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NOTES

On the Reactivity of Spiltover Hydrogen

In a recent paper, Baumgartner *et al.* (*1*) reported that hydrogen which is spiltover on an alumina (Degussa, type C) surface, from Pt/Al_2O_3 catalyst, is not able to hydrogenate to a detectable degree unsaturated compounds such as benzoic acid, cyclohexene carbonic acid, acetylene dicarbonic acid, maleic acid, and acrylic acid. This conclusion was based on the absence of a change in IR absorption spectra of the adsorbed unsaturated reactants. These unsuccessful attempts at the hydrogenation of these compounds were performed in a hydrogen–helium stream (H_2 partial pressure 100 Torr) at temperatures from 320 to 620 K (47 to 347°C), within a reaction time of 120 min. The occurrence of hydrogen spillover was however detected by the exchange (with D_2) of alumina surface hydroxyls and by formation (with WO_3) of a tungsten bronze. By generalizing these results of unsuccessful hydrogenations the authors question the importance of the spiltover hydrogen in direct reactions during catalytic conversion of hydrocarbons, at least for alumina as a carrier.

It is of interest to draw attention here to the care which must be exercised in pretreating catalysts or supports so as to show up the phenomena produced by hydrogen spillover, in order to reconcile apparently conflicting results.

Two cases should be distinguished. (i) The migration of hydrogen (spillover) from the metal to the support (silica, alumina) can be detected (by OH–OD exchange) already at room temperature (*2, 3*). This spiltover hydrogen is inactive at room temperature toward the hydrogenation of unsaturated compounds. Even at 170°C its ability to reduce ethylene, acetylene, benzene, or cyclohexadienes is very much restricted (*4, 5*). The same conclusion concerning the lack of reactivity at 80°C toward benzene of hydrogen spiltover from rhodium on various zeolites has been presented recently (*6*). (ii) The spiltover hydrogen creates on the oxide new types of catalytic centers. A temperature above 400°C for 12 h, in the presence of H_2 and Pt, is required for this activation of alumina or silica (*7, 8*). In the case of silica, hydrogenating and cracking sites are formed, probably of superbasic and superacidic nature (*9*), whereas on alumina only hydrogenating sites are created (*10*). These are able to activate molecular hydrogen for the hydrogenation of unsaturated hydrocarbons. The nature of this reactive molecular hydrogen is not the same as that of the spiltover hydrogen required for the creation of active sites on alumina or silica (*11*).

As the experiments of Baumgartner *et al.* (*1*) were performed between 47 and 347°C for 2 hr, the support was probably not activated by spiltover hydrogen. Now the lack of reactivity of this spiltover hydrogen toward unsaturated hydrocarbons shows that the *indirect* contribution of spillover to catalysis seems to be more important (*8*). This involves the induction of activity on seemingly inert supports and the retention of activity on sites that would deactivate (by coke formation, by oxidation, etc.) without spillover.

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