

SINCLAIR REFINING COMPANY

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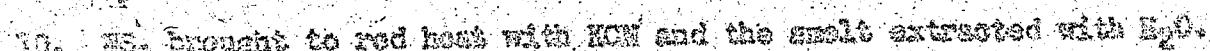
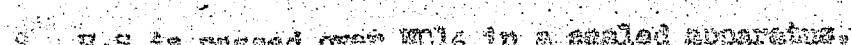
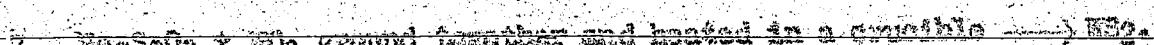
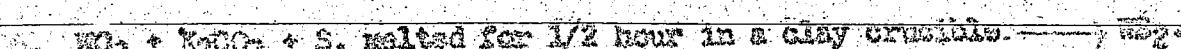
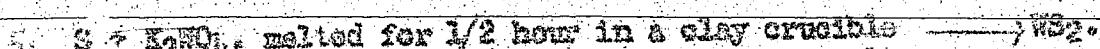
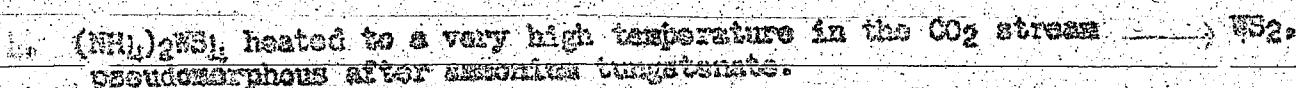
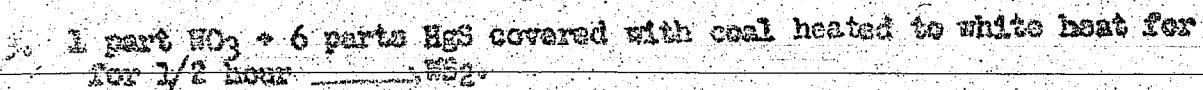
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S-107

The Preparation of Catalytically Active Tungsten Sulfide

May 22, 1943

Caslin's text book enumerates ten methods of preparing WS₂:



In this fascicule, only a few of these methods appear suitable for the preparation of large-area active WS₂. Nearly all of these processes are based on the effects of high temperatures, for neither the oxide nor the metal are transformed into WS₂ at a low temperature. In 5.), 6.), 7.) and 10.) alkali is present, too.

Our investigations on the cementia catalysts have taught us that the presence of even very slight quantities of alkali impairs the catalytic activity of Mo and W; this observation has also been verified for WS₂. Neither by reacting WO₃ and H₂S at 600°, nor by preparing WS₂ from WO₃ + HgS, did we succeed in preparing an active catalyst. Then we tried to prepare it from the sulfonate, in accordance with method 4.), and by precipitating WS₂ and further by the pressureless reduction of WS₃. These attempts were negative, too. The latter fact failed probably because WS₃ oxidizes most readily, and thus there was not the pure compound available; the former experiment failed probably because the temperature was too high. For this reason, we continued our efforts to find ways and means of preparing WS₂ at lower temperatures. In preparing catalysts a well developed surface area is of great importance. In producing metal catalysts, thin large area is usually obtained by reducing the oxides, provided that the reduction temperature of the oxides in question is not too high, for otherwise, the porous metal may start

intering. (e.g. Fe from Fe_3O_4 , the NH_3 catalyst, Co from $Co(OH)_2$ in the Fischer catalyst).

If this fine distribution does not suffice for the catalytic effect desired, compounds of still more complicated structures, (e.g. with Ni-nickel formate, Ni-acetate, or Ni-oxalate are subjected to the reduction at particularly low temperatures (less than 250°). In preparing an active oxide or another metal compound, such as sulfide, we shall usually proceed via the intermediate stage of preparing a hydroxide or a precipitated sulfide and converting them into the corresponding oxide by gentle drying and gentle extraction of the water of constitution. It is of importance for the catalytic activity of an oxide or an oxide-hydroxide catalyst that the hydroxide or oxide hydrate is present in a certain modification or can be converted into it under certain conditions, e.g. active alumina, active silica gel. For some catalytic reactions it will be sufficient if an oxide of higher valence is readily converted into one of lower valence (Mn, Cr-catalysts). In preparing active coal we are also starting from a very complicated high-molecular carbon compound, producing a particularly porous carbon structure by gentle degradation.

For the preparation of Fe_2 , process (1) has been modified. The decomposition of ammonium sulfotungstate with H_2 is carried out at temperatures up to $100^\circ C$. Thus, the particularly active catalyst 5055 has been obtained.

Later on, we were able to prepare a Fe_2 of equal activity by reacting Fe_2 or ammonium tungstate with H_2S for about 15-10 (sic!) hours under pressure (5-10 atm.) at a temperature rising up to $110-120^\circ$. By the time H. G. was here we succeeded in carrying out the reaction at a low temperature and in a comparatively short time, whereas at normal H_2S pressure the reaction proceeds only at high pressure and only very slowly. Technically, the H_2S -pressure method has not been applied. The method via the sulfosalts has been developed.

W. Böhr
May 12, 1940