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FUSED IRON CATALYSTS FOR CO - H_2 SYNTHESES

The subject of this report are the iron catalysts which were developed by Dr. Ed. Linckh for the CO - H_2 synthesis at elevated temperatures and pressures with reference to the ammonia catalysts. These catalysts are fused from metallic iron in a stream of oxygen in the familiar manner with addition of the desired promoters. As pure oxides the resulting hard compact masses markedly resemble natural ores, in particular, magnetite.

I. Optical Investigations

In 1936 Dr. Winkler asked me whether it was possible to evaluate the fused iron catalysts by microscopic investigation and whether in so doing any facts could be found to substantiate the effectiveness of these catalysts. According to the character of these catalyst masses it seemed possible that microscopic investigation based on the methods used with ores would offer the answers to the questions raised.

Up to that time about 1200 varieties of catalysts had been developed by Dr. Linckh. The bulk of these consisted of fused iron catalysts. Of these the most typical and the most interesting were selected for investigation. Sections were ground and provisional investigations were started with a makeshift ore microscope.

The initial orientation investigations revealed distinct optical differences in the individual catalysts. Consequently we hoped to attain practical results as in the above project with systematic investigations.

The planned investigations were initiated on procurement of a suitable ore microscope.

1. Dr. Linckh's Fused Catalysts

The series which was investigated comprised 44 catalysts. No information was furnished on the effectiveness of the catalysts in order not to influence the optical investigations. Sections of natural hematite and magnetite were compared.

With the unaided eye these catalysts reveal the typical appearance of fused catalysts, such as ammonia catalysts. They are compact, hard and friable masses splintery to jagged cleavage of a gray color with a light reddish to bluish cast in the fresh cleavage. They tarnish ~~with~~ a light brownish color and often exhibit more or less white efflorescence.

In the case of the bulk of the catalysts little crystals can be observed with the unaided eye. The blocks of the hardened melts contain for the most part one or more cavities (contraction cavities) which are generally lined with well-formed crystals or crystal skeletons. The complete crystal formation of the coarse cleavages can be satisfactorily recognized with a hand lens.

Three separate types were clearly differentiated by the microscopic investigation. These were designated as Types I, II and III. This type of designation is employed to characterise the catalysts. In Type I the crystal grains have solidly coalesced and are partially indented into each other. There is no "binder", that is, no substance which lies between the crystals and fills the fissures. Types II and III, on the other hand, follow this pattern. In these cases the crystals are separated from each other by narrow fissures. These are filled with such a "binder". Type II is uniformly vitreous with no special properties, whereas Type III exhibits little crystals in the vitreous mass, or is devitrified. The crystals are then practically vertical to the cleavage planes.

I should therefore like to conceive the catalysts of these two types as "supersaturated", i.e. the amount of the additions exceeds the absorbing or dissolving power of the magnetitic base crystals or, as a result of their type and make-up, they are so different and foreign to the base crystal that only a narrowly restricted absor tivity occurs. In this connection individual elements appear to act as "dissolving agents", i.e. in their presence a more extensive or completer incorporation of the additions into the base crystals occurs. An image of Type I can thereby be formed. The elements of the earth alkaline group, particularly calcium and barium, appear to exert this action.

The base crystals themselves alwasy exhibit a more or less strong optical anisotropy. The real magnetite, natural Fe_3O_4, is normally ~~an~~isotropic as a purely cubic mineral, that is does not show any double refraction in polarised light. All the crystal grains exhibit the same degree of darkness irrespective of how they were ground. On being rotated in polarised light they show no brightening or extinction. Magnetites of various orignis exhibit weak anisotropy which is ascribed to a more or less high content of Fe_2O_3. This occurs in its natural state as hematite rhombohedral crystals and consequently possesses strong optical anisotropy. This may also be true with fused catalysts.

Polished sections were completely satisfactory for the comparison investigation. Etching experiments with various reagents led to no utilisable results. The crystals were coated with various colors, particularly in various shades of brown, but the sections were attacked so vigorously that they could no longer be used for microscopic investigation. The etching experiments were therefore discontinued, particularly since investigation of the simple polished sections sufficiently revealed the properties.

These older catalyst can be divided into two groups on the basis of the material available to me on their make-up and catalytic action.

The first group is derived from Catalyst No. 142 by a variation. It consists of a simple mixture of iron with 4.5 per cent uranyl nitrate and 4.5 per cent TiO_2. These catalysts all belong to Type I, i.e. they do not contain any binders. The crystal grains are all intimately coalesced and exhibit vigorous anisotropy and marked extinction. As far as I can gather from the data they possess good catalytic properties, especially as regards the formation of hydrocarbons. The lack of the vitreous or crystalline binder leads to the conclusion, in view of the existing homogeneity, that the added promoters are absorbed into the crystal. The optical anisotropy points to the fact that more or less intense lattice disturbances are brought about by the incorporation of molecularly-foreign substances into the crystal union. The homogeneity of the structure leads to the conclusion that a homogeneous "discrete" dispersion of the lattice-distrubing promoters obtains here. However, the chemical make-up of these promoters conditions the direction in which the catalyst acts. And furthermorethe intensity of the lattice disturbance conditions the catalytic intensity of the catalyst, depending on the type and amount of the promoters. This appears to progress up to a cetrain threshold which is located just before the start of the formation of new crystallographic units. These can then be recognized as deposits of the most varied kind.

Attached are photographs of two typical catalyst sections of this group.

(Photographs on page 4)

<u>K 142</u>

Homogeneuos crystalline mass in which the individual crystals are almost jointlessly coalesced. The individual crystal grains are frequently recognizable only as a result of the anisotropy. Intense anisotropy with pronounced extinction. In places lamellar formation which may possibly be caused by beginning disintegration and twinning.

Very active catalytically, especially with respect to hydrocarbons.

<u>K 319</u>

Here the coalescence is even more intimate. The boundaries of the grains are practically no longer recognizable. Very intense anisotropy and pronounced extinction.

Yields even better. Also favors hydrocarbons.

The second group, to which Types II and III are to be classed, is derived from Catalyst No. 997 which is essentially described in German Patent 708512.

In these catalysts the individual crystals are not intimately coalesced but are almost always separated from each other by fissures. These spaces are filled with a vitreous binder containing a multitude of fine, strongly double refractive, colorless or nearly colorless crystalline needles. This is the normal Type III. In individual cases the binder may be completely crystalline. Those catalysts in which a purely amorphous-vitreous binder exists are thought of as a type in itself, Type II. This binder, partcularly the amorphous form, is strongly attacked when the sections are etched with acid reagents. In general, a slighter anisotropic is exhibited by the magnetitic base crystals, even in the catalysts possessing good catalytic action; However, they do not exhibit as marked an extinction as the homogeneous catalysts of Type I. It is unclear to what extent the binder participates in catalytic action. It is assumed that the other silicatic or compounds of similar make-up separated out insofar as the base crystals could not absorb them. A crystalline mixture of petrological character is formed. After reduction of the catalyst to metallic iron the binder can no longer be recognized. I should like to assume that we now have a mixture in the most intimate dispersion which is now in a position to react catalytically. Quantitative statements cannot be made since suitable optical equipment for this purpose is not available.

Type II

K 1159

Irregular, partially sharp-edged granules with purely vitreous binder. This completely amorphous base crystal weakly anisotropic.

Effectiveness good. Oil enriched with oxygen compounds.

Type III

Coarse to middle-grained, strongly flaked crystals. Moderately to intensely anisotropic. Considerable vitreous binder containing abundant quantities of fine needle crystals.

Parent catalyst to which the others are compared. Efficiency good, even though appreciably exaggerated.

K 1243

Small to middle-grained. Very porous. Markedly segmented. Weakly anisotropic.

Abundantly vitreous, almost colorless, transparent binder with many markedly double-refractive little crystals between the crystals.

Good yields, particularly with oil.

K 1259

Middle-grained. Partially coarse.

All spaces filled with vitreous binder with strongly double-refractive little crystals. Base crystals distinctly anisotropic.

Yields moderate to good. Marked tendency to oil formation.

K 1259

Same area in polarized light .

2. Own Experiment Series

In this connection the purely empiric method of working which had been employed up to that time was abandoned.

The point of departure for these ideas was the fact that the fused catalysts on an iron base essentially possess a spinel structure, deriving from magnetite. In the characteristic catalyst No. 997 the addition of SiO_2 and TiO_2, that is, "acidic" oxides, appear to exercise the strongest influence. Consequently, a new catalyst, titanium magnetite, i.e. a magnetite containing titanic iron or ilmenite in a solid solution, was selected as a model for the planned series of experiments. Melts 1287 and 1288 were formed, containing 26 per cent by weight, 17 per cent TiO_2, apart from iron. Analysis of the melts gave

1287 - 51 mol % Fe_3O_4 49 mol % $FeO\text{-}TiO_2$

1288 - 66 mol % Fe_3O_4 33.3 mol % $FeO\text{-}TiO_2$

These melts which contained extremely high contents of TiO_2 produced sections exhibiting very marked anisotropy.

Distinct disintegration phenomena appear in 1287 which practically disappear in 1288. Since natural titanium magnetites exhibit a slight content of CaO for the most part, the following Melt No. 1289 was fused from a batch containing 2 per cent $CaCO_3$. The result was a practically homogeneous melt which no longer disintegrated but still exhibited strong anisotropy. It seems that, despite the high content of 18 per cent of TiO_2, an equilibrium is achieved by the addition of calcium, the calcium acting to a certain extent as a dissolving agent.

After the success with 1289 a batch corresponding to the old Catalyst 997 was used with an addition of $CaCO_3$. This resulted in a highly-porous catalyst mass with distinct anisotropy of the base crystals and a practically completely crystalline binder. Because of a deficient conception the iron content was too small. This resulted in marked supersaturation and the added substances were very incompletely absorbed by the base crystal. The fault of conception seems to be as follows.

It was assumed with the new melts that the added substances reacted with each other and were partly absorbed by the base crystal in this form, but for the most part separated out in the form of the "binder". This assumption, however, appears to be incorrect. It would appear that the basic additives (MnO, $CaCO_3$, K_2CO_3 etc.) react to form ferrites, whereas the acidic additivies (SiO_2, TiO_2, ZrO_2) form corresponding iron compounds, e.g. $Fe.TiO_2$ etc. Following the example of Catalyst 1290:

According to the old conception:

10 FeO . Fe_2O_3	31 mol Fe
1 FeO . TiO_2	2 mol TiO_2
1 MnO . K_2O . SiO_2	1 mol MnO
1 CaO . TiO_2	1 mol Si
	1 mol $CaCO_3$
	1 mol K_2CO_3

According to the new concept:

10 FeO . Fe_2O_3	39 mol Fe
1 MnO . Fe_2O_3	1 mol MnO
1 CaO . Fe_2O_3	1 mol $CaCO_3$
1 K_2O . Fe_2O_3	1 mol K_2CO_3
1 FeO . SiO_2	1 mol Si
2 FeO . TiO_2	2 mol TiO_2

This means that the iron content was too low in the former concept, that is, not enough Fe_3O_4 was formed to absorb the new compounds. This had to result in a "supersaturated" melt with a vitreous or crystaline binder.

The following melts proposed to produce a magnetite-zinc ferrite-calcium ferrite mixed crystal with a partial content of TiO_2. All told 4 melts were produced of which half contained twice the amount of iron as the first half. Along with a base crystal of moderate anisotropy the two titanium-containing ferrite mixtures show new-type crystals with marked double refraction and even extinctionx which form lamellar poli-twins. We are certainly not dealing here with cubic spinels. A new compound has been formed about whose chemical structure nothing can be said. Conversely, the titanium-containing ferrites exhibit the normal picture of anisotropic, still cubic base crystals. The anisotropy is certainly intense but no new formations have been observed. In all cases, however, any trace of vitreous binder is missing. It is clear from the microscopic picture that the titanium-containing mixtures, in particular, are fused to satisfactory, spinel-like masses.

The next group is derived from the already described Catalyst No. 1290 . TiO_2 is replaced by ZrO_2 and SiO_2 by TiO_2 and ZrO_2, so that finally only ZrO_2 is used. The two last catalysts 1299 and 1300 contain BaO instead of CaO. In the presence of TiO_2 plus SiO_2 binders appear which completely disappear from 1297 onwards. However, new formations of a chemically and crystallographically unknown type appear. 1297 shews the groundmass of the crystals of the type known since then to be clearly anisotropic. Dispersed in this mass are intensely, double-refractive crystals with sharp, even extinction which form poly-twins for the most part. They appear to be uniaxial, presumably tetragonal crystals. At 1298 the previous base crystals ahve completely disappeared. In their place appear narrow ridges and spiky crystals which coalesce below 60 or 120 deg C. The picture is very uniform. The crystals exhibit sharp, even extinction and intense anisotropy. It appears that regular, spinel-like crystals no longer occur here, but rather pseudo-regualr, supposedly tetragonal new formations. In the crystals themselves finely-divided separations appear, as in a eutectic decomposition.

1299. Here CaO is replaced by BaO. Again a completely crystalline binder appears. The total picture is quite similar to 1298 even though the anisotropy is not so intense and the extinction not so sharp. Numerous ridge-shaped crystals with pronounced twinning. Only with 1300, which also contains only BaO and only ZrO_2 as an acidic addition, do we receive the predominant impression of the formation of a new form of base crystal. Generally marked anisotropy, even sharp extinction of the crystalline ridges which are markedly twinned. Almost the same picture as with 1298, only completely crystalline binders again appear.

In this group 1290, 1295 - 1300 it is clear that a modification of the properties of the base crystals appears which is apparently not far-reaching by the replacement of SiO_2 plus TiO_2 by ZrO_2. The following group 1301 to 1306 inclusive exhibits corresponding modifications. SiO_2 plus TiO_2 no longer appera to to exercise decisive influnece. The jump to ZrO_2, however, seems to be very much greater. This might be explained by the difference in atomic weights (Si = 28.3, Ti = 48.1, Zr = 90.6).

The following group is differentiated from the one described above only by the fact that its iron content is double. The first two, 1301 and 1302, which correspond to 1290 or 1295, exhibit no marked optical modifications thanks to their content of SiO_2 plus TiO_2.

In 1302, which contains SiO_2 along with ZrO_2, the influence of ZrO_2 appears to be markedly inhibited by the SiO_2. In 1303, which contains ~~xx~~ TiO_2 along with ZrO_2, marked modifications appear, such as the formation of markedly anisotropic, markedly twinned ridges which apparently no longer have anything to ~~it~~ do with cubic crystal forms. The same impression is also offered by the following catalysts, 1304 - 1306, as in the case of 1299 and 1300. The last two~~x~~ (1305 and 1306) visibly show a distinct coarsening of the newly-formed crystal shapes by the replacement of CaO by BaO and, if possible, with intensification of anisotropy and twinning. It is peculiar that all the catalysts, despite a doubled amount of iron, carry "binders" against all expectation. The binder is completely crystalline but occurs in noticeably greater quantity than in the previous group. The contraction cavities of the fused blocks always contain octahedral crystals with a marked growth of edges.

The next group, 1307 to 1312 inclusive, is derived from 1297 or 1299 in which CaO or BaO is replaced with rare earths. Lanthanum sesquioxide, "Auer oxide mixture" (Gemischoxyd Auer) and "didymium - Auer oxide" were employed. The "oxide mixture" consists primarily of lanthanum oxide and neodymium oxide; didymium oxide consists of about equal parts of neodymium oxide and praseodymium oxide with some lanthanum oxide. Thus, there is actually very little difference between the three oxide mixtures. Correspondingly, the pictures of the three melts are not very different. Although otherwise of the same composition, 1310 to 1312 contain double the amount of iron of 1307 - 1309. Along with a comparatively small proportion of base crystals of the familiar type, there also occur large flaky units of markedly anisotropic,.

narrow crystal ridges with sharp even extinction which are considered to be new-type tetragonal crystals. These appeared in very much the same manner in all 6 melts. Thus, the oxide mixtures exhibit a marked influence without bringing about distinctly specific actions.

In the following a group of modified catalysts are treated. The bulk has been modified by the addition of copper together with potassium in an equal molecualr proportion. These catalysts differ externally from the original catalysts by a peculiar, light bluish coloration in the fresh fracture, whereas the fresh cleavage plane ordinarily is of a dark gray color with a weak brownish red cast.

In general the addition of copper to the mixture appears to effect a simplification of the section picture, i.e. the melts were all very all uniform and homogeneous. For the most part the vitreous binder markedly receded or completely disappeared; the anisotropy in the individual sections was similarly very uniform and apparently somewhat intensified as compared to the copper-free melts. The peculiarities of the melts 1301 - 1312, i.e. the intensely anisotropic new crystal formations, have disappeared and the sections resemble each other to a great extent. It appears as if the copper, similarly to the CaO, acts as a "dissolving agent" to a certain degree and thereby accomplishes this simplification and standardization. In the catalysts which exhibit marked inhomogeneity, i.e. in which new formations openly occur, only slight decomposition phenomena appear on addition of copper to the mixture which otherwise remains the same.

In further modification experiments melts were produced where the alkali was omitted, the mixture otherwise remaining the same (997 ff. 1300 ff., 1306 ff.). The melts produced in this fashion show no differences in their section picture from the normal, alkali-free melts.

The following experimental series was produced by modification of the two initial catalysts 1288 and 1289.

First potassium and then potassium and copper together are introduced. 1288 K, 1288 CuK plus 1289 K showed practially no differences. Small cubic crystals combined to form treelike units. The spaces were filled by a metal-white, lustrous mass which was markedly anisotropic and exhibited sharp extinction. The crystals themselves were weakly to moderately anisotropic. This boundary separation was interpreted as Fe_2O_3 (hematite) by comparison. Apparently the formation of abundantly excess Fe_2O_3 was promoted in the presence of K_2CO_3, at least to a certain degree. On the other hand, 1289 K serves as a connecting link between the initial melts and the following ones which were planned according to another principle. This catalyst exhibits a granular-spiky formation without any binder, that is, a very divergent picture. The intimately coalesced granules are weakly anisotropic. In spots small quantities of Fe_2O_3 appear. The overall picture of this section, however, is the same as the other melts of the series 1313 to 1324 which belong to it.

This series was produced by modification of Catalyst No. 1289, CaO being replaced by BaO, MgO and ZnO. K_2O or K_2CO_3 was then added, then CuO, and then K_2O plus CuO together in the end members. Thus, 3 catalysts belong together. The same sequence is always maintained: BaO, MgO and ZnO. The sections of the first three catalysts 1313 - 1315 do not exhibit any great differences. The closely coalesced base crystals exhibit distinct anisotropy and extinction. There is an absence of binder in all instances.

The three following melts 1316 - 1318 contain K_2CO_3, otherwise remaining the same. Again the sections show pretty much the same picture, 1317 which contains MgO deviating the furthest. Very little anisotropy can be proved here. In all three, however, a completely crystalline, strongly double-refractive binder occurs. This vitreous binder appears to be immediately formed whenever K_2O is added in any form when SiO_2 plus TiO_2 are the acidic additives.

In the next three catalysts 1319 - 1321 K_2O is replaced by CuO. This results in a marked modification. The melts become coarse to semi-fluid; the base crystals are coalesced practically without any joint. Binders are completely absent. Anisotropy is distinct and the sections show practically no differences.

The three last melts of this series 1322 - 1324 contain K_2O plus CuO together. Again the sections resemble each other to a great extent. Anisotropy of the base crystals is clear. There is only slight formation of joints but they contain a completely crystalline binder. We received the impression that a far-reaching homogenisation of the melts is brought about by the CuO content which even promotes the absorption of acidic additions in the presence of K_2O.

The melts prepared since then give the impression that the acidic additions are better absorbed with rising molecular weight. In the presence of two acidic additions, e.g. SiO_2 plus TiO_2x together, the one with the lower molecular weight exerts its influence, i.e. the absorption of the higher one, which is ordinarily extensive, is diminished. In particular, the separation is promoted by the content of K_2O in the melt, i.e. larger quantities of separations designated as "binding agents" appear between the magnetite-like base crystals. If only one acidic constituent is present, then the separation in the presence of K_2O is substantially smaller and in the case of TiO_2 alone it practically disappears. This can be determined by addition of ZrO_2. The corresponding catalysts that have already been described show no binders in the presence of ZrO_2 alone, or practically none. If, however, SiO_2 or TiO_2 are used in addition, the separation will immediately start all over again.

This becomes clear in the two following series 1325-1330 and 1331-1346.

1325-1330 are based on catalysts 1288 and 1289 and supplemented by addition of K_2O. 1325, which consists of iron with an addition of ZrO_2 (corresponding to 1288 with TiO_2), reveals a very simple section: closely coalesced crystals with moderate to weakanisotropy and without binders. Also 1326, which corresponds to the earlier 1289~~x~~, appears to have an appreciably simpler structure with considerably less disturbances by the replacement of TiO_2 by ZrO_2 for the anisotropy is much less. No noticeable modification occurs in the base crystals on addition of K_2O, but instead individual, small, for the most part twinned crystals appear with intense double refraction and sharp even extinction. There is no binder~~x~~(1327). If to the previous melt CaO is added, the picture will become even simpler: weak anisotropy and a very uniform picture of base crystals without binders (1328). If the CaO is replaced by BaO, the anisotropy becomes more intense (1329) and, in commom with (illeg) O_2, swarms of small twinned crystals of the same type as in 1327 appear in spots along with the normal base crystals (1330).

The next and last group is derived from 1288-1289 by the introduction of CuO plus K_2O and by the replacement of CaO by BeO, MgO and ZnO, i.e. in every instance the original TiO_2 is replaced by ZrO_2. The introduction of CuO or CuO plus K_2Odiminishes the anisotropy even further in contrast to the corresponding previous melts, i.e. optical homogeneity is further improved, i.e. the action of CuO, which was observed previously, is again confirmed here. The following melts are modifications of 1289. CaO is replaced by BeO, MgO plus ZnO, then K_2O, then CuO, and finally both together are introduced. The first three of the series are hardly differentiated from each other. The ground masses have compact homogeneous catalyst masses without binders, jointless coalescence, moderate to weak anisotropy, and sharp extinction. Disintegration phenomena are clearly visible in spots (1333-1335). The next three (1336-1338) were modified in the same sequence with addition of K_2O. The disintegration phenomena have disappeared. The granule boundaries are barely visible principally as a result of the weak anisotropy of the base crystals. The pictures offered by the sections are very similar. The anisotropy appears to possess gradual differences; it is most marked on addition of MgO.

In the following melts 1939-1941 a gradual rise in anisotropy appears to take place with the increasing molar weight from BeO to ZnO. Disintegration phenomena are visible in the sections in spots.

1339 exhibits disintegrations quite clearly along with very weak anisotropy. Disintegration forms are no longer present in 1340. Anisotropy is appreciably more intense along with sharper extinction. In 1341 there is an even more noticeable increase. It appears as if uniaxial crystals are present which are vertical to the optical axis and are isotropic along with even extinction. 1342-1344 contain CuO plus K_2O together. Optically the three melts can hardly be differentiated. All three exhibit practically the same section picture: sharp even extinction along with moderate anisotropy. The existence of other optical phenomena is doubtful. 1345 contains BaO as earthe alkali; 1346 contains CaO. There is very little optical difference between the two. Both are moderately to distinclly anisotropic with sharp extinction.

Many sections of this series 1331-1346 give the impression that the original cubic symmetry has been changed into something pseudecubic. The sharp even extinction leads us to the conclusion that umiaxial crystals, which are presumably tetragonal, are present but in a pseudocubic form. Further, none of the melts exhibit any binders, i.e. the 9-12 per cent ZrO_2, the approximatley 1.5-3 per cent CuO, as well as the approximately 1 per cent K_2O are directly absorbed into the crystal. The addition of CuO appears to simplify and and render uniform the structure even further so that hardly any deviations of simple magnetite are optically visible in the individual melts although we are dealing with 5-substance systems (1328, 1331, 1343, 1344,1345 and 1346). We receive the impression, despite the accepted assumption, that multi-substance systems with the simplest optical structures are most efficient.