III. "Corrected" Catalysts

In developing the catalysts described until now certain assumptions and ideas on the structure of the unreduced catalysts was of decisive importance. As has previously been stated, titanium magnetite was considered as a base: x $FeO.Fe_2O_3$ plus y $FeO.TiO_2$. It was correspondingly assumed in developing further catalysts that, along with Fe_3O_4 as the predominant ground mass, the other additions were introduced in the shape of zirconates or titanates, e.g. K 1298:

10 Fe_3O_4 plus 1 $FeO\ .\ ZrO_2$ plus 1 $(MnO.K_2O)\ ZrO_2$ plus 1 $CaO\ .ZrO_2$.

It was assumed that the vitreous or crystalline "binder" consisted of these additions.

Conversion to mol %, based on the concept as explained in the above example, yielded discrepancies. If, on the other hand, it was assumed that the basic additions were absorbed in the form of ferrites, and the acidic additions in the form of the corresponding ferrous compounds, no difficulties are then encountered, e.g.

10 Fe_3O_4 plus 1 $MnO.Fe_2O_3$ plus 1 $CaO.Fe_2O_3$ plus 1 $K_2O.Fe_2O_3$ plus 3 $FeO.ZrO_2$.

Conversion to mol % resulted in simple numerical ratios which can be reduced apparently to ideal simplified formulas if divided by 2.5. The following examples demonstrate this:

In this manner the compositions of the following catalysts were converted: 997, 997 CuK, 1298, 1302 CuK, 1308 CuK, 1328, 1337, 1343, 1344, 1345 and 1346. A series of 24 new catalysts were obtained which were designated as "corrected catalysts" , as a result of transposition by conversion, by simplification in the composition, and, finally, by the replacement of ZrO_2 by TiO_2 in the case of individual catalysts.

There sections were subjected to optical investigation and then, after reduction, they were investigated as to their catalytic efficiency in a 1-liter reactor. The sections of these catalysts exhibited very simple pictures throughout. Type I is almost exclusively represented, i.e. there is no vitreous binder. The base crystals are homogeneous and uniform with, for the most part, medium to moderate anisotropy. This corresponded to previous experience so that good catalytic efficiency was to be expected.

Indeed these catalysts proved to be quite practibable medium catalysts, with individual performances exceeding the 100-g threshold. However, we were thoroughly disappointed in our expectation that new and even better catalysts than the original ones would be created with the aid of this conversion. Interestingly enough, the ThO_2-containing catalysts, as compared with the ZrO_2-containing catalysts, either fell below or remained at the same or almost the same values. A leap, such as was caused by the transition from TiO_2 to ZrO_2, was not observed in a single instance. Later on perhaps individual experimental melts will be produced to test the efficiency of ThO_2.

Since these corrected catalysts were thoroughly disappointing despite all our hopes, a new conversion was undertaken to find out the reasons, and the series was considerably expanded. The melts as well as the analyses of the unreduced catalysts were reconverted to mol % and compared against each other.

This table shows that it is necessary to divide by 2 and not as was originaelly thought, by 2.5, in the reconversion of the analyses and also in many melts in order to arrive at "simplified numerical ratios". This important, inasmuch as a good many shifts occur in favor of the $FeO.Fe_2O_3$, and often also in favor of the $FeO.ZrO_2$ in most cases. It is possible that this can explain why the already tested series of corrected catalysts was so disappointing. Conversions had been effected by division by 2.5 and the compositions of the melts computed according to numerial ratioms thus obtained. The circumstance that the catalysts, which fused after this incorrect calculation, dropped so much in efficiency as compared with the original ones would appear to lead to the conclusion that the catalysts were rather markedly dependent on the ratio of their consituents and reacted very sensitively to changes.

The "simplified numerical ratios" or the mol % shows the following mean values for the most important catalyst components:

magnetite proportion	$FeO.Fe_2O_3$:	36-38	or in mol %	72-76
earth alkali proportion e.g.	$CaO.Fe_2O_3$:	1		2
potassium proportion	$K_2O.Fe_2O_3$:	1		2
heavy metallic ferrite e.g.	$CuO.Fe_2O_3$:	2		4
"acid" proportions e.g.	$FeO.ZrO_2$:	10		20

To date the 4-substance catalysts have been the most practicable, but individual 3-substance and 5-substance catalysts have also come between the same boundaries.

We receive the impression from all this that a quite specific ratio which can be fixed in whole numbers is necessary for optimum performance of the catalysts. This is seen from the above figures and can be converted to an optimum mixture. In this connection the heavy metallic portion $(CuO . Fe_2O_3 , MnO . Fe_2O_3)$ should be included in the magnetite portion, i.e. the heavy metllic component shoul be reduced in the computation. As was already stated before, variation of the earth alkalis appears to have a less marked influence; on the other hand, the variation of the "acid" component is decisive. As was previously indicated, the qualitative change corresponding to the molar weight exercises a far-reaching influence on the quality of the catalyst, i.e. reduction of the acid component has the effect of a shift toward hydrocarbon formation; conversely, an increase has the effect of boosting alcohol formation along with increased gas formation (chiefly methane). These variations also appear to occur within relatively narrow boundaries. To this should be added the influence of the poxtassium, for without potassium the efficiency even of copper-containg catalysts is slight. In any case potassium appears to promote a certain tendency toward hydrocarbon formation. Combined with copper the potassium exercises an effect which none of the other components possess in themselves.

Unfortunately, accurate experimental checks of these conclusions are still missing and are not possible to the author at the moment because of conditions, particularly inview of the fact that the pilot plant has been damaged by air raids.