Surface P–OH Groups on Impregnated Silicas

By M. J. D. LOW* and P. RAMAMURTHY
(*School of Chemistry, Rutgers—The State University, New Brunswick, N.J.* 08903)

ALTHOUGH the use of phosphorus compounds as catalyst-promoters has been frequently mentioned during the past few decades and phosphate materials have been used for olefin polymerizations, relatively little is known about the nature and surface properties of phosphorus-containing catalysts or silica–phosphate solids. We now find that some surface P–OH groups are formed if high-surface-area silicas are impregnated with P_2O_5.

The spectrum of a highly degassed silica such as Cab-O-Sil shows a prominent absorption band generally ascribed to the O–H stretching fundamental of isolated surface silanols (spectrum A). If such a material is slurried with P_2O_5 solution, dried, and degassed, a second sharp band is observed in the OH region near 3665 cm.$^{-1}$, *e.g.*, spectrum B. A similar band is formed with porous Vycor glass (spectrum C).

The 3665 cm.$^{-1}$ band is considerably reduced in intensity on degassing above 500° and can be eliminated after 10 hr. at 800°, but can be reformed by sorbing H_2O or shifted to 2698 cm.$^{-1}$ by sorbing D_2O. The 3665 cm.$^{-1}$ band is ascribed to the O–H stretching fundamental of surface P–OH groups. As the P–OH band is relatively sharp, there is little interaction of P–OH groups and their surface environment. Some phosphorus atoms could become incorporated in the silica, but aggregates of phosphorus oxide may exist on the surfaces.

When gases become physically adsorbed, the behaviour of the P–OH groups is much like that of surface Si–OH or B–OH groups. If chemisorption is involved, however, the spectra show the occurrence of surface interactions in which P–OH groups play a predominant role. Surface P–amine groups are formed on reaction with ammonia, for example. Studies with a variety of adsorbates, to be described in detail elsewhere, show that surface phosphorus can act as specific adsorption or reaction sites, and may modify the reactivity of the silica carrier.

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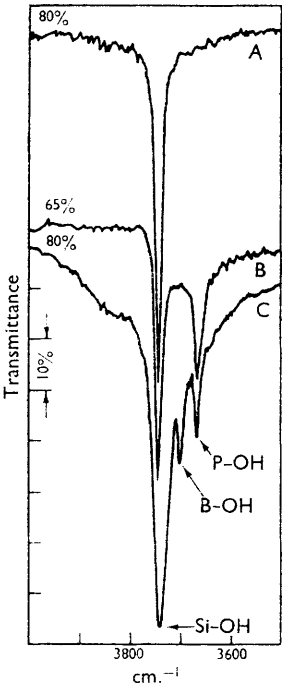

FIGURE. *Infrared spectra of surface* OH *groups.* (A) *Cab-O-Sil degassed at* 750° *for* 10 *hr.* (B) *Cab-O-Sil impregnated with* 5% P_2O_5 (*by weight*) *after degassing for* 2 *hr. at* 100, 200, 300, *and* 400°. (C) *porous Vycor glass, boiled in* 2% P_2O_5 *solution, dried, degassed at* 750° *for* 11 *hr. and at* 800° *for* 5 *hr. Ordinates are displayed to avoid overlapping. The numbers next to each spectrum indicate the* % *transmittance of the sample at* 4000 *cm.*$^{-1}$.

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