Surface Boranes on Boria–Silica. A Method for Producing Surface Hydride Species

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Summary Three types of surface $=$B–H groups arise from the pyrolysis of B–OCH_3 groups, the thermal collapse of chemisorbed alkoxy-groups being a method of producing surface hydride species.

WE have recently shown that the pyrolysis of Si–OCH_3 groups on the surface of silica leads to the formation of surface $=SiH_2$ groups. When these are removed, the silica becomes highly activated and will react with molecular hydrogen to form surface $=SiH_2$ and $\equiv$SiH structures.[1] We have carried out similar studies with boria-impregnated silica (Figure).

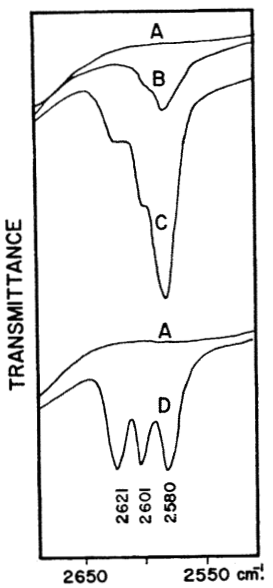

FIGURE. *Absorptions of surface boranes.* A: *Background spectrum of a boria-impregnated Aerosil* (1 *wt.* % *boria*) *after methylation.* B: *After degassing at* 700° *for* 2 *min.* C: *After degassing at* 700° *for* 12 *min.* D: *After exposure to* 30 *torr* H_2 *at* 700° *for* 3 *hr., subsequent to complete removal of* $=$B–H *groups by degassing.*

Pyrolysis of B–OCH_3 groups[2] led to an absorption at 2580 cm.$^{-1}$ (spectrum B) which then broadened and formed three distinct absorptions at 2621, 2601, and 2580 cm.$^{-1}$ (spectrum C). These could be eliminated by high-temperature degassing. The "reactive boria" formed in this fashion could react with molecular hydrogen, causing three distinct bands to be formed (spectrum D). In view of the positions of the bands, band shifts observed when CD_3OD was used or when D_2 was used for exchange, as well as the intensity relations of the three bands under different conditions, there is little doubt that each of the three bands can be attributed to the B–H stretching of a distinct surface $=$B–H species.

The three surface boranes were not formed when boria-impregnated silica which had not been subjected to the methylation–pyrolysis activation procedure was exposed to hydrogen under severe reaction conditions, so that it seems that the formation of the boranes on the boria portion of the adsorbent is a localized phenomenon directly connected with the particular conditions set up by the pyrolysis of B–OCH_3 groups. The thermal collapse of chemisorbed methoxy-groups, and probably of other alkoxy-groups, thus appears to be a powerful method for producing surface hydrides which are not obtainable by means of direct reactions with molecular hydrogen.

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[2] M. J. D. Low and Y. Harano, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 1968, **16**, 271.