Efficiency of grafting of Al₂O₃, TiO₂ and ZrO₂ powders by perfluoroalkylsilanes

Joanna Kujawa, Wojciech Kujawski, Stanislaw Koter, Anna Rozicka, Sophie Cerneaux, Michel Persin, André Larbot

Faculty of Chemistry, Nicolaus Copernicus University, 7 Gagarina St., 87-100 Torun, Poland
Institut Européen des Membranes, 1919, route de Mende, 34293 Montpellier Cedex 5, France

HIGHLIGHTS
- Efficient modification of ZrO₂, TiO₂ and Al₂O₃ by various perfluoroalkylsilanes.
- Modification the hydrophilic surface of metal oxides to the hydrophobic one.
- Characterization of grafting process with PFAS by various analytical techniques.
- Determination the impact of several parameters on the grafting efficiency.
- Evaluation and optimization of grafting conditions by chemometric simplex method.

ABSTRACT
Metal oxides powders of Al₂O₃, TiO₂ and ZrO₂ were modified by two types of perfluoroalkylsilanes (PFAS) molecules 1H,1H,2H,2H-perfluoroctyloxytrimethylsilane (C₆) and 1H,1H,2H,2H-perfluorotetradecyltrimethoxysilane (Cl₂). Studies showed that surface of oxide powders can be efficiently hydrophobized. Grafting efficiency of oxide powders was determined by TGA and FR-MIR techniques. Strong influence of ratio of amount of PFAS to amount of metal oxide powder, type of grafting molecules, grafting time and concentration of PFAS solution were observed on the grafting efficiency of all powders.

The highest grafting efficiency occurred for alumina, what is related with the highest specific surface area of Al₂O₃. However, zirconia should the lowest grafting efficiency by PFAS molecules.

The mechanism of grafting process was suggested and confirmed by ²⁹Si NMR and FT-MIR techniques. Analyses results revealed three possible types of bonding of the hydrophobic chains to the materials surface. It was found that C₆ molecules were attached mainly by siloxane bonds, whereas C₁₂ molecules were attached by geminal silanol bonds.

The results obtained for alumina modification were additionally approached using chemometric simplex method, what allowed to determine the optimal grafting conditions. The highest grafting efficiency of Al₂O₃ was obtained using 0.75 mmol C₆ g⁻¹ of Al₂O₃. Concentration of C₆ molecules has only a minor influence on the grafting efficiency.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction
Ceramic materials are more stable than other materials especially at elevated temperatures and in more corrosive environment. Among ceramics oxides are the most commonly used materials because they are more stable in the air than non-oxide ceramics...