CATALYSIS IN HYDROCARBON CHEMISTRY (Parts IV. to VII.).

BY R. H. GRIFFITH.

Received 14*th December*, 1936.

PART IV.—THE ADSORPTION OF HEXANE ON CATALYSTS.

(With S. G. HILL.)

The fact that benzene, cyclohexane and hexane are adsorbed by molybdenum oxide catalysts at temperatures as high as 450° has already been demonstrated,[1] and the present investigation was carried out to compare the behaviour of a number of other metals or metallic oxides under similar conditions. A brief note of the results obtained has been given,[2] and this communication is concerned chiefly with recording the experimental data.

[1] Griffith and Hill, *Proc. Roy. Soc. A*, 1935, **148**, 194.
[2] Hollings and Griffith, *Nature*, 1932, **129**, 834.

The catalysts were prepared in the form of an oxide, hydroxide or carbonate, either precipitated as such or purchased in the purest commercial grade available. The hydroxides of Al, Cr, Co, Cu, Fe, Mn and Ti were precipitated; Ca, Th, Zn, Zr, Mg, Pb and Sn were employed as oxides; vanadium was obtained by careful heating of pure ammonium vanadate, and tungsten was used as tungstic acid. In all cases the materials were carefully washed with distilled water until free from soluble matter. The dried solids were then finely powdered and made into a paste with water, extruded from a small handpress into threads, and broken into granules which were reduced in a stream of hydrogen at 450° for 50 hours.

The hexane was dried and redistilled before use, the same material being used throughout the whole series of experiments.

The adsorption apparatus was similar to that previously employed,[1] and gave the results recorded in Table I.; negative values appearing in this table indicate that decomposition of hexane has occurred, and the substances producing this effect are collected in group 1. The remaining substances did not lead to decomposition of hexane at 450°. In the expression of the volume of hydrocarbon adsorbed, the vapour is regarded as a true gas.

TABLE I.—C.C. (CORRECTED TO 0° AND 760 MM.) OF HEXANE ADSORBED BY 100 GRAMS OF CATALYST.

Group 1.	20°.	100°.	200°.	300°.	400°, 0 Hours.	400°, 2 Hours.	450°, 0 Hours.	450°, 2 Hours.
Cr	250	208	126	66	98	7·8	—	—
Zn	8	—	1·6	2·3	1	−16·4	—	—
Fe	46	16	8·5	6	12	−63	—	—
Cu	23	17	16	−11 (after 1½ hours).			—	—
Charcoal	—	—	140	85	47	−3·8	—	−38
Ti	—	—	57	27	29	—	22	−178
Mn	50	24	20	20	16·6	−19·5	—	—
W	28	25	10·5	8·7	6·0	−11	—	—
Co	—	—	14·6	15	12	−13	—	—
Al	130	45	19	17	19	—	17	−36
V	79	—	35	30	11	−108	—	—
Th	37	19	7·5	3	1	−6	—	—
Group 2.	**20°.**	**100°.**	**200°.**	**300°.**	**400°**	**450°.**		
Pb	11	5·4		5·2	5·4	4·1		
Mg	134	19	8		7·1	15		
Zr	92	30	18	16·2	16·4	16·6		
Ca	121	34	22	19	19	18·7		
Cd	82	47	51	54	60	63		
Sn	14	4		3·8	7	6·1		

It is clear that several types of adsorption of hexane can take place, varying in intensity, velocity and character. Although the existence of activated adsorption in the case of hydrocarbons is not nearly so obvious as it is with hydrogen, there is little doubt that it often takes place, but where decomposition occurs, the true effects are masked. There is also a qualitative relationship between activity for decomposition and one particular type of adsorption,[3] but it is evident that adsorption may lead to one of four results:

---

[3] *Cf. The Mechanism of Contact Catalysis,* Oxford University Press, 1936, page 45.

(1) Vigorous decomposition causing extensive deposition of carbon on account of secondary reactions brought about by adsorption of primary reaction products;

(2) decomposition involving the loss of much hydrogen from the molecule;

(3) decomposition by loss of methane;

(4) holding of the molecule without decomposition.

Catalytic activity is therefore always accompanied by adsorption, but the existence of adsorption does not necessarily involve activity. These observations agree with the fact that decomposition of hydrocarbons is brought about by a very wide range of catalysts, and that the products obtained with the various contact materials employed are often very different one from the other.

Summary.

Comparative data are presented for the adsorption of hexane on a large number of catalysts at temperatures between 20° and 450°. Activated adsorption can be detected in many cases, and its relation to catalyst activity is discussed.

PART V.—PROMOTER CONCENTRATIONS.

In a previous communication,[4] the effect of the addition ot small amounts of silica was studied in relation to the activity of molybdenum oxide catalysts for the decomposition of hexane and cyclohexane.

A wide range of promoters has now been investigated by using the same method, in order to determine whether any regularity could be observed in the optimum concentration of the several substances. The results obtained have been described in outline,[5] and their significance has been discussed briefly.[6] The present communication is intended to provide experimental data supplementary to the previous notes.

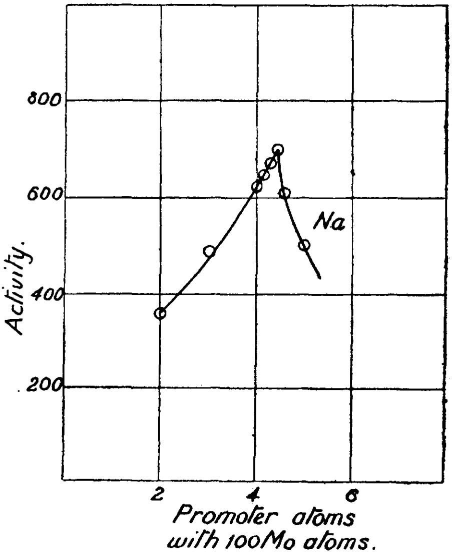

FIG. 1.

The substances employed as promoters were sodium, chromium, iron, copper, cerium, aluminium, barium, lead, boron and thorium. Sodium was added in the form of carbonate and reacted to give sodium molybdate; boron was added as boric acid. In the case of all the other substances, the molybdic acid was first treated with ammonia in order to give just sufficient ammonium molybdate to react

---

[4] Griffith and Plant, *Proc. Roy. Soc. A*, 1935, **148**, 191.

[5] Griffith, *Nature*, 1936, **137**, 538.

[6] *The Mechanism of Contact Catalysis*, Oxford University Press, 1936., p. 77.

with the promoter salt, which was either a nitrate or an acetate. This was found to be necessary in order to obtain uniform admixture of the promoter in such a form that it could not become unevenly distributed during subsequent drying and heating. With mixtures containing sodium and boron, the catalyst threads were dried at room temperature, but the others could be dried in a steam oven.

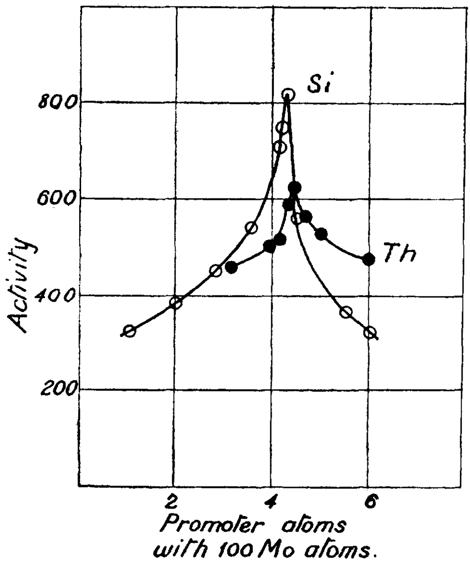

FIG. 2.

The granules employed were of the same size as before, the reaction temperature, method of experiment and expression of activity were also identical. Reduction was carried out at 500° for one hour with hydrogen at 100 c.c./minute before a test was begun.

Experimental results in addition to those previously published are shown in the accompanying drawings, which indicate the change in catalyst activity as the concentration of promoter was increased. The activity was determined by measuring the volume of permanent gas formed from hexane at 500° in unit time. In Table II. the positions and activity of the optimum are given. The latter are all corrected for the composition of the promoter compound as determined by analysis.

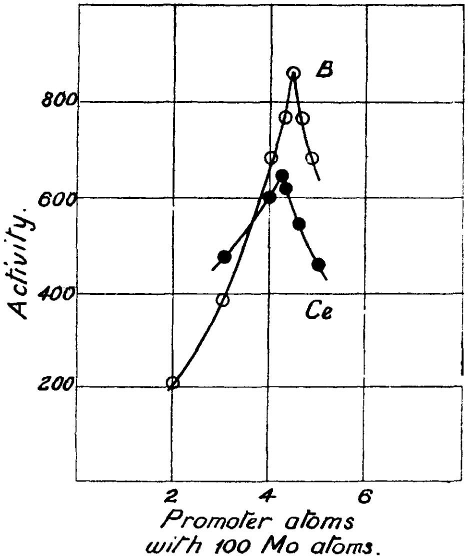

FIG. 3.

It is clear that the ten new promoters, and the silicon previously investigated, all fall into two classes. One of these has an optimum ratio of 4·3 to 4·4 atoms of promoter element to 100 atoms of molybdenum, and the other has a peak at half that concentration.

Also, it can be seen that those substances which are reduced to metals under the conditions of the experiments are all required in the smaller concentration, while those giving the peak at 4·4 atoms are all oxides. No difference in the optimum concentration can be observed with change in valency, density or crystal structure, and basic or acidic oxides behave similarly.

The actual value of the maximum activity, the rate of rise to this point, and of fall from it, does vary appreciably from case to case. It is probable, in view of the relatively high activity shown at points well beyond the maximum in the case of copper and thorium, that this final figure is determined by the activity of the promoter when employed alone as a catalyst. This means that the molybdenum surface has become completely covered with the promoter and is simply acting as a carrier for it.

The volume of catalyst obtained from a given weight of molybdic acid, the initial activity measured at the beginning of a test, and the rate of fall to a final steady activity were found to vary considerably with the different promoters, but these factors do not affect the final results.

TABLE II.—Position of Maximum Activity.

Promoter.	Concentration for Maximum.	Value of Maximum.
Na . .	4·3	694
Cr . .	4·3	898
Ce . .	4·25	618
Al . .	4·6	950
Ba . .	4·3	833
B . .	4·3	841
Th . .	4·5	613
Si . .	4·3	825
Fe . .	2·1	1000
Cu . .	2·1	687
Pb . .	2·35	744

The promoter concentration required to give the optimum result with a given catalyst, for a particular reaction involving a single reactant, is therefore primarily a characteristic of the catalyst and not of the promoter. It follows that, once the position of the peak is known for any promoter for a given reaction with a single reactant, that of the others can be predicted.

A further deduction is that no higher activity can be obtained by the addition of a second promoter to the most active concentration of the first promoter, once the latter has been properly established. This point was confirmed by the addition of 0·1 atom of silicon, in the form of colloidal silica, to the chromium-promoted molybdenum catalyst of greatest activity. The result was a change of activity from 898 to 830.

Summary.

When a molybdenum oxide catalyst is promoted by the addition of another oxide, the concentration of the latter which gives the greatest activity is found to be the same in every case examined. The amount of promoter required is therefore a characteristic of the catalyst and not of the promoter oxide which is used. If the promoter is present as a metal, the concentration required is only half that which is necessary with an oxide. The prediction of the proper concentration of any promoter is therefore possible when that of any single one has been thoroughly established.

The significance of these results in connection with the general theory of catalysts is discussed.

PART VI.—THE CONVERSION OF PHENOL TO BENZENE.

The present investigation was carried out to determine the influence of changes in promoter concentration when two reactants were involved. The conversion of phenol to benzene, by treatment with hydrogen, appeared to be a particular interesting reaction of this type, as the products—water and benzene—were both of a different class from the two reactants, and were less likely to give rise to retardation similar to that previously observed in the hydrogenation of hydrocarbons.[7] The use of molybdenum oxide as a catalyst for this reaction is described by Fischer, Petrick and Bahr.[8]

Experimental Method.

An apparatus similar to that employed for the decomposition of hexane [9] was used with slight modifications. The saturator was constructed of copper, owing to the rapid attack of glass by hot phenol. The reaction tube was made of monel metal. A stream of dry hydrogen was passed at atmospheric pressure and at constant rate (207 c.c. per min.) into the phenol saturator at 100°, and thence to the catalyst tube at 440°. The catalysts were employed in the form of pellets and were prepared by the procedure previously described. The catalyst was reduced with hydrogen, not containing any phenol, for 30 minutes at 440° prior to each experiment.

The reaction products were cooled in a condenser and then passed to an electrostatic precipitator and through a tower packed with active charcoal, to a gas-collecting burette. As the vapour pressure of phenol at 100° is about 44 mm., the maximum contraction per minute would be about 13-14 c.c., depending somewhat on barometric pressure. No cyclohexane is produced from benzene under the conditions employed.[10] No liquid benzene would separate but its vapour was completely retained by the charcoal; strict precautions were taken that the latter did not become saturated and allow benzene vapour to pass to the gas collector. The course of the reaction was followed by measuring the volume of hydrogen collected per minute.

The volume of catalyst was chosen so that complete conversion to benzene was not quite achieved, and the results were then corrected to a standard catalyst volume of 10 c.c. measured after use. The activity is thus expressed as the contraction in volume of hydrogen per minute caused by 10 c.c. of catalyst. Although with molybdenum oxide alone the activity fell rapidly to zero in a few hours, generally it remained steady over periods of several hours in the case of catalysts containing appreciable concentrations of promoter (*e.g.* more than 2 atoms per 100), but for comparative purposes the experiments were continued for minutes in every case.

TABLE III.

Catalyst.	Absorption of H_2, c.c./minute.	Catalyst Volume, c.c.	Activity.
Ce 4 * .	6·6	5·0	13·2
8 .	7·5	6·0	12·5
12 .	6·0	4·6	13·1
16 .	6·0	4·0	15·0
66·6 .	7·0	4·8	14·6
Ce oxide	1·5	5	3·0
Na 4 .	0	4·5	0

* The compositions are given on the usual basis of promoter atoms to 100 molybdenum atoms; Ce 66·6 is cerium molybdate.

Results Obtained.

The two cases most fully investigated were molybdenum oxide promoted by silica and by alumina; the former was added as colloidal silica, and in the case of aluminium the nitrate was added to the molybdic acid containing just sufficient ammonia for its precipitation. A sharp peak in the concentration-activity curve [11] appeared at 15·0

[7] *Proc. Roy. Soc. A*, 1935, **148**, 186.

[8] *Brennstoff-Chemie*, 1932, **13**, 45.

[9] *Proc. Roy. Soc. A*, 1935, **148**, 191.

[10] Sabatier and Mailhe, *Compt. Rend.*, 1903, **137**, 240; Burrows and Lucarini, *J. Amer. Chem. Soc.*, 1927, **49**, 1157.

[11] *Cf. The Mechanism of Contact Catalysis*, Oxford University Press, 1936, p. 79.

atoms of Si to 100 atoms of Mo, and at 16·5 atoms of Al. Experiments were also carried out with boric acid, but although a promoting effect was observed, it was erratic and not reproducible. The catalysts containing boric acid were also found to be covered with a fine crystalline deposit after use, and it was evident that volatilisation of boric acid, by means of the steam formed in the reaction, was leading to these irregularities.

Other experiments, with sodium added as carbonate and with cerium, precipitated as molybdate, are recorded in Table III. ; the former gave no promoting effect and the latter gave an activity figure which remained practically unaltered between atomic ratios of 4 and 66·6 to 100.

Discussion.

From these results it is possible to draw the following conclusions : (1) the concentration of promoter required to give the maximum effect is different from that observed in the case of hydrocarbon decomposition ; (2) the optimum concentration does not remain unaltered by the use of different promoters, although the results are still close together.

(1) This fact indicates that different classes of reactants are absorbed by different parts of the catalyst surface.

(2) Two alternative explanations of this effect may be suggested : (*a*) that the small differences previously observed in the case of hexane decomposition are real differences. It is interesting to observe that the ratio of Al to Si in the former case is 1·07 and in the present case is 1·10 ; (*b*) that the observed promoting effect, when two reactants are involved, is primarily due to the increase in the rate of adsorption of that reactant which is normally more slowly adsorbed. When the maximum promoting effect, with regard to the latter, is approached, its adsorption velocity may become of the same order as, or even greater than, that of the second reactant, so that the influence of promoter concentration on the latter also plays its part. This would lead to displacement of the observed optimum unless every promoter gives the same degree of effect as well as the same position.

It has already been shown (Part V.) that the degree of effect obtained varies with the promoter employed, and it seems that the second alternative is the more likely explanation of the results now recorded.

The behaviour of sodium and cerium may at first appear to disagree with earlier statements that any oxide can act as a promoter, provided that it is added in uniform distribution. In fact, however, they can be readily explained as cases of compound formation in which the compounds have a specific effect and excess molybdenum oxide simply acts as a carrier ; the substance obtained by reduction of sodium molybdate is inactive, while that from cerium molybdate gives a fairly high activity. This is confirmed by the fact that cerium oxide alone is also found to have a very small activity.

It is interesting to observe that aluminium is stated not to form a molybdate.[12]

It is therefore evident that although both sodium and cerium molybdates appeared to be completely decomposed at 500° in contact with hexane, since they gave true promoter curves, yet they retain their intimate association in the form of a compound at 440° in contact with phenol and hydrogen. Unfortunately comparative experiments at 500° in the present case are not possible as the catalysts lose their activity

---

[12] *J. prakt. Chem.*, 1854, **61**, 453 ; 1860, **81**, 411.

so rapidly at that temperature, owing to the deposition of decomposition products. This fact greatly limits the number of possible true promoters in the present case.

The results described in this paper should be compared with those obtained by Kingman and Rideal[13] when using heteropoly acids containing molybdenum, as catalysts for phenol reduction. These authors showed that the compound acids fell into two classes, those containing P, Ni, Cr and Si giving increased activity, while those with Sn and Th in the molecule were less effective than molybdenum oxide alone. The catalysts obtained in this way cannot, however, be considered as promoted in the sense used above, and they must be classified as compound catalysts instead, each compound having its own characteristic activity.

Summary.

The effect of promoters on molybdenum oxide as a catalyst for the deoxidation of phenol by means of hydrogen at atmospheric pressure is discussed.

It is found that the optimum concentration of promoter is different from that required in the case of hexane decomposition, and is also slightly dependent on the particular promoter employed.

Compound formation is found to occur in certain cases, and give effects which can be easily distinguished from those of true promoter action.

PART VII.—CARRIER ACTION AND MOLECULE SIZE.

In a previous communication,[14] attention was called to the fact that with molybdenum catalysts, used for the hydrogenation of tar oils under pressure, no change in activity was observed when an appreciable quantity of an inert material was added to the pure catalyst. A similar observation is recorded in an annual report of the Fuel Research Board (1934, p. 80).

The most likely explanation of this phenomenon appeared to be that the reacting hydrocarbon molecule was so large relatively to the distance between the active centres of the catalysts that only a small proportion of the latter were actually effective in the case of the pure catalyst, and that addition of the inert material showed no diluting effect because there was still a sufficient number of active centres.

A closer study of this point has now been made by following the dehydrogenation of dekalin, decane, hexane and cyclohexane in contact with various catalysts at ordinary pressures. The experimental method was that previously employed with hexane, slightly modified to suit a wider range of conditions.

A stream of nitrogen (83 c.c. per minute dry at 0° and 760 mm.) was passed over the hydrocarbon in a saturator maintained at such a temperature that the vapour pressure of the latter was 160 mm. in each case, and the mixture then came in contact with the catalyst at 500°. The catalyst was previously reduced with pure hydrogen. The activity of the catalyst was expressed as the volume of permanent gas, dry at 0° and 760 mm., produced by 100 c.c. of catalyst per minute. In every case experiments were continued until a steady activity of the catalyst was shown for at east two ho urs.

[13] *Nature*, 1936, **137**, 529.

[14] *Proc. Roy. Soc. A*, 1935, **148**, 186.

Hydrocarbons Used.

Dekalin was redistilled before use, and the product actually employed was found to contain both cis- and trans-dekalin, as well as a small quantity of tetralin. Separate experiments carried out with very carefully prepared samples of the two stereoisomers showed that cis- form was decomposed slightly more easily than the trans-, as would be expected. It was also found that tetralin was more reactive than either form of the fully saturated molecule, but the rigorous purification of the hydrocarbons was not necessary for the series of experiments on carrier action.

Decane was prepared from a commercial " white spirit " by washing with strong sulphuric acid, extracting the residue with warm aniline and fractionating the product to a boiling-point of 171-173°. It was not pure hydrocarbon but representative of a long-chain type. Hexane and cyclohexane were redistilled commercial products.

Preparation of Catalysts.

Titanium hydroxide was prepared by precipitation from a solution of titanic chloride, followed by washing of the precipitate until free from chloride. The air-dried product was ground in a paint mill before use. (This method was applied in every subsequent case as well.) Copper oxide, of analytical reagent quality, was used for preparation of copper catalysts, and chromium hydroxide was obtained by precipitation from chrome-alum, also of analytical reagent quality.

As carrier, pure magnesium oxide was chiefly employed. It was selected on account of its inert character towards hydrocarbons (*cf.* Part IV.), but a few parallel experiments were carried out with molybdic acid, and with china clay as carriers. The carriers were all incorporated by mechanical mixing with the catalyst. In every case the catalyst was used in the form of small pellets, as described in previous publications.

Experimental Data.

In Table IV. are given results obtained with titanium and copper catalysts used with dekalin. It is evident that, with the former, a

TABLE IV.—DECOMPOSITION OF DEKALIN.

Catalyst.	C.c. Gas, per Min.	C.c. Catalyst.	Activity.
100 per cent Titanium oxide . . .	23·0	8·0	287
80 ,, ,, ,, 20 per cent. MgO	19·0	8·1	234
70 ,, ,, ,, 30 ,, ,,	16·5	8·1	203
60 ,, ,, ,, 40 ,, ,,	14·5	8·2	177
50 ,, ,, ,, 50 ,, ,,	11·0	7·9	139
20 ,, ,, ,, 80 ,, ,,	6·0	8·2	73
10 ,, ,, ,, 90 ,, ,,	4·0	8·8	45
0 ,, ,, ,, 100 ,, ,,	0·5	10·0	5
100 per cent. Copper oxide . . .	0		0
90 ,, ,, ,, 10 per cent. MgO	9·0	10·5	85·7
80 ,, ,, ,, 20 ,, ,,	9·75	11·2	85·7
70 ,, ,, ,, 30 ,, ,,	10·8	12·8	84·4
50 ,, ,, ,, 50 ,, ,,	12·2	14·2	85·5
30 ,, ,, ,, 70 ,, ,,	16·2	18·3	88·5
10 ,, ,, ,, 90 ,, ,,	8·5	13·2	64·4
5 ,, ,, ,, 95 ,, ,,	4·6	13·6	33·8
60 per cent. Titanium oxide . . 40 ,, Molybdic acid . .	9·5	6·4	150
30 ,, Chromium oxide . . 70 ,, Molybdic acid . .	5·7	5·9	97

straight dilution effect sets in on the addition of carrier, and it may be concluded that this catalyst only contains a small number of active centres. With copper, however, the results are different. The pure oxide is found to give a catalyst whose activity rapidly falls to zero and this is due to sintering of the metallic copper. With the addition of 10 per cent. of magnesia, however, this change is prevented. On the further addition of magnesia a steady activity persists until the mixture contains only 10 per cent. of copper oxide; the 5 per cent. mixture is again lower.

The case of copper, therefore, appeared to be suitable for further study except for the fact that the 10 per cent. and 5 per cent. mixtures were not reduced to metallic copper during the experiment. This is undoubtedly a disturbing factor, and renders the substance useless for the present investigation.

Chromium Catalysts.

The results obtained with chromium oxide are given in Table V. It is here clearly indicated that the concentration of inert carrier which may be added, before dilution sets in, depends on the size of the reacting molecule. As would be expected, the greater dilution is possible the larger the molecule, the whole catalyst surface being accessible to hexane but only a small proportion to dekalin. The case of cyclohexane (Table VI.) is anomalous, as the catalyst was not reduced to the same oxide. The black oxide was formed in every case but that of cyclohexane, the colour appearing equally intense even with high concentration of carrier, but the change in intensity with the green-brown oxide was pronounced. If previously reduced black oxide was used with

TABLE V.—DECOMPOSITION OF HYDROCARBONS WITH CHROMIUM OXIDE CATALYSTS CONTAINING MAGNESIA AS CARRIER.

Hydrocarbon.	Catalyst, per cent., Cr Oxide.	C.c. Gas, per Min.	C.c. Catalyst.	Activity.
Dekalin .	100	9·0	9·0	100
,, .	50	17·0	17·0	100
,, .	30	17·1	17·6	97
,, .	10	16·1	16·2	99
,, .	5	13·8	18·0	77
,, .	0	0·5	10·0	5
Decane .	100	5·1	9·0	56·7
,, .	50	9·1	16·5	55·1
,, .	20	5·7	16·8	34·0
,, .	10	3·1	17·5	17·7
,, .	0	0	—	0
Hexane .	100	2·15	8·6	25
,, .	80	2·95	13·4	22
,, .	50	2·0	16·2	12·4
,, .	10	0·35	17·5	2·0
,, .	0	0	—	0
Cyclohexane .	100	18·0	9·0	200
,, .	50	7·7	16·8	46
,, .	10	0·35	17·6	2
,, .	0	0	—	0
,, .	100 after dekalin	0·35	9·6	4

cyclohexane the activity was so low that the dilution effect could not be followed.

TABLE VI.—DECOMPOSITION OF DEKALIN WITH Cr OXIDE-SILICA CATALYST.

Carrier.	C.c. Gas per Min.	C.c. Catalyst.	Activity.
0 per cent.	13·0	4·8	271
10 per cent. MgO	11·95	5·3	225·5
20 ,, ,,	9·8	6·1	160·7
30 ,, ,,	8·0	7·4	108
50 ,, ,,	8·6	8·1	106
70 ,, ,,	7·7	8·8	87·5
80 ,, ,,	7·0	8·9	76·7
90 ,, ,,	5·6	9·3	60·2
95 ,, ,,	2·75	9·0	30·6
20 ,, Molybdic acid	6·9	3·0	230
40 ,, ,, ,,	6·3	4·0	160
60 ,, ,, ,,	4·0	4·8	83·3
70 ,, ,, ,,	6·15	8·8	70
80 ,, ,, ,,	2·15	3·6	58·3
25 ,, China clay	7·65	6·3	121·5
50 ,, ,,	5·5	6·4	85·9
80 ,, ,,	4·2	9·8	42·4

Promoted Chromium.

These observations suggested that parallel experiments with a promoted chromium catalyst would indicate whether the latter contained a larger number of active centres than the unpromoted catalyst. Mixtures of chromium oxide and colloidal silica were therefore prepared in order to discover the optimum promoter concentration. The promoted catalyst was mixed, as before, with carrier.

The results given in Table VI. show that an entirely different state of affairs exists on the surface of the promoted catalyst. Regardless of the nature of the carrier an immediate dilution sets in in every case. It must, therefore, be concluded that the promoter does not increase the number of active centres but produces others of an entirely distinct type. This deduction agrees with those arrived at by other methods.[15]

Summary.

(1) The most active catalyst does not necessarily have the largest number of active centres.

(2) The lowering effects observed with carriers cannot be due to compound formation with the catalyst as similar results are given by substances of widely different character.

(3) With a catalyst containing a large number of active centres the addition of a carrier will produce a lowering of activity at a concentration which depends on the size of the reacting molecule.

(4) The addition of a promoter does not increase the number of active centres but produces a surface of a different type from that of the pure catalyst.

---

[15] *Cf. The Mechanism of Contact Catalysis*, Oxford University Press, 1936, p. 177.

(5) Changes in activity occur if the degree of reduction of an oxide catalyst varies; this type of change is associated with visible colour differences.

(6) A carrier may produce an initial increase in the activity of a catalyst by prevention of sintering.

Fulham Laboratory.
The Gas Light and Coke Co.