ISGC 2019
May 13th - 17th

N°452 / OC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Design of innovative nanocomposite materials by spray-freeze drying process: efficient catalysts and photocatalysts preparations

AUTHORS
STEFANIA ALBONETTI / UNIVERSITÀ DI BOLOGNA, VIALE RISORGIMENTO 4, BOLOGNA
Giuseppe FORNASARI / UNIVERSITÀ DI BOLOGNA, VIALE RISORGIMENTO 4, BOLOGNA
Simona ORTELLI / ISTEC-CNR, VIA GRANAROLO 64, FAENZA
Alice LOLLI / UNIVERSITÀ DI BOLOGNA, VIALE RISORGIMENTO 4, BOLOGNA
Anna Luisa COSTA / CNR-ISTEC, VIA GRANAROLO 64, FAENZA
Magda BLOSI / CNR-ISTEC, VIA GRANAROLO 64, FAENZA
Riccardo BACILE / UNIVERSITÀ DI BOLOGNA, VIALE RISORGIMENTO 4, BOLOGNA
Sara ANDREOLI / UNIVERSITÀ DI BOLOGNA, VIALE RISORGIMENTO 4, BOLOGNA

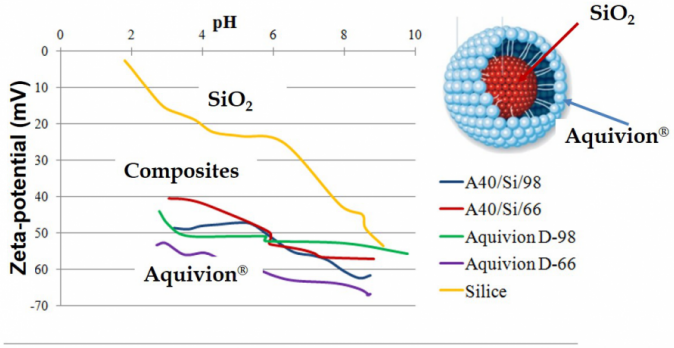
PURPOSE OF THE ABSTRACT
Spray-Freeze-drying (SFD) is a drying method often encountered in pharmaceutical industry as well as in the processing of food. With this procedure, thermo-labile compounds can be dried at low temperatures to produce spherical porous particles and forming high-surface area systems. Indeed, using this method, a solvent can be removed without exposing the systems to tensile forces of a receding meniscus. Therefore, it is a suitable drying technique to develop porosity in inorganic and polymeric materials.
For catalyst preparation, freeze-drying has been suggested to reduce precursor solution mobility during drying and therefore control the location of deposition of the precursor phase [1]. Moreover, the technique can be utilized to the homogeneous embedding of the active phases into the support, minimizing the possibility of phase separation on a molecular scale, as also demonstrated for drugs. Nevertheless, few applications have been reported in the catalytic field until now.
In this work, SPD was successfully applied for the preparation of nanostructured mixed oxides (TiO2/SiO2, Pt containing systems) and polymer/oxides composites (perfluorosulfonic superacid resin- Aquivion PFSA with SiO2) with very high surface area and homogeneous dispersion of different components. The prepared materials were tested in various reaction such as: 1) the gas-phase dehydration of ethanol to ethylene (Aquivion /SiO2 systems) [2]; 2) the oxidation of hydroxymethyl-2-furfural (Pt containing catalysts) [3]; 3) the photodegradation of rhodamine B, used as a stain model (TiO2/SiO2 materials) [4].

Results and discussion
The mixed-oxides and polymer/oxide composites were produced at different compositions using a colloidal heterocoagulation method - expected to give rise to matrix encapsulation - associated with the spray-freeze drying. Sols containing the different oxides, latex or metal precursors were characterized by zeta-potential analyses and Dynamic Light Scattering (DLS) measurements to evidence the effect of particles charge and dimension on the materials synthesis. Moreover, the study of the effect of different synthesis parameters used during the colloids mixing permited to optimize the properties of the final powders.
The zeta potential (zeta-pot) was measured using an electrophoretic light scattering (ELS) method and was very useful to investigate the organization of the different components in the composites and mixed oxides. As an example, pristine SiO2 NPs and Aquivion PFSA were both negatively charged (Figure 1) but the resin-modified silica showed a significant decrease in ?-pot suggesting a reorganization of the SiO2 with a perfluorosulfonic superacid resin shell, which could indicate that polymer encapsulated structures are obtained (drawing in Figure 1).

In the process of SFD , the evaporation induced condensation of the sols containing the different nano-oxides or polymeric latex, intimately mixed, occurs during a very short time, forming a stable network.

As-synthesized and calcined catalysts were lightweight flowable powders with low bulk density as well as very high specific surface area, also in the case of perfluorosulfonic superacid resin utilization. Active species were demonstrated to be incorporated and well dispersed in the matrix network. The SEM-FEG micrograph of the samples (Figure 2, reporting the TiO_2/SiO_2 systems) reveals a primary structure that is very fine, but organized in the form of diffused aggregates. The dispersion of the different components was very homogeneous in all the studied systems. Prepared catalysts and photocatalysts were very active in the targeted reaction; in particular, acid resin-based catalysts gave much higher conversion and selectivity in ethylene at very low temperature respect to catalysts prepared by conventional impregnation methods.

FIGURES



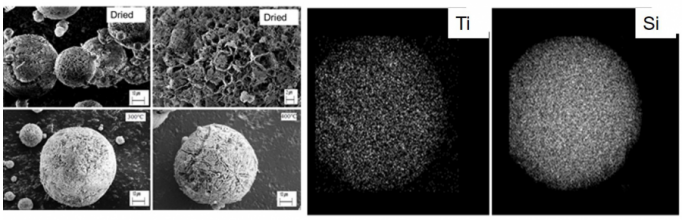


FIGURE 1

Figure 1

FIGURE 2

Figure 2

SEM-FEG images of SFD powders from TiO2-SiO2 sol with a SiO2:TiO2 weight ratio 1:1.

KEYWORDS

Spray-freeze-drying | catalysts | nanostructured composites | Aquivion®

BIBLIOGRAPHY

[1] T.M. Eggenhuisen, P. Munnik, H. Talsma, P.E. de Jongh, K.P. de Jong J. Catal. 297 (2013) 306–313.

[2] S. Albonetti, G. Fornasari, S. Andreoli, R. Bacile Patent P64747IT00, 2018 assigned to the Bologna University

[3] A. Lolli, S. Albonetti, L. Utili, R. Amadori, C. Lucarelli, F. Cavani Appl. Catal A 504 (2015) 408-419.

[4] A.L. Costa, S. Ortelli, M. Blosi, S. Albonetti, A. Vaccari, M. Dondi J. Photochem. Photobiol. 276 (2014) 58– 64.