II. Catalytic Efficiency

There are practically no experimental results available to me on the efficiency of the catalysts produced by Dr. Ed. Linckh. With the exception of some qualtitative material I cannot use this experimental material.

Only the parent catalyst 997, which has been tested many times, is employed for comparison.

The catalyst were employed entirely similar conditions in order to obtain utilisable comparison values. The " spiral (illeg) reactor", which was developed by Dr. Ed. Linckh, was employed. This is a (illeg) reactor 120 mm in diameter and 120 cm in length. An H.P. copper tube 8 mm in diameter and with a wall thickness of 1.5 serves as catalyst carrier. The tube is bent into 8 spirals each 65 mm in diameter at intervals of 95 mm. Little baskets made of brass wire gause 70 mm in diameter and (illeg) in height are fastened around the spirals. These baskets receive the catalyst which has been grained to 6-12 mm. A high pressure copper tube, which encloses 4 thermoelements for recording the internal temperature, is introduced through the central opening of the spirals. The catalyst carrier is free in the interior of the reactor and contains about 1 liter of catalyst. The gas is admitted at the head of the reactor, sweeps ~~past~~ freely past the catalyst, thus starting the conversion, and then leaves the oven at the base. The condensable products are precipitated in an adjoing high pressure spiral cooler and then collected in a separator. After the separaotr the end gas is depressured through a control valve and measured with a gas meter and a flow manometer. 1 m^3 per (illeg) of the end gas is sent through an activated carbon tower daily to determine the end gas gasoline and the Gasol. The furnaces are heated or cooled with steam, which can be superheated in a simple superheater, by means of the spiral coils.

A mixed gas of 16 - 18 per cent CO plus 84 - 82 per cent of zero gas. The pressure is maintained at 100 atm. The reactors are run at an internal temperature of 270 deg C and with a reduction in pressure of the end gas of 100 liters/hr. After 2 days the temperature is raised to 280 deg C and the end gas rate increased to 250 liters/hr. Each batch is run for two days and then the temperature is raised by 10 deg C. The end gas quantities are raised from 100 to 250, 500, 750, 1000, 1500 and 2000 up to 2500 or 3000 liters/hr. In addition to the end gas and the Gasol - or the quantity of gasoline in the end gas - the oil and water drawn off daily from the separator is recorded. The content of alcohol is determined by specific gravity and distillation. Day to day gas analyses of the end gas are also taken.

All these conditions were rigidly maintained in the comparison experiments. The following tables contain the yields obtained by the catalysts which have been described up to this point with the above indicated method of operation. The catalysts have been assembled according to the "relationship" of the meltsin order to render possible conclusions on the influence of the added substances. Every catalyst is run at 450 and 650 deg C after a preliminary reduction.

Catalyst No. 997, which was furnished by Dr. Ed. Linckh, is the comparison catalyst (see German patent 708512). It is fused from the following mixture: 89.5 per cent iron, 2.24 per cent TiO_2, 2.24 per cent silicxon powder, 2.24 per cent MnO and 1.80 per cent KOH. The companion catalyst 997 CuK contains 2.08 per cent copper powder added in the same mixture.

1290 is the same in principle with the addition of 4.5 per cent $CaCO_3$ to the mixture. 1295 contains ZrO_2 instead of TiO_2, the rest of the mixture being the same as 1290. 1297 replaces silicaon with TiO_2 and TiO_2 with ZrO_4 until finally, at 1298x, all the"acidic" additions have been repxaced by ZrO_2. In 1301 to 1304 all the previously described catalysts are modified by doubling the quantitxy of iron in the mixture. By this change 1301 compares with 1290, 1302 with 1295, 1303 with 1297, and 1304 with 1298. In 1302 CuK the melt is enlarged to same mixture as 1302 by the addition of 0.8 per cent of copper powder.

The modicications bring about the following effects as far as can be seen from the table:

1. Copper

Copper as a replacement for alkali causes a sharp diminsihment of action. Conversely, an appreciaxble increase in the alcohol yield yield along with an appreciable increase in temperature-stability is brought about if it is employed jointly with KOH in an equivalent quantity. In general, a marked increase in the yield occurs for the most part.

2. Calcium

The effect of CaO is uncertain. However, we are under the impression that calcium renders the melt more homogeneous and causes the absorption of the added substances to more uniform and more complete ("dissolving agent").

3. ZrO_2

If SiO_2 is replaced by TiO_2, and TiO_2 by ZrO_2, and finally both by ZrO_2, a general increase in yield will be observed as well as an increase of the alcohol yield in particular. An increase in the molar weights of the additives appears to cause an increase in catalytic efficiency and, consequently, of yield.

4. Increase of the iron content, it appears, similarly results in an increased output, insofar as is perceptible.

1288 is the model which substantially served as a point of departure for the newer catalysts. It is derived from titanium magnetite Fe_3O_4 plus $FeO.TiO_2$ by addition of KOH and copper. It was modified here by ZrO_2.

1288, which is composed of 83.0 per cent iron plus 17 per cent TiO_2, is a very poor catalyst. 1288 K contains only half the amount of TiO_2 plus 1/5 mol K_2CO_3, a significant improvement being thus attained. 1288 CuK contains an added 1/4 mol copper powder but there is no noticeable alteration, at the very most a certain tendency towards "smearing" of the catalyst, i.e. slackening of catalyst efficiency by introduction of higher molar organic substances. In 1325 TiO_2 is already replaced by ZrO_2. 1327 has the same composition as 1325 with an addition of K_2CO_3; 1331 has an addition of copper powder instead of K_2CO_3; and

1332 has copper as well as K_2CO_4 in addition to the composition of 1325.

The following conclusions can be drawn form these instances:

1. KOH causes a violent increase.

2. ZrO_2 similarly increases the yields appreciably.

3. The effect of copper as an addition is not clearly discernible.

In contrast with previous experiences, the catalysts reduced at 450 deg C in this group are substantiably better than those reduced at 650 deg C.

Base catalyst No. 1289 corresponds to catalyst 1288 which is supplemented by $CaCO_3$ as a "dissolving agent":

79.92 % iron

18.03 % TiO_2

2.05 % $CaCO_3$

1289 K is supplemented by 1.7 per cent K_2CO_3; copper is added in 1289 CuK. 1326 contains ZrO_2 instead of TiO_2. 1328, the best catalyst of this group, adds K_2CO_3 to the 1326 composition. In 1329, which has the same compostion as 1326, the $CaCO_3$ is replaced by $BaCO_3$. In 1330 K_2CO_3 is again added to the previous composition. 1291 - 1294 are conceived of as iron-zinc-calcium spinels; it is hoped that they will provide a better catalysis for alcohol. 1291 had a composition of 76.2 per cent iron, 13.2 per cent $ZnCO_3$, and 10 per cent $CaCO_3$. 1292 contains 66.7 per cent iron, 13.6 per cent $ZnCO_3$, 11 per cent $CaCO_3$, and 8.73 per cent TiO_2. 129~~5~~3 and 1294 contain double the amount of iron.

1345 is prepared according to the model of titanium magnetite, TiO_2, however, being replaced by ZrO_2, $CaCO_3$ by $BaCO_3$, and, in addition, copper and K_2CO_3 are added. 1346 is prepared like 1345 with calcium replacing barium.

As could be determined before, a material improvement is achieved with copper and calcium. It is true that copper tends to decrease efficiency somewhat, but it makes the catalysts more resistant, primarily against soot formation. ZrO_2 boosts outputs appreciably as compared with the TiO_2-containing catalysts. Calcium and barium appear to possess equal efficiency.

The zinc-containgin mixed spinels were very disappointing although it is hoped that sysyematic modification may still lead to utilizable results.

In any case, this group contains the catalysts with the best alcohol values, 1289 K, and, above all, 1328. In addtition, there are 1345 and 1346.

Here catalysts 1299 and 1300 are modified, that is, catalysts which chiefly contain ZrO_2 as the acidic component. 1299 corresponds to the already described catalyst 1298, that is, a ZrO_2-containing catalyst with an addition of calcium with replacement of the calcium with $BaCO_3$. From this 1300 is further developed. The remainder of TiO_2, which is still present in 1299 is replaced by ZrO_2 so that ZrO_2 is the only acidic addition present. 1305 and 1306 correspond to 1299 or 1300 but with double the amount of iron.

1307 to 1312 correspond to 1299 or 1305; the $BaCO_3$ is replaced by La_2O_3, "Aure oxide mixture" or didymium oxide. These are catalysts 1307 to 1309. The "Auer oxide mixture" is essentially a mixture of lanthanum oxide and neodymium oxide.

In 1310-1312 the iron is again doubled, the composition otherwise remaining the same. 1308 CuK, 1310 CuK and 1311 each contain an admixture of about 1 per cent of copper.

It can be seen from these results, especially in the table, that the modifcation of the acidic addtions has a much greater effect than the modification of the basic additions, apart from KOH or copper. The substitution of calcium by barium causes a slight impairment, and the introduction of rare earths does not exercise any noticeable influence. As was already mentioned, the marked influence of copper together with K_2O is again clearly demonstrated here.

This group is derived from catalyst 1289 which is composed of 80 per cent iron, 19 per cent TiO_2, and 2 per cent $CaCO_3$. The $CaCO_3$ is here alternatley replaced by $BeCO_3$, MgO and zinc in equivalent amounts. Variations are then obtained by addition of K_2CO_3, then copper, and, finally, the two togehter. Thus, 1313-1315 contain BeO, MgO and ZnO instead of CaO. Addition of K_2O in 1316-1318; in 1319-21 a content of CuO, and, finally, in 1322-1324 K_2O and CuO together.

The success of the CaO substitution is dubious. The results are the same as those obtained with the unmodified 1289.

BeO plus MgO appear to be distinctly superior to ZnO. This finding corresponds to the experiences obtained by the experiments assembled in Table 4 on the basis of which it is clear that the variation caused by the basic additions is of slight influence only.

This group, in its structure and variations, corresponds fully with the previous one, with the exception that the equivalent amount of ZrO_2 is added instead of TiO_2. The first three again contain BeO, MgO and ZnO; the next three contain K_2O as the additive; the following CuO; and the last three contain both.

Here, too, the appreciably stronger influence of the acidic component, ZrO_2, is clearly discernible. The values obtained are far superior to those of the previous group and, in part, yield very good results which rise above the 100 g threshold. The increase on addition of K_2O is clearly discernible. Again there is a distinct drop when CuO alone is added, whereas CuO and K_2O together again bring about the best results. In contrast to previous experiences, reduction is apparently more favorable at 450 deg C in this group.

An important result of previous experiments, as is represented in the following tables, may be stated:

It has been demonstrated that the "acidic" additives exercise the substantially more marked influence in the synthesis of alcohols with fused iron catalysts. It is clear that increasing molar weight exercises a favorable influence. The presence of two acidic substances, SiO_2 along with TiO_2, generally lowers the influence of the higher molar proportion.

The influence of the basic additives is noticeably slighter. CaO appears to yield the most favorable values. K_2O plus CuO are an exception. Thus, it appears to refer principally to the earth alkaline metals. For the most part K_2O effects an appreciable increase in yield, especially favoring the hydrocarbons. CuO, which was introduced as a replacement for K_2O, clearly effects a homogenization of the melts and appreciably reduces soot formation, even obviating it entirely in some instances. CuO, which in itself tends to lower efficiency for the most part, brings about an appreciable increase in catalytic activity when combined with K_2O.

The previous results were obtained by experiments with the 1-liter reactors (spiral shelved reactors) in a simple straight pass. These figures must not be considered to be the maximum values. The experience of experiemtns in a larger reactor with a content of 16 - 18 liters with gas recirculation, that is, under pilot conditions, gave much better outputs throughout. Of the available catalysts to date 16, which have been demonstrated to be the best so far, have been selected for testing undet semi-works conditions. On restoration of the equipment, which was partially destroyed by enemy air raids, the experiments will be carried out. It is to be hoped that more favorable experiemntal results will be partially obtained.