyridine	None	48.4[a]	None	1.2	0.3	1.6
Quinaldine	None	47.8[a]	None	1.3	0.1	0.6
Quinoline	None	48.0[a]	None	1.4	0.3	0.8
Aniline	None	48.4[a]	None	1.5	0.2	1.1
Decylamine[c]	23.7	19.3[a]	None	4.5	4.9	0.86

[a] Calculated. [b] Due to small amount of gas formed gas gravity values are not accurate. [c] Based on the ammonia absorbed by standard HCl, 57.4 wt.% of the decylamine cracked.

Ammonia was produced from decylamine quite readily in the presence of the catalyst. Decene was identified as the main hydrocarbon product, although there were other products which may be attributed to the cracking of decene. Tests for thermal stability of decylamine under the same conditions except for absence of catalyst, showed only minor cracking without selective deamination. The observations made by Bradley and Grim[8] on heating bentonite containing octadecylamine to 400° can be interpreted on the basis of these results.

An experiment was carried out to determine the distribution of quinoline on a partially poisoned catalyst. Two-hundred cc. (120 g.) of fresh catalyst was charged to a glass case, the catalyst being divided into three equal sections by means of glass–wool plugs. Two-tenths cc. of quinoline was charged from a buret to the case. This was followed by nitrogen flushing. The catalyst was removed and each section analyzed for nitrogen by the Kjeldahl procedure. The results in Table VIII show that under these condi-

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[7] S. B. Hendricks, *Ind. Eng. Chem.*, **37**, 625 (1945); *J. Phys. Chem.*, **45**, 65 (1941).

[8] W. F. Bradley and R. E. Grim, *J. Phys. and Coll. Chem.*, **52**, 1404 (1948).

tions there is a fairly even distribution of quinoline on a partially poisoned catalyst. The total quinoline charged was sorbed by the catalyst. It was thought that with a partially poisoned catalyst, the top section of the catalyst might be completely poisoned and that the degree of poisoning would decrease gradually down the catalyst bed.

TABLE VIII

DISTRIBUTION OF QUINOLINE ON A PARTIALLY POISONED CATALYST IIIA[a]

Catalyst section	Me. quinoline/g. cat.	Me. quinoline
Top	0.018 × 40 g.	0.72
Middle	.011 × 40 g.	.44
Bottom	.013 × 40 g.	.52
Total quinoline found on catalyst		1.68
Quinoline charged		1.7

[a] Quinoline chemisorption capacity of CAT. IIIA = 0.027 me./g.
Total quinoline capacity 0.027 × 120 = 3.25 me.

Poisoning of Cracking Catalysts by Potassium Ions.—The exchange of potassium ion onto an uncalcined synthetic silica–alumina caused loss of activity. The results are given in Table IX.

TABLE IX

			Catalytic properties	
Catalyst	Description	Capacity to chemisorb quinoline, me./g.	CAT-A % Gasoline	Cumene % Benzene
IA	Calcined Houdry synthetic	0.06	45	39.7
XI	Uncalcined Houdry syn. partially exchg. with K^+ 5.37% K_2O = 1.14 me./g.	.03	11	3.6
XII	Uncalcined Houdry syn. partially exchg. with K^+ 8.21% K_2O = 1.75 me./g.	.024	6.1	..

That inactivation was not due to the fluxing action of potassium oxide was established from the fact that the surface area remained high; for example, 262 sq. m./g. for catalyst XI compared to 273 sq. m./g. for catalyst IA. Furthermore, on re-exchanging the potassium ion from the calcined catalyst by means of hydrogen or ammonium ion the activity was largely regained. Before testing the ammonium ion exchanged catalyst, it was recalcined. A calcined silica–alumina catalyst was also exchanged with potassium ion (Table X).

TABLE X

EFFECT OF POTASSIUM ION EXCHANGE ON CALCINED SiO_2–Al_2O_3 CATALYST (IA)

			Cracking activity test A			
Catalyst	Exchg. *p*H	K_2O, me./g.	Gasoline	Coke	Gas	Gas gravity
IA	..	0	45.1	3.2	10.1	1.58
XIII	3.62	0.04	21.5	1.1	1.8	1.35
XIV	4.55	.25	15.9	1.1	1.3	1.17
XV	5.60	.30	11.7	1.0	0.7	1.05

In the case of the calcined catalyst as little as 0.04 me. of potassium ion per g. of catalyst causes a severe loss of activity. To bring about a given reduction of activity a smaller amount of potassium ion is necessary for calcined than for uncalcined catalyst and a still smaller amount of quinoline is necessary. These differences are attributed to structural changes which occur to the oxide catalyst during treatment with the aqueous salt solution. This will be discussed in a future paper.

The deleterious effect of inorganic ions on activity has been recognized in catalyst preparation.[9] During the course of this work, Bitepazh[10] has published similar results on poisoning silica–alumina catalyst by alkali metal ions.

General Discussion.—An estimation for any given catalyst of the fraction of the total surface occupied by the active sites can be made from the amount of basic nitrogen chemisorbed by the catalyst. The exact area covered by a quinoline molecule is questionable depending upon whether or not it lies flat on the surface. However, taking 36 sq. Å. as the area of the flat-lying quinoline molecule, in the case of the Catalyst IA only about 4% of the surface is covered. Hence, by far the major part of the surface does not contribute to the cracking activity of the catalyst.

In one experiment employing catalyst IIA at 425°, 8 LHSV, and a catalyst to cumene volume ratio of 0.25, there was obtained, in wt. % of the cumene charged: benzene, 25.7; coke, 0.1 and gas, 9.4 (1.38 gravity compared to air). Using the number of millimoles of cumene cracked per g. catalyst (10.1), the number of active centers per g. of catalyst as measured by quinoline chemisorption (0.03), the average number of scission reactions catalyzed per active center was calculated to be about 340. Thus, each active center is able to promote the decomposition of a large number of molecules.

Physical properties, notably surface area, have been proposed as a measure of activity for catalysts. This correlation is successful only when the composition and the method of preparation through the partial deactivation are the same. That surface area is not basically related to activity is demonstrated by the rather extreme examples given in Table XI. On the other hand, the fact that the quantity of quinoline chemisorp-

TABLE XI

Catalyst	Area sq. m./g.	Cracking activity % gaso. CAT-A
VIIS Silica gel	366	5
VIA 1% Alumina-silica	390	28
IA 12.5% Alumina-silica	280	45
XVI 10% Alumina-silica	2	19

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[9] J. R. Bates, U. S. Patents 2,283,172-3 (1942), to Houdry Process Corporation.

[10] Yu A. Bitepazh, *J. Gen. Chem. (U. S. S. R.)*, **17**, 199-207 (1947).

tion is related to catalyst activity is shown by data (Table I and Fig. 5) obtained with catalysts of various compositions, methods of preparation and activities. The amount of quinoline chemisorbed thus measures a fundamental property of the catalyst which is related to its ability to act as a catalyst.

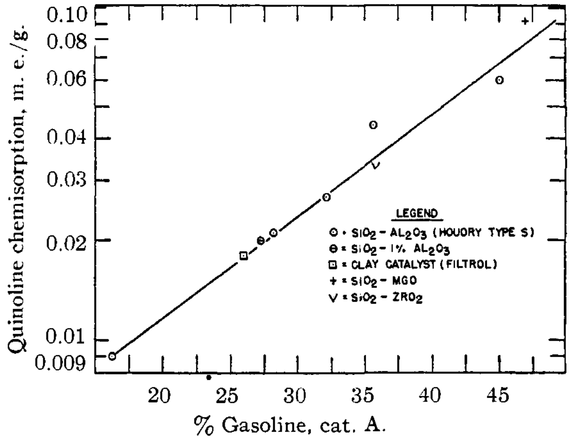

Fig. 5.—Quinoline chemisorption at 315° as a function of activity for cracking light East Texas gas oil.

Considering the chemical nature of the substances found effective for deactivating catalysts (alkali metal ions and basic nitrogen compounds), the conclusion is drawn that it is the acidic characteristics of cracking catalysts which are fundamental to their activity. The ability of silica–alumina catalyst to show an acid reaction to indicators,[11] to release carbon dioxide when contacted with carbonate solution and to catalyze the inversion of sucrose (unpublished data from this laboratory) verifies the acid nature of the catalyst.

Actually (excluding the free radical reaction), most hydrocarbon reactions are acid catalyzed, although some are more difficultly so than others. For instance, such a comparison might include, starting with the most easily catalyzed: double bond shifting in an olefin, skeletal isomerization of olefins, polymerization, cracking of olefins and alkyl aromatics, cracking of paraffins and isomerization of paraffins. The physical and chemical properties of each hydrocarbon must be taken into account in determining the nature of catalyst–hydrocarbon complexes and the mechanisms of reactions.

The mechanism of several reactions which proceed during catalytic cracking, may be visualized through the formation of a carbonium ion.[12] Indeed, from the fact that olefin polymerization and alkylation of aromatics are acid catalyzed reactions it follows that the depolymerization and dealkylation are also acid catalyzed. In any consideration of the mechanism of the reactions brought about by silica–alumina the ability of silica–alumina to catalyze hydrogen exchange in hydrocarbon molecules must be taken into account.[13]

The idea of a straight-forward chemical relationship between catalyst and substrate is not new.[14] Frequently catalytic reactions have been interpreted through the formation of a complex, where such unstable complexes are known or where prototypes have been recognized. However, the idea of discerning the functionality of molecular groupings responsible for catalytic activity and determining quantitatively the effect of poisons on catalytic activity by means of chemical reactions does not appear to have been appreciated fully.

The structure of siliceous catalysts, the detailed chemical nature of the active centers of these catalysts and the mechanism of the reactions they catalyze will be discussed in future papers in this series.

Acknowledgment.—Permission by the Houdry Process Corporation to publish this work is acknowledged with appreciation. Contributions of other members of this laboratory are also acknowledged and particularly those of S. G. Hindin.

Summary

1. Basic organic nitrogen compounds, such as quinoline, are held on silica–alumina (–magnesia, –zirconia) catalyst surfaces by physical and chemical forces. These forces are widely different so that at 250–500° the physically-held quinoline can be distinguished from that chemically-held. At a given temperature the amount of physically-held nitrogen compound is increased with an increase in its partial pressure. The amount chemisorbed is decreased with an increase in temperature.

2. The cracking activity of the catalysts studied was proportional to their capacity to chemisorb quinoline at cracking temperatures.

3. Catalysts which have basic nitrogen compounds chemisorbed or which have potassium added by base exchange are poisoned for cracking. From a study of partial poisoning an exponential relationship was found between the amount of certain nitrogen compounds chemisorbed and the yield of benzene from the dealkylation of cumene.

4. A relatively small fraction of the total surface of silica–metal oxide cracking catalysts is responsible for catalytic activity. The chemical properties exhibited by this part of the surface identify the active principle as an "acid."

MARCUS HOOK, PA. RECEIVED MARCH 12, 1949

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