V. Catalysts Derived from Oxides

To avoid the uncertainties occurring when the mixtures are fused in a stream of oxygen, experiments were initiated to produce the catalysts directly from the oxides.

The experiments were carried out in the following manner:

Pure, finely-pulverized iron oxide was mixed as imtimately as possible with the oxides or carbonates corresponding to the mixture of the desired catalyst. The best method of mixing was attained by wet grinding in a ball mill. The watery slurry withdrawn from the mill was carefully mixed with the suitable quantity of KOH and the entire mass was dried. This product was now pressed into 15 x 15 mm pellets or the cake which had received a somewhat better consistency by the previous addition of some dextrine (about 1-2 per cent), was broken up into pieces about 10 mm long. A less successful attempt was made at a suitable granulation by forming in a compress.

At first an unsuccessful attempt was made to achieve the oxide reaction by ignition. However, since such reactions in a solid state procede appreciably better in the presence of water or steam at high temperautres, the experiments were continued in an atmosphere of steam. Pellets of a suitable oxide mixture were ignited in an iron tube at 800-850 deg C and superheated steam conducted through the tube. After 2 hours the pellets were withdrawn . Even externally they were strongly modified. The substances had undergone marked contraction and were tinged a dark grey color. The cleavage exhibited the same metallic lustre and dark grey color with a reddish cast as fused catalysts of the same composition. The desired conversion was therefore successful. The iron tube that was employed was naturally strongly attacked by the steam at the high temperatures and had been converted into iron oxide. Therefore, a porcellan tube was employed in further experiments with the result that the conversion in the steam atmosphere failed to occur. It was evident that hydrogen was neccessary in addition to the presence of steam. Therefore, the steam was heated in a preheater over glowing steam and only then conducted over the pressed catalyst substances. In this manner the desired conversion was immediately attained.

Consequently, we see that the desired catalysts cannot be produced by ignition alone, or in pure steam, or in hydrogen, but by by heating the oxidic substances in an atmosphere of steam and hydrogen (file number 11123). Further experiments showed that pellets of powdered iron with suitable additives, that is, practically the same mixture as was previously employed for the fused catalysts, also allow conversion of the desired catalysts in this treatment (file number 11964).

Microscopic examination of the section showed that the desired effect had been attained. The samples disclosed practically the identical structure and optical behavior as the corresponding fused catalysts, i.e. by conversion of the oxides in hydrogen-containing steam the same catalysts are obtained as by melting down metallic masses in an oxygen stream. The structure, however, is much more fine-grained with greater porosity. In this manner the catalysts so produced receive a greater internal surface which conditions an increase in activity. In general, these catalysts are activated at much lower temperatures than the fused catalysts; also, as far as can be seen from previous experiments, the yields are noticeably better. It is true, of course, that this is accompanied by a greater sensitivity toward all fluctuations of pressure, temperature, or gaseous state. In addtion, they have a tendency toward "smearing", i.e. high-molecular compounds, mostly hydrocarbons, which are formed within the catalysts, fillup the catalyst substances from inside outwards and thus eliminate the active surface. This is especially true in the case of the so-called "shortened" catalysts. A coarseflour (up to 1 mm grain size) derived from scraps of the fused catalyst in question was added to the oxide mixture in quantities of 50 to 75 per cent of the batch and, after the process, subjected to the above-described treatment. Catalyst masses of the porosity of pumice were obtained. The initial activity of these catalysts is very good but diminishes very rapidly as a result of this "smearing". To date only orientation and comparison laboratory experiments with these catalysts are available so that only qualitative statements can really be made about them. These masses appear to be very suitable for many purposes, particularly if the technical problems of production have been solved.