Cost-effective Surface Modifications of Silica and Alumina
Achieved by Way of a Simple In-house Set-up
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Introduction

Highly porous silica or alumina was surface-functionalized in up to kilogram amounts by means of reactions that combined the inorganic-organic chemistry and the practicality of a stepwise, reduced-pressure approach. Oven-dried silica or alumina was placed inside a reaction vessel having one or more types of organosilane reagent. A vacuum was applied and the system was heated to an elevated temperature, during which time organosilane vapors had transferred onto the native, high-surface-substrate. Aqueous vapor was subsequently introduced, thereby, hydrolysing surface-bound silanols and generating the activated alanol species. Following a final condensation step, the new surfaces were analyzed. As anticipated, BET surface analyses illustrated a decrease of area following the procedure. Chromatic analyses indicated that the reactivity of surface-pendent functional groups was consistent with the type of reagents used, and carbon-13 and silicon-29 CP-MAS NMR analyses disclosed characteristic chemical environments. The chemical environment was probed further by 13C- & 29Si-CPMAS NMR using an Inova 500MHz Varian system, and surfaces by chromogenic analyses. Interestingly, its reactivity with lead ion was completely different. Secondly, the gas phase TEOS reaction clearly had not hydrolyzed to completion, as evidenced by the etchability of the carbon in the NBR (right). This finding, coupled with a higher BET value, suggested a different structural arrangement. CP-MAS NMR analyses coupled to BET and color analyses were peculiar in the sense that not all tests were consistent. For example, a significant loading according to BET analysis was met with a weak NMR signal or no color formation. The underlying reasons are currently under investigation.

Summary

Reactive Reagents

Reagent: APTMS: amino-propyltrimethoxysilane; TEOS: tetraethylorthosilicate; MPTMS: mercaptopropyltrimethoxysilane; PMPMS: glycyl-propyltrimethoxysilane; NMMTMS: N-methylamino-propylmethoxysilane; APMDES: amino-propylmethoxy-diethoxysilane; GOES: glycidoxypropyltrimethoxysilane. Gas-phase method: Dry silica and alumina samples were treated with organosilane vapor (50 °C, 48 h) (130 m2/g), and the system was heated to an elevated temperature, during which time organosilane vapors had transformed onto the native, high-surface-substrate. Aqueous vapor was subsequently introduced, thereby hydrolysing surface-bound silanols and generating the activated alanol species. Following a final condensation step, the new surfaces were analyzed.

Experimental

Materials surface composed of glass, metal oxide or potentially any oxide/hydride functional group are routinely tailored using organosilane reagents, affording new physico-chemical surface properties and enabling diverse application. The classical modification is based upon a hydrolysis-condensation mechanism. Reactive reagents such as TEOS, (1:1 molar ratio), and APTMS, were incubated with water under an ambient conditions, at 75 °C, for 48 h. Concurrently, the aqueous reaction mixture was analyzed by 1H NMR to determine the extent of organosilane hydrolysis and condensation. The resulting solutions were characterized by FTIR and visible spectrophotometry. The hydrolyzed organosilane solutions were then applied to silica gel for chromogenic analysis, which was characterized by the development of a specific color. The chromatography was performed on a silica gel plate using different solvent systems, followed by UV irradiation at 254 nm. In addition, the coloration was recorded by scanning the silica gel plate with a spectrophotometer. The resulting spectra were then analyzed to determine the color forms of the surface-bound functional groups. The color forms of the surface-bound functional groups were determined by comparison with aqueous standards such as dithioerythrol, mercaptopropyltrimethoxysilane, and gas-phase deposited and hydrolyzed samples.

Results and Discussion

BET surface analysis showed a loss of surface area in alumina samples in the range of 4-19% in either material, the gas and aqueous phase methods appeared to afford high loadings with certain reagents and poor loadings with others. Additionally, the fact that the reagents had occurred via gas-phase deposition and hydrolysis was conclusive. The loss of surface area, assuming a spherical or cylindrical mesopore structure of 60Å diameter and a homogeneous monolayer coating of 10Å, was approximated at 56% and 33% respectively. On the basis of BET measurements, therefore, the reaction clearly had not afforded complete monolayer coverage. Interestingly, its reactivity with lead ion was completely different. Secondly, the gas phase TEOS reaction had not hydrolyzed to completion, as evidenced by the etchability of the carbon in the NBR (right). This finding, coupled with a higher BET value, suggested a different structural arrangement. CP-MAS NMR analyses coupled to BET and color analyses were peculiar in the sense that not all tests were consistent. For example, a significant loading according to BET analysis was met with a weak NMR signal or no color formation. The underlying reasons are currently under investigation.

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