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Part 2, Section 3

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The Preparation of Catalytically Active Tungsten SulfideMay 22, 1913Osolin's text book enumerates ten methods of preparing  $WS_2$ :

1.  $W + S$  strong heating  $\rightarrow WS_2$ .
2.  $WO_3$ , or  $W + S$ , or  $H_2S$ , or  $CS_2$  strong heating (incandescent)  $\rightarrow WS_2$ .
3. 1 part  $WO_3 + 6$  parts  $HgS$  covered with coal heated to white heat for 1/2 hour  $\rightarrow WS_2$ .
4.  $(NH_4)_2WS_4$  heated to a very high temperature in the  $CO_2$  stream  $\rightarrow WS_2$ . pseudomorphous after ammonium tungstate.
5.  $S + K_2WO_4$  melted for 1/2 hour in a clay crucible  $\rightarrow WS_2$ .
6.  $WO_3 + K_2CO_3 + S$ , melted for 1/2 hour in a clay crucible  $\rightarrow WS_2$ .
7.  $Hg_2S_2O_7 + WO_3$  ground together and heated in a crucible  $\rightarrow WS_2$ .
8.  $H_2S$  is passed over  $WO_3$  in a sealed apparatus.
9.  $WS_3$  brought to red heat  $\rightarrow WS_2$ .
10.  $WS_3$  brought to red heat with  $KOH$  and the melt extracted with  $H_2O$ .

Prima facie, only a few of these methods appear suitable for the preparation of large-area active  $WS_2$ . Nearly all of these processes are based on the effects of high temperatures, for neither the oxide nor the metal are transformed into  $WS_2$  at a low temperature. In 5.), 6.), 7.) and 10.) alkali is present, too.

Our investigations on the ammonia 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  $WS_2$ . Neither by reacting  $WO_3$  and  $H_2S$  at  $600^\circ$ , nor by preparing  $WS_2$  from  $WO_3 + H_2S$ , 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  $WS_2$  and further by the pressure-less reduction of  $WS_3$ . These attempts were negative, too. The latter test failed probably because  $WS_3$  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  $WS_2$  at lower temperatures. In preparing catalysts a well developed surface area is of great importance. In producing metal catalysts, this large area is usually obtained by reducing the oxides, provided that the reduction temperature of the oxide in question is not too high, for otherwise, the porous metal may start

intering, (e.g. Fe from  $Fe_3O_4$ , the  $NH_3$  catalysts, 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  $250^\circ$ ). 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  $WS_2$ , process (1) has been modified. The decomposition of ammonium in sulfotungstate with  $H_2$  is carried out at temperatures up to  $450^\circ C$ . Thus, the particularly active catalyst 5058 has been obtained.

Later on, we were able to prepare a  $WS_2$  of equal activity by reacting  $WS_3$  or ammonium tungstate with  $H_2S$  for about 36-40 (eight) hours under pressure (5-10 atm.) at a temperature rising up to  $410-430^\circ$ . By reacting  $H_2S$  under pressure 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 sulfosalt has been developed.

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