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IN
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VOL. V

ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME V

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PREFACE

Advances in Catalysis is now entering into its fifth year. It is, in the editors' opinion, an encouraging and significant fact that the past volumes are finding increasing use in scientific and industrial laboratories and that the *Advances* are frequently quoted as literature sources on various topics of catalysis.

Thus, the editors present this fifth volume with confidence that it too may serve the purpose of fully informing those interested or active in catalytic studies on scientific and practical progress in this field.

In the current volume a variety of subjects is treated by competent authors. These subjects deal with new techniques of surface investigations with the microbalance, with the elucidation of reaction mechanisms by the concept of intermediates, and with specialized studies of the ammonia synthesis, hydrogenations, carbon monoxide oxidation and hydrocarbon syntheses. In addition, Volume V contains an extensive critical review of Russian literature in catalysis.

The correlations established in recent years between the electronic structure of metals and of semiconductors with their activities as surface catalysts will be dealt with in future volumes of the *Advances*.

VLADIMIR NIKOLAEVICH IPATIEFF

1867–1952

Vladimir Nikolaevich Ipatieff, one of the truly great men of chemistry and a pioneer in the field of catalysis, passed away on November 29, 1952.

Our admiration of this man should be based not only on the success of his scientific work but also on the wonderful balance between his academic and industrial achievements.

Ipatieff was, first of all, a brilliant and able teacher who preferred the title of Professor to any other. His research activity of a purely scientific nature brought with it unusual industrial success, and many plants, operating all over the world, are based on catalytic reactions discovered by him. Among the most important of his contributions are the introduction of high-pressure techniques in chemistry and chemical industry, destructive hydrogenation, the production of acetone from propyl alcohol, and the production of high-octane aviation fuel by the reactions of polymerization, alkylation, and isomerization. He was the first to demonstrate the specificity of catalysts and the use of mixed catalysts and promotors.

Professor Ipatieff was born in Moscow in 1867. He worked in Russia under both the Czarist and Soviet Governments before coming to the United States. His scientific and industrial achievements were independent of his political environments. He was promoted to the rank of a general by the Czar and later was awarded a government title by the Soviets. In 1930 he came to the United States where his scientific and industrial achievements received complete recognition.

Among the many international honors he received were the Butlerow Prize and the Lavoisier, Berthelot, and Willard Gibbs medals. He was cited by the United States Government for his work on the production of aviation gasoline, which was credited with establishing the air superiority of the Allied Forces.

All his life his activities were rewarded by more material wealth than his own simple personal tastes required. He spent it instead on the promotion of his beloved science—chemistry. To honor and encourage the work of young chemists in catalysis, he established the Ipatieff Prize. To provide better facilities for teaching students, he built and guided the Ipatieff High Pressure and Catalysis Laboratory at Northwestern University.

During the years of my association with Professor Ipatieff in Russia and in the United States, I grew to know him as a lively man with a wonderful sense of humor, whose enthusiasm, patience, and understanding made him an ideal director and teacher of research workers.

The life, work, and achievements of this great man can serve as an inspiration to us all.

V. I. Komarewsky

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I. INTRODUCTION

1. Background

The development of an industrial ammonia synthesis was one of the early achievements of catalytic chemistry. The ammonia industry is still a key industry, with U.S. annual production at present almost two million tons. In view of this fact it deserves to be mentioned that the catalysts used today are of the same types as those developed forty years ago by Bosch and Mittasch. This does not mean that the latest developments in ammonia synthesis are only of theoretical value, because the increased knowledge of the catalysts and of the kinetics of the reaction has resulted in improved performance and increased lifetime of the catalysts owing to refinements in manufacture, reduction, and operation of the catalysts. It will be the object of this paper to discuss our present knowledge of the catalysts and of the kinetics, and from this information combined with the latest published data on high-pressure conversion measurements to give a brief survey of the dependence of efficiency and lifetime of catalysts upon synthesis conditions.

2. *Scope*

A number of substances show considerable activity as ammonia catalysts. Fe, Os, and Re and nitrides of Mo, W, and U are the best known. Iron in the form of promoted iron catalysts is by far the most important, maybe the only type in industrial use, and except for a few comparisons, iron catalysts will be the only type dealt with in this paper. Furthermore, the discussion will be limited to the type of catalysts made by fusing iron oxides together with the promoter components and subsequently reducing the catalysts. This limitation is not too important, since this type of catalyst is the one most widely used and also the type on which most fundamental work has been done.

Reference is made to earlier surveys by Emmett (1) and by Frankenburg (2) as this paper deals mainly with later developments.

The progress during the last twenty years in our knowledge of the solid state, which resulted from the introduction of quantum mechanics, was the prerequisite to the improved understanding of catalysts that is now in sight.

The state of iron ammonia catalysts is dealt with in the following chapters, and x-ray, magnetic, and electric data will be discussed together with adsorption measurements. Information about the catalysts combined with kinetic experiments has led to a fairly good qualitative understanding of ammonia synthesis on iron catalysts, but owing to the extremely complicated nature of the catalyst surface during reaction, a quantitative treatment based on data of catalyst and reactants will not be attained in the near future.

II. UNREDUCED STATE OF CATALYSTS

1. *Composition*

The iron catalysts for the ammonia synthesis discussed in this article are manufactured in form of oxides, which are subsequently reduced to their active state. Normally the reduction is performed in the converters. The unreduced catalysts consist mainly of iron oxide, but one or more other oxides are usually added to serve as stabilizers and activators of the reduced catalyst. The iron oxide used may be a natural oxide, such as magnetite, or it may be a synthetic oxide made from Armco iron or similar materials. The composition of a catalyst is determined both by the type and amount of promoters and by its degree of oxidation. In the following we shall discuss nonpromoted, singly, doubly, and triply promoted catalysts; catalysts called nonpromoted may, however, contain small amounts of promoters originating from impurities in the raw materials. All available evidence suggests that a ratio of Fe^{II} to Fe^{III} equal to 0.5, or in the promoted catalysts at least near to this ratio, is optimal. Almquist and Crittenden (3) have examined the dependence of activity of pure iron catalysts on the degree of their state of oxidation prior to reduction and found maximum activity with samples corresponding to Fe_3O_4. They found the dependence to be more pronounced when the catalysts were used at 100 atm. than when used at 30 atm. Similar results were obtained by Bridger, Pole, Beinlich, and Thompson (4) when investigating K_2O-Al_2O_3-promoted catalysts at 100 atm., 450°, and S.V. = 10,000.

A large number of papers have appeared which deal with the type and amount of promoters which preferably should be used.

A survey of some of the more important promoters is given in a monograph by the author (Nielsen, 5). The author believes that our knowledge concerning this point can be expressed in the following way.

Nonpromoted catalysts rapidly lose their activity, particularly under severe conditions of operation. This is in no way contradicted by reports stating that reduced magnetites are good catalysts without addition of promoters. The author had made a spectrographic analysis of an octahedron crystal of Ural magnetite, and the examination disclosed a content of calcium, not less than 1%, of titanium between 0.5 and 1% and smaller contents of magnesium and aluminum, which proves that well-known promoters were present in the magnetite matrix.

It is impossible to define an optimal catalyst composition, because the composition which is most effective for one set of synthesis conditions will be far from optimal for other conditions. Thus Telegin, Sidorov, and Shpulenko (6) have shown that the amount of Al_2O_3 necessary to stabilize a catalyst for work at 450° and 1 atm. is far from sufficient to give it stable activity at 500° and 300 atm. The difference may be so great that if 0.1% Al_2O_3 is sufficient in the former case, up to 5% Al_2O_3 may be required in the latter. This is not only a problem of stability of the catalysts; it is also a question of activity. A series of catalysts do not necessarily have the same relative activity under different synthesis conditions, which may be explained by the assumption that, at different conditions, not always the same surface elements are the most active for the catalytic conversion.

It is a generally accepted view that for industrial application the doubly promoted catalysts are superior to the singly promoted types. The promoter pair should consist of an oxide of an alkaline metal and of a difficultly reducible oxide of amphoteric or acidic character. Commonly K_2O-Al_2O_3 is accepted as the best activator pair. The ratio of K_2O to Al_2O_3 should not exceed certain limits. Oxides easily reduced, such as copper oxide, decrease catalyst activity and/or stability. It is stated that promoted iron catalysts are superior to promoted iron-molybdenum catalysts. The author holds the view that triply promoted K_2O-CaO-Al_2O_3-iron catalysts are superior to doubly promoted types. This is especially true in respect to thermostability, which property largely determines the lifetime of a given catalyst in industrial application. It is generally assumed that MgO may partly substitute CaO of the triply promoted catalyst. MgO and CaO enter the magnetite matrix in solid solution, replacing iron oxide. As will be mentioned in the next section this substitution increases the amount of other promoters which can enter the spinel lattice. It ought to be emphasized that a catalyst should not be stabilized for more severe conditions than those at which it is scheduled to operate, because a decline in activity will result if a too high promoter concentration is used. In addition a too high promoter content may cause a deterioration of the mechanical properties of the catalysts.

2. Structure

It can be readily understood that the structure of the oxide, from which the reduced catalyst is prepared, plays an important role for the properties of the catalyst. This dependence has been proved experimentally by the influence which the rate of cooling of the oxides of a given catalyst composition shows upon the catalytic properties of the reduced catalyst. This effect can be interpreted by considering that in the reduced catalyst the promoters are distributed all over the surface and that it is, of course, highly important how they are distributed. This distribution cannot be independent of the way in which the promoters are present in the oxidic state, whether in solid solution in the magnetite, as separate crystals or as amorphous glassy layers.

It should also be mentioned in this connection that the reduction process exerts a considerable influence on the behavior of the catalysts and that the course of this process is intimately connected with the structure of the oxide.

In Table I, x-ray data are listed for various iron oxides relevant to this type of catalysts. A few words will be said about these pure oxides before discussing the more complicated promoted catalysts.

TABLE I

Structures of Iron Oxides

Compound	Structure	Dimension	References
Fe_3O_4	Spinel	$a_0 = 8.37$	Wyckoff and Crittenden (7)
		$a_0 = 8.37_{4\pm3}$	Clark, Ally, and Badger (8)
γ-Fe_2O_3	Spinel	$a_0 = 8.33$	Lihl (9)
γ-FeO	Spinel	$a_0 = 8.37_5$	Lihl (9)
α-FeO	Sodium chloride	$a_0 = 4.2820$	Bénard (10)
FeO	Rhombohedral deformation		Rooksby and Tombs (11)
α-Fe_2O_3	Rhombohedral	$a = 5.42$	
		$\alpha = 55°17'$	Strukturberichte

a. Magnetite. The unit cell of this spinel consists of a framework of oxygen ions which deviates slightly from cubic close packing and which forms 64 tetrahedral and 32 octahedral interstices per unit cell. In the case of stoichiometric Fe_3O_4, 24 iron ions are distributed in the interstices. According to de Boer, van Santen, and Verwey (12) magnetite is an inverse spinel as eight Fe^{III} occupy tetrahedral interstices and eight Fe^{II} and eight Fe^{III} occupy octahedral interstices. Its formula should be written $Fe^{III}(Fe^{II}, Fe^{III})O_4$. This special distribution of the iron ions explains the high electric conductivity of magnetite, because according to Verwey and de Boer (13) semiconductors of this type owe their conductivity to the presence, at equivalent crystallographic positions, of ions of the same element but of different valency. This structure also conforms with the theory by Néel (14) explaining the magnetic properties of Fe_3O_4 and γ-Fe_2O_3.

It should further be mentioned that Néel (15,16) investigating the magnetic properties of α-Fe_2O_3 observed small regions, almost two-dimensionally extended, of Fe_3O_4 deformed so as to join the α-Fe_2O_3 matrix. This is, of course, a lattice distortion which can be observed very accurately.

b. γ-Fe_2O_3, γ-FeO. When considering the small deviation in unit cell dimension between Fe_3O_4, γ-Fe_2O_3, and γ-FeO it may well be possible that the same type of lattice imperfection as that found by Néel in a rhombohedral matrix may exist in spinel structures, so that regions with a deviating number of iron ions per unit cell exist coherently with the normal lattice.

c. Rhombohedral FeO. A rhombohedral deformation of FeO leads to a doubling of x-ray reflections, and this point is of some interest in connection with discussion of x-ray diagrams of unreduced catalysts.

d. Oxidic State of the Catalyst. In a microscopic examination of a great number of promoted fused iron catalysts for Fischer-Tropsch synthesis three general types of grain structure were observed (Klemm, 17). In the first type of catalysts the grains joined without separate interfacial phases, indicating that the promoters are completely dissolved in the magnetite matrix. In the two other types, interfacial phases were observable either as an amorphous glassy material or as separate crystals, which means that more promoters are present than the amounts soluble in the magnetite matrix. The catalysts investigated were not ammonia type catalysts, since they contained considerable amounts of acidic promoters such as SiO_2, TiO_2, and ZrO_2. Some information relevant to ammonia catalysts is, however, obtainable from this investigation. It appears that oxides of the alkaline earth metals enter the matrix easily and that the presence of these oxides leads to better solubility of other promoters in the matrix, so that unreduced catalysts of the first type result. It also appears that CaO or $CaO \cdot Fe_2O_3$, when entering the matrix, makes the phase less anisotropic as observable by polarized light. Further, as should be expected, the simultaneous presence of K_2O and acidic oxides, especially of SiO_2, favors the formation of glassy layers. In this connection attention is also called to the large diameter of the potassium ion.

Wilchinsky (18) using a technique based on grinding, separation according to particle size, and chemical analysis, concluded that in a K_2O-SiO_2-Al_2O_3-promoted iron catalyst, Al_2O_3 is found as solid solution of either γ-Al_2O_3 or $FeO \cdot Al_2O_3$ in the magnetite, whereas K_2O and SiO_2 are concentrated between the layers of a mosaic-like structure. This picture was supported by microscopic examination. Wilchinsky states that particles smaller than about 30 microns are normally single celled. They are, however, most likely themselves built of much smaller mosaic blocks.

Maxwell, Smart, and Brunauer (19) drew the conclusion from thermomagnetic measurements that in singly promoted (Na_2O, K_2O, BaO) and in one doubly promoted (K_2O-Al_2O_3) catalysts, a maximum of one mole per cent promoter is present in solid solution in the magnetite. However, in some other doubly promoted catalysts, including a second catalyst promoted with K_2O-Al_2O_3, a greater amount of promoters was found to be in solid solution in the magnetite. In a number of highly promoted catalysts there was an indication of two coexisting magnetic phases. The somewhat intricate behavior of K_2O-Al_2O_3-promoted catalysts may mean that some unaccounted factor, such as the cooling rate of the oxides when prepared from the molten state, may play a role.

When compiling the information gathered by different techniques of various investigators, the view can be expressed that the promoters, among them especially CaO and Al_2O_3, are uniformly distributed in one or more spinel or distorted spinel phases, the latter partly existing as separate phases. This view is confirmed by the available x-ray data.

Wyckoff and Crittenden (7), using the Debye-Scherrer technique, have investigated Fe_3O_4, and Fe_3O_4 promoted with $FeO \cdot Al_2O_3$ and with $K_2O \cdot Al_2O_3$. Their results indicate that the promoters do not produce separate phases, but form solid solution with magnetite.

Brill (20) has taken powder photographs of unreduced and reduced Al_2O_3-promoted catalysts and of the Al_2O_3 residue formed by dissolving the catalyst in acetic acid. The residue found was always γ-Al_2O_3 independent of the special methods used in the preparation. As α-Al_2O_3 is the stable modification and as the catalyst had been heated during preparation to a temperature at which transition from the γ- to the α-form takes place rapidly, this, as pointed out by Brill, means that Al_2O_3 forms a solid solution with the magnetite.

The present author has carried out a series of x-ray examinations of unreduced iron synthetic ammonia catalysts and related substances. Details of results and techniques are found in reference (5). In Figs. 1, 2, and 3 of Plate I the diagram of a K_2O-CaO-Al_2O_3-promoted commercial catalyst (KM II) is compared with diagrams of a Ural magnetite and of a synthetic spinel $FeO_{1.311}$. All three substances show the lines of a magnetite structure and their lattice constants agree within the limits of experimental accuracy. The following values were found.

Ural magnetite	8.377_9 kX units
Ferro-ferric-oxide	8.377_8 kX units
KM II	8.377_7 kX units

When considering the lattice constants it may be recalled that the Ural magnetite, although a nice octahedral crystal, was not pure Fe_3O_4.

It may be seen from the figures that the catalyst pattern differs from the pattern of Ural magnetite in three ways. There are some fuzzy extra reflections somewhat removed from the magnetite lines. These reflections may be satellites or may originate from separate phases. There are satellites quite near the (311) reflection, and there is a broadening of the main reflections. In patterns of other catalysts a number of weak satellites are observed nearer to the main reflections.

The extra lines are not due to promoter phases, since they are also found in the pattern of the synthetic spinel $FeO_{1.311}$, neither are they due to Fe_2O_3. The doubling of some of the lines noticed in Fig. 2 could be due only to FeO if this had been rhombohedrally distorted; such a structure has actually been observed by Rooksby and Tombs (11). The satellites, however, cannot be due to FeO and can best be explained by the existence of a modulated magnetite structure.

The dependence of line broadening upon the Bragg angle of reflection was determined. When line broadening is due to small crystal size, the broadening increases proportionally to $\lambda \sec \theta$. When it is due to certain types of strain, as found in patterns of cold worked metals, it increases proportionally to $\tan \theta$. No such simple relationship could be found, the $\beta \cot \theta$ values being highest for reflections with low indices. Line broadening dependent in an individual way on the indices, although of a much more regular type, has been observed by Edwards and Lipson (21) in the pattern of an imperfect structure of Co. Similar observations have been made with Co-Fischer-Tropsch catalyst by Hofer, Peebles and Bean (21a).

In summarizing, the view may be expressed that the different types of anomalies found in the patterns of unreduced catalysts are due to a complicated variation in scattering power and lattice geometry brought about by promoters entering the magnetite matrix. The regions in which a certain modification of the matrix exists need not occupy whole crystals, as the differences in oxygen spacing may be small enough for coherence between modulated and nonmodulated phases. It should be mentioned in this connection that catalysts of a high CaO content give patterns with pronounced line broadening. This fits well with the microscopic data.

Satellite reflections have been encountered previously in alloy structures and reference is given to articles by Preston (22), Daniel and Lipson (23), and Hargreaves (24).

Before concluding this section attention is called to the spotted character of reflections from unreduced catalysts obtained when the samples are not finely ground. The crystal dimensions indicated hereby are in agreement with the single cell dimensions found by Wilchinsky (18)

III. REDUCED STATE OF CATALYSTS

1. *Structure*

When the oxidic catalysts are reduced with hydrogen, no or only slight shrinkage of the external volume of the particles takes place simultaneously with the rebuilding of the material. Reduced catalysts have a density of about 2.7 g./cc. after correction for void space, and are thus a porous form of iron.

The author has made an x-ray examination of a number of doubly and triply promoted reduced catalysts. The method and results have