Colloids and Surfaces A: Physicochem. Eng. Aspects 420 (2013) 64–73

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Efficiency of grafting of Al_2O_3, TiO_2 and ZrO_2 powders by perfluoroalkylsilanes

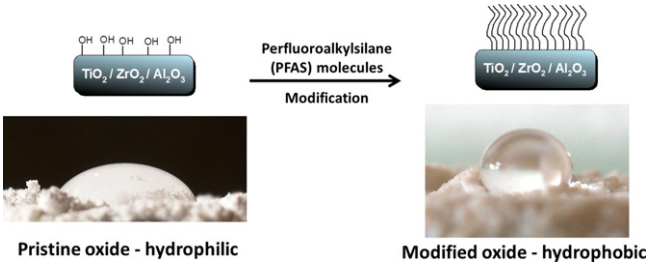
Joanna Kujawa[a], Wojciech Kujawski[a,*], Stanisław Koter[a], Anna Rozicka[a], Sophie Cerneaux[b], Michel Persin[b], André Larbot[b]

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

HIGHLIGHTS

- Efficient modification of ZrO_2, TiO_2 and Al_2O_3 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.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 September 2012
Received in revised form
13 December 2012
Accepted 18 December 2012
Available online 26 December 2012

Keywords:
Al_2O_3
TiO_2
ZrO_2
Surface modification
Perfluoroalkylsilane
Simplex method

ABSTRACT

Metal oxides powders of Al_2O_3, TiO_2 and ZrO_2 were modified by two types of perfluoroalkylsilanes (PFAS) molecules 1H,1H,2H,2H-perfluorooctyltriethoxysilane (C6) and 1H,1H,2H,2H-perfluorotetradecyltriethoxysilane (C12). 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 Al_2O_3. However, zirconia should the lowest grafting efficiency by PFAS molecules.

The mechanism of grafting process was suggested and confirmed by ^{29}Si 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 Al_2O_3 was obtained using 0.75 mmol C6 g^{-1} of Al_2O_3. Concentration of C6 molecules has only a minor influence on the grafting efficiency.

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

* Corresponding author. Tel.: +48 56 611 43 15.
E-mail address: kujawski@chem.umk.pl (W. Kujawski).

0927-7757/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2012.12.021