

NOTE

Reactions of Radical-Anions and Ethyllithium with Silica

A numbers of papers (1-11) have been devoted to the structure and reactivity of porous silica gel, a catalyst carrier for polymerization of alkenes. The surface is formed by siloxane bonds, free and hydrogen-bonded hydroxyl groups, and adsorbed water. Controversial views on the surface composition and reactivity of various samples of silica gel can be found in the literature. The structure and reactivity of silica gel are dependent on its preparation procedure and further processing (usually dehydration and dehydroxylation). The present paper deals with the interaction of silica gel with radical-anions in tetrahydrofuran and with ethyllithium in *n*-heptane. These organic compounds of alkali metals have been employed due to their high reactivity, the small size of their molecules or ions, and the ease of determining their concentrations.

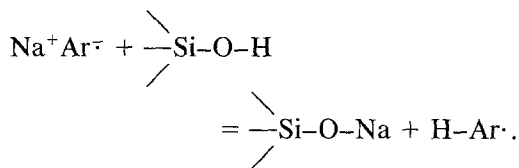
Silica gel (Davison, grade 952 (U.S.A.)), was dehydrated in a quartz vessel in a purified nitrogen stream for 6 h at 200-900°C or by 100-h evacuation under 10^{-2} Pa at 20°C. Specific surface area was measured using the BET method and the following values were obtained at various temperatures of heat treatment: 285 m² g⁻¹ (20-600°C), 278 m² g⁻¹ (800°C), and 218 m² g⁻¹ (900°C). Pore volume values calculated using nitrogen desorption isotherms were 1.8, 1.7, and 0.85 cm³ g⁻¹, respectively, and a maximum of the pore size distribution was observed at 10 nm.

Tetrahydrofuran, *n*-heptane, lithium, sodium, carbon tetrachloride, ethyl chloride, naphthalene, phenanthrene, and benzophenone were effectively purified of traces of impurities, especially oxygen and water. Radical-anion solutions in tetrahydrofuran

(10^{-2} - 10^{-1} mol · liter⁻¹) were prepared according to the procedure described elsewhere (12) and their concentrations measured by acidimetric titration or from electrical conductivity. Ethyllithium was prepared as a 0.05 mol · liter⁻¹ solution from ethyl chloride and metallic lithium in *n*-heptane according to the method of Gilman *et al.* (13).

Infrared spectra of silica gel in the 4000-8000 cm⁻¹ range were measured using a Perkin-Elmer 377 instrument. Silica gel was placed in a 1 cm quartz cell and dry carbon tetrachloride was added to obtain a slurry of 16-17 wt% concentration. Bands at 4425, 4505, and 7140 cm⁻¹ due to hydroxyl groups were measured.

The reaction of radical-anions with hydroxyl groups of silica gel can be described as (Ar is arene)



Radicals H-Ar· may combine mutually or with other radical-anions (14), thus consuming one molecule of radical-anion per hydroxyl group. During titration by radical-anion solution, silica gel first decomposes Na⁺Ar⁻ according to the above equation; excess of radical-anions then brings about their adsorption causing intensive coloration, turning finally black.

Titration of silica gel by radical-anion solution was performed as follows: To a slurry of dry silica gel in pure tetrahydrofuran at 25°C, ca. 0.1 M solution of radical-anion in tetrahydrofuran was added slowly under magnetic stirring. At the beginning

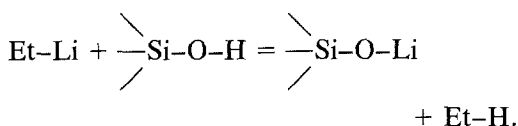
of titration, the solution discolored fast; thereafter the color disappeared slowly and the silica gel began to acquire color, but the turning point could not be determined; at a certain point of titration, a weak coloring of the solution was permanent while the silica gel was intensively colored. The color of the silica gel corresponded to that of the radical-anion and it could be removed immediately by adding Brønsted acids (e.g., water, alcohols); thus an adsorption of radical-anions on silica gel can be visualized. The adsorption may be chemical due to a nonzero amount adsorbed at zero concentration in solution. Further addition of radical-anion solution to the silica gel slurry brought about a deepening of color in both solution and the silica gel. The color of the silica gel under an excess of radical-anion solution turned to black. Titration of the silica gel to the turning point of appearance of a permanent weak color of solution (equilibrium between radical-anions in solution and those adsorbed on the silica gel) revealed the total amount of radical-anions reacting with hydroxyl groups (and possibly with siloxane bonds) and chemically adsorbed on the silica gel at virtually zero concentration of radical-anions in solution. The amount of chemically adsorbed radical-anions was determined by back titration of the silica gel slurry by 0.1 *M* water solution in tetrahydrofuran up to discoloration of the silica gel.

A reverse titration was also carried out. A known amount of silica gel (0.5–2.0 g) was added to 20–50 ml of radical-anion solution of a known concentration (max 0.05 mol · liter⁻¹) in tetrahydrofuran. The slurry was stirred vigorously and the drop in conductivity was measured. After reaching equilibrium (30–60 min) the concentration of radical-anions was redetermined through acid-base titration: the slurry was titrated slowly by a solution of water in tetrahydrofuran (0.1 *M*), first to discoloration of the solution (and simultaneous drop of conductivity) and then to discoloration of the intensively colored silica gel.

From the difference between the total amount of radical-anions captured from solution by the silica gel (i.e., those having reacted with hydroxyl groups and siloxane bonds and physically adsorbed radical-anions) and the amount loosely adsorbed on the silica gel (reacting with water), the amount of radical-anions having reacted with the acidic hydrogen of hydroxyl groups and siloxane bonds of the silica gel was determined.

The amount of radical-anions consumed in the reverse titration procedure was the same as that found in the standard procedure, including the chemically adsorbed amount. Benzophenone, phenanthrene, and naphthalene were used as the aromatic components of radical-anions; the results obtained were independent of the aromatic type.

Reaction of ethyllithium with silica gel in *n*-heptane can be described by the equation



The amount of ethane formed corresponds to the quantity of acidic hydrogen and was measured by manometrically applying the solubility correction.

The amounts of Na⁺(phenanthrene)⁻ and Et-Li reacted with silica gel activated at 20–900°C are shown in Fig. 1. These two quantities do not differ from each other within experimental error (5–10%). Both substances are subjected to the reaction with acidic hydrogen in hydroxyl groups. However, they differ substantially in molecular sizes and in polarity of the carbon-metal bonds. Considering the extremely high reactivity of these substances and the proportional drop of the hydroxyl group signal in the infrared spectra of the silica gel (4505 and 7140 cm⁻¹) after the interaction with radical-anions and ethyllithium, it can be concluded that both substances react quantitatively and stoichiometrically with hydroxyl groups on the silica gel surface. A

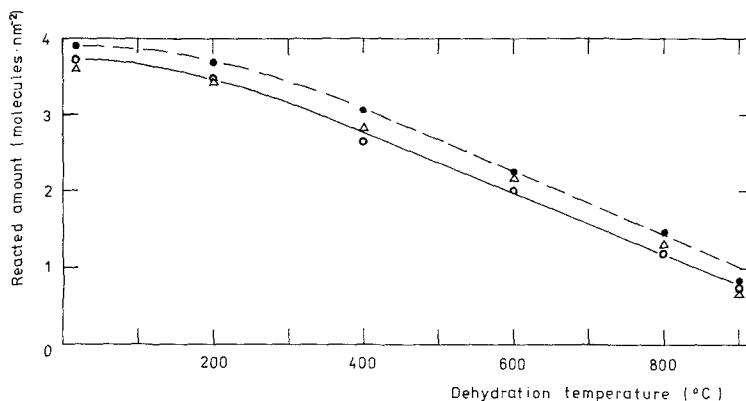


FIG. 1. Influence of the dehydration temperature of silica gel on its reaction with Na^+ (phenanthrene)⁻ in tetrahydrofuran and with ethyllithium in *n*-heptane at 20°C. (O) Consumed amount of Na^+ (phenanthrene)⁻; (●) sum of consumed and adsorbed amount of Na^+ (phenanthrene)⁻; (Δ) evolved amount of ethane.

certain portion of the hydroxyl groups (2–5%) is left intact in reactions with radical-anions and ethyllithium according to infrared spectra (Fig. 2). These may be inaccessible hydroxyl groups, the presence of which has been demonstrated, e.g., in pressed disks of silica gel (2).

The thermally untreated Davison 952 silica gel exhibits 3.6–3.8 OH-groups/nm²

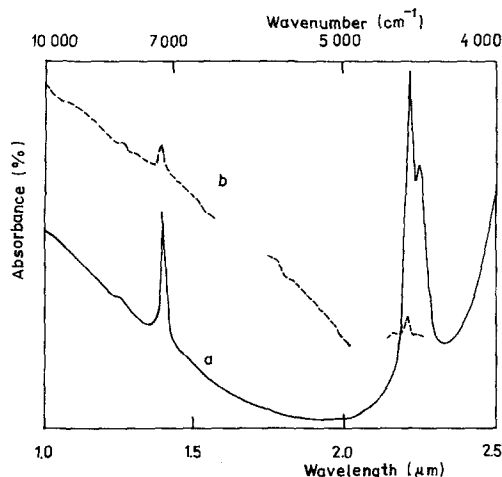


FIG. 2. Infrared spectrum of (a) silica gel dehydrated for 6 h at 800°C and (b) the same silica gel after its reaction with Na^+ (phenanthrene)⁻ (0.96 mmol · g⁻¹) in tetrahydrofuran. Conditions: 1 cm quartz cell, dry samples added to CCl_4 , 16 wt% slurry concentration.

(Fig. 1) and this value decreases slightly with increasing temperatures of activation up to 200°C. The heat-untreated silica gel exhibits a maximum amount of hydroxyl groups. This was documented by refluxing silica gel in water for 8 h followed by 100 h evacuation at 20°C; after these treatments silica gel again contained 3.6–3.8 OH-groups/nm². Published values of maximum amounts of the surface hydroxyl groups of the silica gel are 2.9–5.5 OH/nm² (1, 2, 4–8), rarely higher (10, 15). These values were found after activating silica gel at least at 100°C; thus the extrapolation to room temperature is rendered difficult. The contents of free water have not been reported, which may lead to an overestimation of the OH-group content at low temperatures of activation; see for instance, the dependence on the activation time (6). The agreement of our results with the published data strongly suggests the suitability of titration methods for characterization of the surface composition of silica gel.

The amounts of reacted radical-anions and ethyllithium decrease linearly with increasing temperatures of activation in the range 200–900°C. A steeper decrease with increasing temperatures is usually reported (4, 6, 8), though a linear dependence has also been found previously (15).

The amount of chemically adsorbed radical-anions on Davison 952 silica gel is 0.2–0.3 molecule/nm² and it is apparently independent of the activation temperature (Fig. 1). A certain dependence on the activation temperature, however, cannot be excluded due to the high experimental error involved ($\pm 50\%$).

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