ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME VIII

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CONTENTS

Coal-Hydrogenation Vapor-Phase Catalysts

By E. E. DONATH, *Koppers Company, Inc., Pittsburgh, Pennsylvania*

The Kinetics of the Cracking of Cumene by Silica-Alumina Catalysts

By CHARLES D. PRATER AND RUDOLPH M. LAGO, *Research and Development Laboratory, Socony Mobil Oil Company, Inc., Paulsboro, New Jersey*

Current Problems of Heterogeneous Catalysis

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Only a few decades ago the term *catalysis* in the sense indicated by the title was practically a collective designation for a number of chemical reactions and adsorption processes, the nature and mechanism of which were very little known. Text books dating from the turn of the century, or even a decade or so later than that, usually contain a collection of more or less unsystematic observations and patents. For a long time in the school curriculum a catalyst was defined as a substance which accelerated a reaction without participating in it—a chemical hocus pocus, indeed!

The veils shrouding the mode of operation of the catalyst were rent by the kinetic and thermodynamical investigations by Langmuir, Paneth, Polany, Volmer, Bodenstein, and Taylor. Debye's studies of dipole effects constituted decided progress in this field, and the same may be said of Born, Franck, and London's treatment of these problems from the point of view of wave mechanics. The literature on catalysis at this stage (1) is entirely different from the earlier works;—among modern works may be mentioned Rideal's "An Introduction to Surface Chemistry," Schwab's "Katalyse vom Standpunkt der chemischen Kinetik," the "Handbuch der Katalyse" in six volumes edited by Schwab, and the "Papers Presented for a Discussion at a Joint Meeting of Société de Chimie et de Physique and Faraday Society" (Bordeaux, 1947).

The next steps toward a deeper understanding of the catalytic processes were possible through researches which elucidated the nature of crystal structures and the geometrical positions of electrons, ions, or atom groups and their energetic conditions and that also determined the factors which influence the mobility of these particles within the lattice or at phase boundaries.

Already in his early work Taylor had pointed out that particles at surfaces, edges, corners, or points are not energetically equivalent with particles in symmetrical positions, because of their exposed and, with regard to affinity, unsaturated positions. Taylor held the opinion that those particles had a particularly high catalytic activity ("the active centers"). It was Taylor I think who drew attention to the fact that no phenome-

1

nological differences exist between adsorption processes and chemical reactions at the phase boundaries; he called adsorption processes "faint chemical reactions" (1).

The activity of the particles in unsaturated positions have also a purely physical and crystallographic effect. At places with high activity the recrystallization that usually is inadvantageous for catalytic processes occurs at lower temperatures or at constant temperatures with higher velocity than at less active places on the surface of the solid-state catalyst.

Goetz showed that there exists a block formation on the surfaces of a crystal and that in this formation the distances between particles are slightly different from those in the interior of the structure; and Cohen observed that transitions at low temperatures can occur in such structures (2,3).

There will be occasion to return to these phenomena in connection with the general significance of those crystal states where new phases are formed. It might be pointed out here, however, that far too little is known about the structural and energetic conditions of surfaces, in spite of their fundamental importance not only for catalytic processes, but for chemical reactions in general. After all, those reactions start at surfaces.

The necessity of further studies in the mechanism of formation of nuclei, of changes of modification, and of crystal growth should also be underlined, although a solid foundation for further work on these problems has been laid by the researches of several investigators, for instance Stranski and Volmer (4,5).

Quite recently there was an important advance toward a deeper understanding of the nature of catalytic processes. The mobility of electrons at surfaces and the exchange of electrons at phase boundaries between catalyst and substrate were investigated and rules for these processes formulated.

The liberation of electrons from the surfaces of solids through irradiation or by other means has attracted the attention of several investigators, working with different objects in view. These researches are mentioned here, because, viewed in perspective, they also emphasize the common traits in the mechanism of adsorption, reaction, photochemical, physical, and crystallographic processes, as well as those pertaining to electronics.

Regularly recurring symposia and congresses in several countries, covering the physical and chemical characteristics of the solid state, give further information accentuating these common traits. Among specialists those gatherings are well known and particular references consequently unnecessary.

In 1943 Schwab demonstrated a connection between electron concentration and catalytic activity. Similar problems have been investigated by Hauffe and Wagner, among others (*6,7*). In this connection it is necessary to mention the important ideas and investigations by Weyl on the *screening effect* in crystals (*7a*).

Schwab and Suhrmann and Sachtler have proceeded further along this road and shown that coupling an electron-spending to an electron-accepting substance apparently is a fundamental condition for a process to take place, whether it is a purely chemical reaction or a catalytic process or the preliminary stage of the catalytic process, adsorption (*8,9*). These investigations seem to be a sound basis for further research on catalysis. It should be possible one day to compute the most advantageous combinations of carrier, catalyst, and substrate in order to obtain the desired course of the reaction. Here for instance are common research approaches for flotation and ion exchange processes.

The preceding paragraphs were a rough outline of the gradual dispersal of the miasma veiling the catalytic processes; further, it should once more be underlined that catalysis, from the phenomenological standpoint, does not occupy any specific position in the group of processes which take place at phase boundaries.

Results from recent research are, of course, extensions of earlier results concerning polarization effects in the innermost adsorption layers and consequent decrease of the energy of activation—in the cases where a reaction is facilitated.

Even though the elucidation of the adsorption and reaction mechanism is close at hand, there are still many problems of theoretical interest and great practical importance. The following paragraphs will touch on these matters.

Better methods must be evolved both for determining and for exploiting the surface of the catalyst. Closely allied to these issues is the task of elaborating new methods of preventing recrystallization, which lowers the effect in the purely geometrical and, especially, in the energetic sense. This problem is undergoing intensive study, as the author had opportunity to observe at a recent visit to American research laboratories. In part, at least, the solution lies in introducing into the lattice such guest particles as retard the transport of matter across the boundary lines of the crystallites. It constitutes an urgent problem in the case of both metallic and nonmetallic catalysts (*10*).

Recrystallization is one form of aging in catalysts. There is a further form in the case of the industrially important mixed catalysts. The latter type occurs because there are gradually formed compounds or solid solutions of the components. Theoretically there is nothing to prevent the

new-formed phases from being even better catalysts than the original
one, but it is a remote possibility that an improvement should occur
with reference to the relevant reaction. Aging of this type is consequently
often combined with a change not only in the activity of the catalyst, but
also of its selectivity.

   One type of aging, frequently leading to complete inactivity, is caused
by poisoning. It may consist of a purely chemical change of the catalyst,
but also of a decrease of the active surface, caused by the fact that sub-
stances formed at the reaction are deadsorbed more slowly than the sub-
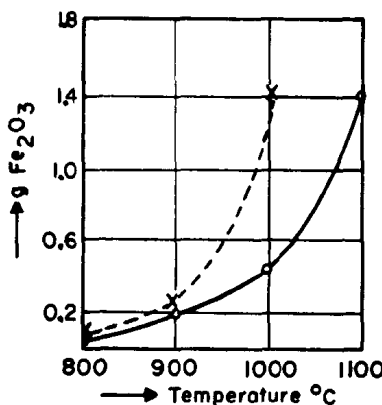strate is adsorbed.

FIG. 1. Changes in the adsorption activity of ferric oxide after heating in oxygen
(curve o) and in nitrogen (curve x). The quantities of ferric oxide required for adsorp-
tion of a fixed quantity of the adsorbate are shown on the abscissa. It will be seen that
the adsorption capacity of a ferric oxide preparation declines more rapidly if it has
been preheated in nitrogen than if it has been heated in oxygen.

   These phenomena are closely connected with the mobility of so-called
surface molecules or *moleculoids*, the mobility of which is also influenced
by energetic or material disturbances in the interior of the lattice (*11,12*).
   It should be pointed out that in many cases it seems uncertain which
substance it is that constitutes the veritable catalyst. Particularly for
metallic and oxidic catalysts each separate case must be investigated for
formation of a monomolecular layer of compounds or adsorbates, for in-
stance, sulfides, carbides, hydrides, etc., which constitutes the real cata-
lyst after an individual activation period of the metal or the oxide. In
such cases the electron exchange between the film and the substrate will,
of course, be the decisive factor (*13*).
   These phenomena underline the necessity of research on the geomet-
ric, structural, and energetic problems of the surface. Interferometric,
radiographic, and X-ray methods as well as determinations of surface

conductivity and electron emission are among the procedures that should be exploited.

The effect of dissolved gases that are not chemically reactive in the ordinary sense on the activity of surfaces and more deeply situated layers has attracted too little attention although it is industrially important. The gases may remain in solid solution or they may be liberated again,
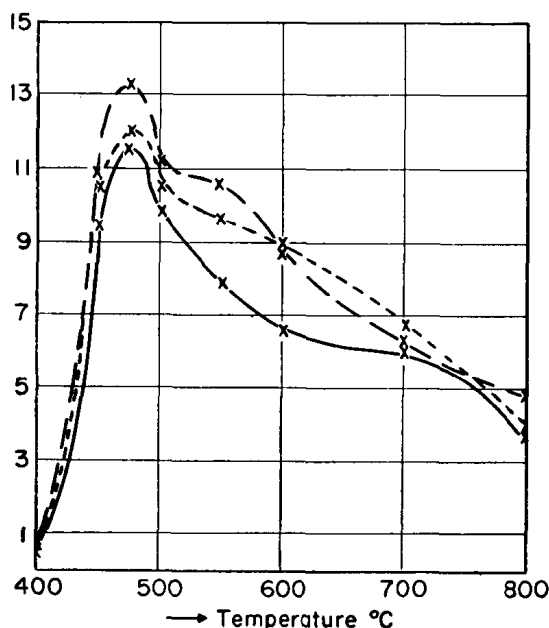
Fig. 2. The change in the dissolution velocity of Al_2O_3 on the heating of kaolin in various chemically inactive gases. The effect consists of a change in the recrystallization velocity and is of interest with reference to the problem of the carrier (- - - - - - air; — ·· — CO; ——— CO_2).

depending on the temperature and the substance. In both cases there is a disturbance of the lattice structure—activating or deactivating according to the composition of the system (14).

Here we approach the group of problems concerning unstable lattice states, brought about in one way or another, problems which are common to adsorption, catalysis, phosphorescence, luminescence, photochemistry, electronics, etc. The geometric distortions of structure, which are naturally combined with energetic changes, are of several types, e.g., "frozen-in" reversible lattice defects, incomplete crystallographic transitions, hereditary lattice imperfections, guest particles of different atomic volume or charge in the lattice, and stoichiometric deviations from ideal formulas. The significance of the latter defects for semiconductors, photo-

reagents, phosphors, and luminophors is common knowledge. Their influence on the adsorption capacity, demonstrated by the author, is perhaps less well known (*14a*).

The influence of the other factors on the activity has been shown by the author in all conceivable cases. With reference to transformations,
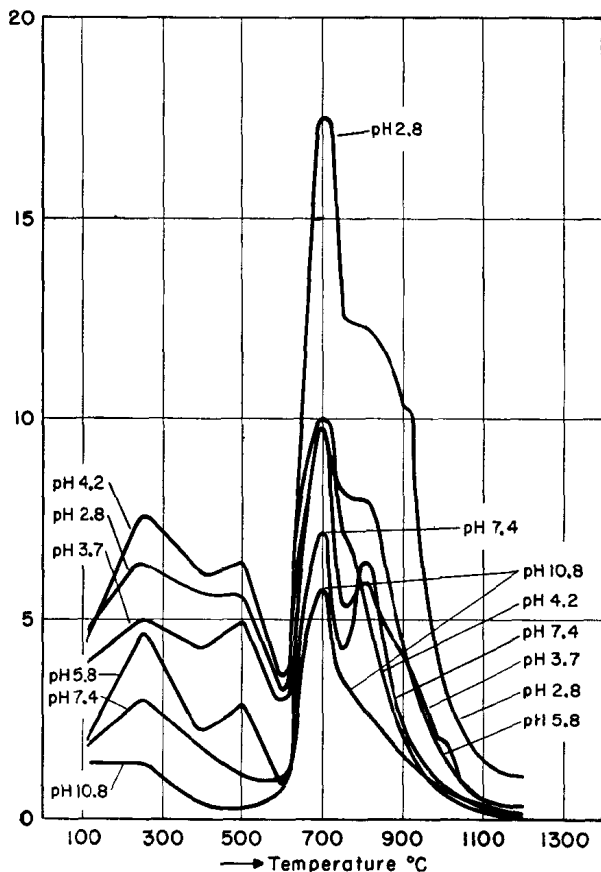

FIG. 3 A. Adsorption of fast red at different pH values as dependent on the heating temperature of pholerite.

the results have been summed up in a rule of general validity: *every kind of transition process or formation of new phases corresponds to a relative maximum of reactivity (15).*

Figures 2 to 6 give some illustrations of this fact. It should be pointed out that though these effects have already demonstrated their usefulness in practice, higher effects and greater selectivity may reasonably be expected through adaptations of the apparatus.

The same may be said with reference to the following considerations.

When an increased yield per unit of time of a chemical reaction in hetero-
geneous systems was desired, temperature, grain size, grain shape, and
contact surface were altered. For catalytic reactions there was further
the method of admixing guest particles to the crystal lattice or creating
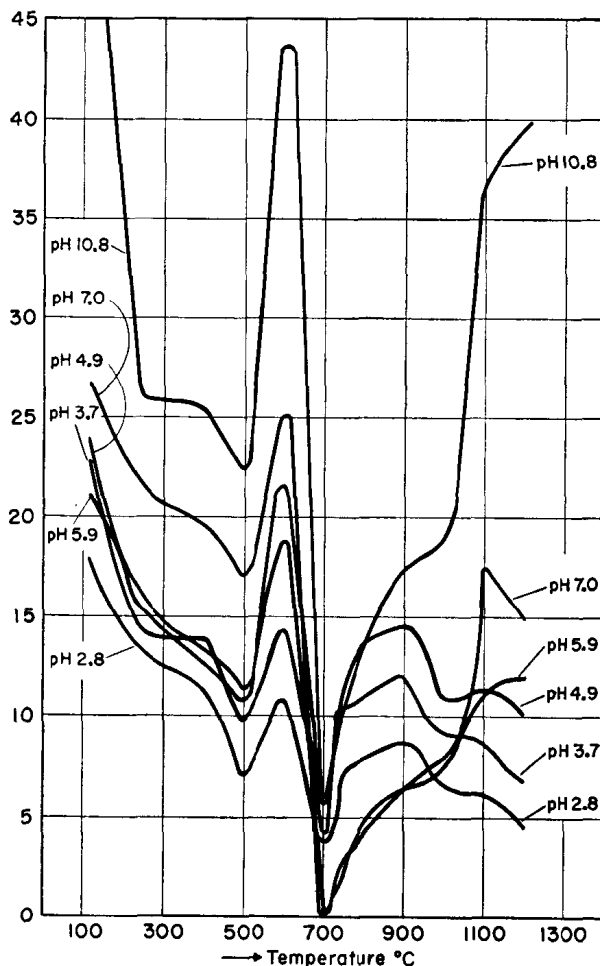

FIG. 3 B. Adsorption of methylene blue at different pH values as dependent on
the heating temperature of pholerite.

phase boundaries by purely mechanical mixture with added substances
(mixed catalysts). Neither at catalysis nor at ordinary chemical reac-
tions, except for photochemistry in the restricted sense of the term, does
there appear to have been a thought that there existed other forms of
energy than heat that might be altered.

When the author started experiments in alteration of energy forms

some twenty years ago, they were generally regarded with marked skep-
ticism. Nobody doubted, of course, that magnetic, electric, or irradia-
tion states should indeed exert an influence on the activity. It was as-
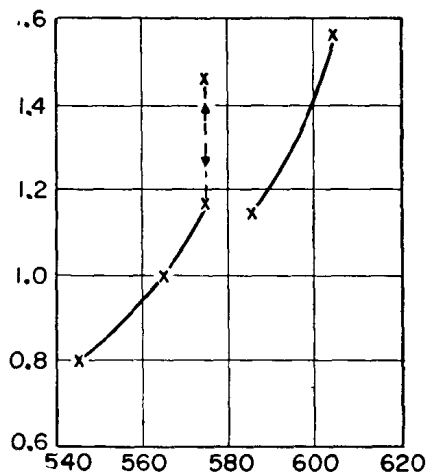sumed, however, that those effects would be extremely small. There were

FIG. 4. The formation of SO_3 with quartz as catalyst in the range of the $\beta \rightleftharpoons \alpha$
transition of quartz (575°). Ordinate: yield in % of theoretical yield.

even mathematical computations that appeared to indicate such a result.
It should be pointed out in this connection that there is a considerable
danger in trying, by starting from a lattice in a state of equilibrium, to
calculate the conditions in a lattice where, from one cause or another, the
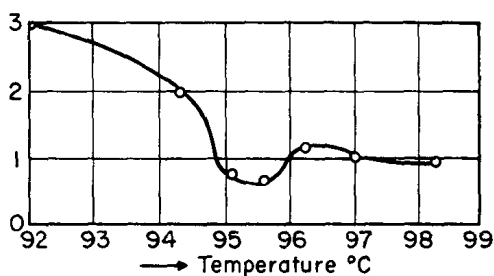

FIG. 5. Maximum of vulcanization velocity of rubber at the transition of sulfur
(minimum of free sulfur). Ordinate: free sulfur in %.

equilibrium has been disturbed. Even the calculations of the states involv-
ing reversible defects depend more on models and ordinary temperatures
(Frenkel, Schottky) than on real—electronographic or roentgeno-
graphic—pictures of the structure. Regarding the real structure of irre-
versible defects, which in practice are immensely important, there do not

exist such investigations, with the exception of a few simple metal lattices. The difficulties naturally increase with heightened temperature and complicated lattices.
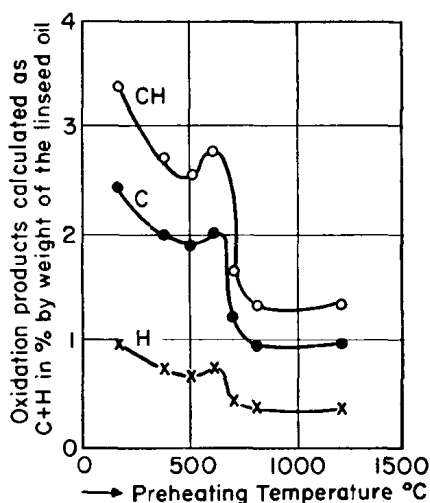

FIG. 6. The influence of the transition from anatase to rutile on the oxidation of linseed oil when TiO_2 is used as pigment.
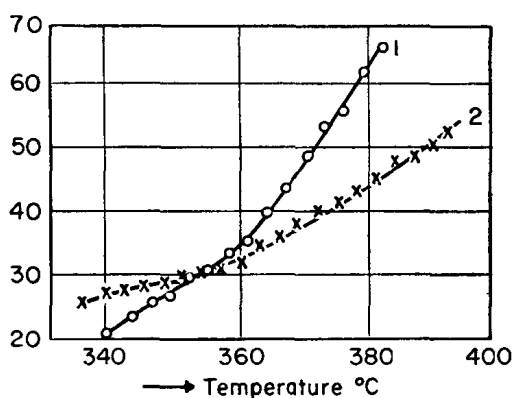

FIG. 7. Abrupt changes in the catalytic decomposition of N_2O on passing the Curie point (360°) of pure nickel. The two curves refer to two experiments with different velocities of the gas currents. Ordinate: yield in % of theoretical decomposition.

To be able to regulate the activity and selectivity of the catalyst, however, is one of the most important problems in research on catalysis. It can be done only through a deeper understanding of the displacement of material particles and electrons.

Results from the experiments are given here by means of a few fig-

ures; these results indicate the great influence exerted on the activity by changes of nonthermal type, i.e., changes in the magnetic, electric, and irradiation state of a substance and the influence of supersonic vibrations (Figs. 7 to 11). In all cases the systems have been selected to ex-
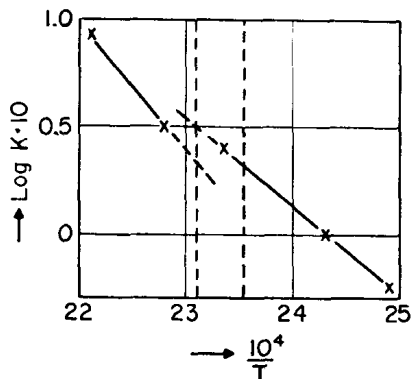

FIG. 8. Similar change observed on kinetic measurement of the catalytic decomposition of formic acid with a Co-Pd alloy as catalyst (Curie interval 135° to 185°).
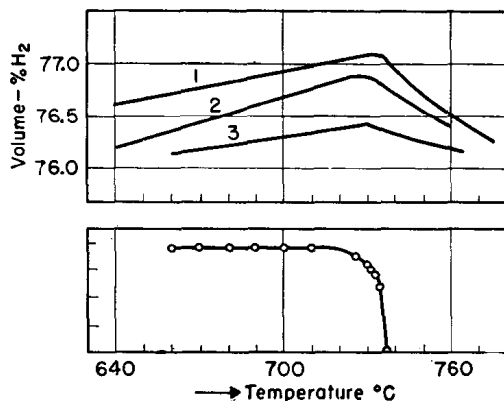

FIG. 9. Changes in catalytic effect on loss of ferromagnetism at the reaction $CO + H_2 \rightarrow CH_4 + H_2O$ with cast iron as catalyst. Reaction mixture: 1 part CO, 3 parts H_2; gas velocity: 3.17 cm.³/min.; temperature increase: curve 1—1.15, curve 2—0.9; curve 3—0.8°/min. The early increase of the H_2 content is caused by the subsidiary reaction $CO + H_2 = H_2O_{liq} + C$. The decreasing percentages above the Curie temperature correspond to the formation of CH_4.

clude the possibility of crystallographical variations. Composite effects are consequently excluded (16). When effects from changes in the magnetic state were investigated, ferromagnetic substances were selected, as there is then no change in modification on passing of the Curie interval.

The influence of the magnetic state was investigated in a large num-

ber of ferromagnetic substances, Ni, Fe, Co-Pd and Heusler alloys, ferrites, etc. In all cases the paramagnetic state exhibited higher catalytic effect. Several different substrates were used. This so-called "magneto-catalytic" effect was later confirmed by Forestier (*17*).
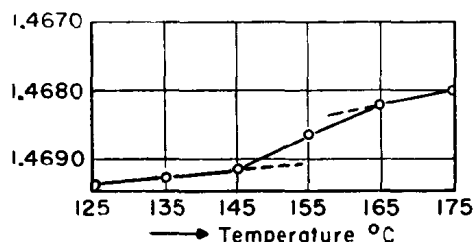

FIG. 10. The change in the velocity of hydration of an unsaturated oil (cottonseed oil) at the passage of the Curie interval of a Co-Pd alloy (152 to 160°). The effect was determined by measuring the refraction index (ordinate).

The result of the kinetic investigations can be expressed as follows: the paramagnetic state has a higher activity than the ferromagnetic state, in spite of the fact that the gross value of activation is smaller in the latter case. It has been pointed out earlier that the interplay of spending and accepting electrons is an essential factor, and the above-mentioned phe-
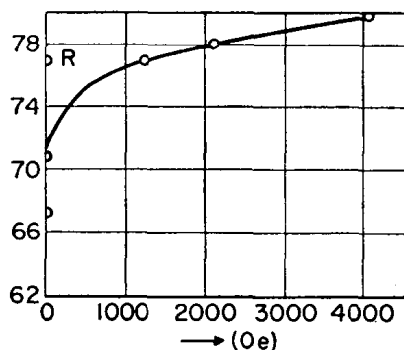

FIG. 11. Effect on the ortho → para transition of hydrogen. [Cf. Justi (*18*).] Ordinate: magnetic field; abscissa: yield in %.

nomena probably mean that this interplay can take place more easily in the paramagnetic state. However, it must be pointed out that further research work must be carried out here, it being too early to explain these phenomenon in details.

Some experiments were made recently in collaboration with Justi in order to ascertain the effect of exterior magnetic fields; an effect on the ortho → para transition of hydrogen was registered (*18*). Similar effects are obtained also in the case of substances with so-called "electrical Curie