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Chemical surface modification of mesoporous silica SBA-15 with a tertiary aminosilane using supercritical carbon dioxide

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ABSTRACT

The surface of mesoporous silica SBA-15 was modified with (*N*,*N*-dimethylaminopropyl)trimethoxysilane (DMAPTS) for the first time in supercritical carbon dioxide (scCO_2). An important requisite in this process is that the precursors have to be soluble in the CO_2. Therefore, the phase behavior of mixtures formed by CO_2 and DMAPTS was investigated. Then, the supercritical surface modification of silica SBA-15 by the silylation reaction using DMAPTS was carried out at several conditions of pressure, temperature, reaction time and concentration of precursor. The modified SBA-15 was characterized using FTIR spectroscopy, thermogravimetric analysis, CHN elemental analysis, N_2 adsorption–desorption isotherms and ^{29}Si MAS NMR. The grafting density of DMAPTS on silica SBA-15 in the supercritical method increased with the reaction time. Typically, values of ca. 2.2–2.4 mmol g^{-1} were reached in 2 h. The effects of pressure and temperature were very weak at the studied conditions. The grafting density increased gradually as the DMAPTS concentration in the CO_2 increased. The structural ordering of silica SBA-15 was preserved in the modified samples. However, the specific surface area and average pore diameter decreased progressively as the amount of DMAPTS attached to the silica increased and they can be controlled choosing the appropriate experimental conditions. In addition, the performance of the scCO_2 modification method was compared to that of the conventional method using toluene. Results indicated that the scCO_2 surface modification of mesoporous silica was faster and yielded larger loads of silane while using a sustainable method.

1. Introduction

Ordered mesoporous silica has performed a significant role in the material chemistry since its discovery in early 1990 [1]. These materials exhibit extremely high surface areas and uniform pore sizes and are interesting as novel catalysts, sorbents, sensors and host materials for large guest molecules. However, the original proposed mesoporous silicates have lower hydrothermal stability and reactivity than zeolites with comparable composition. One way of modifying the physical and chemical properties of mesoporous silica has been the introduction of organic functional molecules on the surface of prefabricated mesoporous silica through the grafting method (post-synthesis reaction) [2,3]. The advantages of this method are that the original structure of the mesoporous support is generally maintained after reaction and that the materials produced show relatively high hydrothermal stability [4]. The grafting method can be performed through a silylation reaction which involves the reaction of the free and germinal silanol groups with organosilane agents such as alkyl, aryl, amino and chlorosilanes on the surface of silica materials. The most common mechanism for the silylation reaction is shown in Fig. 1 for the aminosilane used in this work, (*N*,*N*-dimethylaminopropyl)trimethoxysilane (DMAPTS) [5,6]. Firstly, the adsorbed organosilane is hydrolyzed to the alkylsilanol by the water which is either adsorbed on the surface or dispersed in the solvent. Secondly, the adsorbed alkylsilanol condenses with silanol groups of the surface or with adjacent molecules to produce siloxane bonds (Si–O–Si) plus the by-product water. Under most conditions, condensation may start before hydrolysis is completed. The reactive deposition of trialkoxysilanes from solution can give a number of possible surface structures such as self-assembled polymerization, covalent attachment and vertical polymerization [5]. Self-assembled polymerization refers to the reaction between the alkyltrisilanol with

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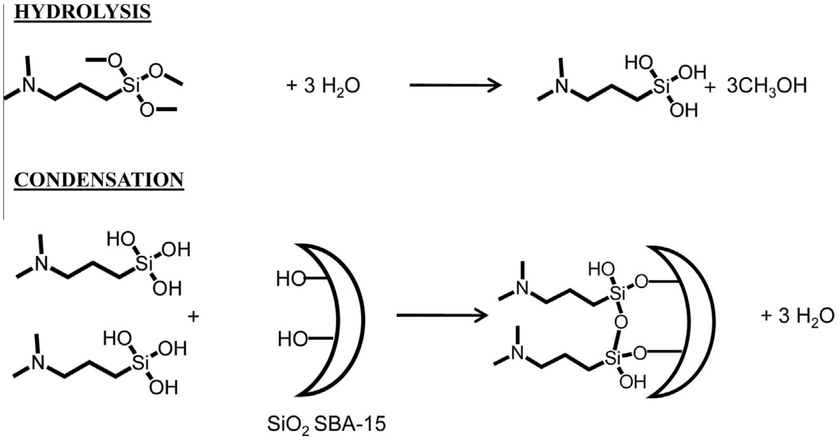

Fig. 1. Simplified mechanism of the silylation reaction.

the surface and simultaneously with neighboring molecules to give lateral siloxane bonds and van der Waals interactions between the alkyl chains, forming a monolayer. If the alkyltrisilanols react predominantly with the surface silanols, then the layer formed has a much lower packing density. This results in a covalent attachment. The vertical polymerization between alkyltrisilanols molecules can also give perpendicular siloxanes grafted to the surface but not a self-assembled monolayer. The competition between the surface reaction and self-polymerization depends on several factors including the nature of the organosilane, the choice of the solvent, the reaction temperature, and, in particular, the amount of water adsorbed on the surface [7].

The two current methods of surface modification by silylation reaction are vapour-phase reaction at elevated temperature or reaction in solution using an organic solvent such as dichloromethane or toluene [5,8,9]. Some drawbacks are associated with both methods. The vapour-phase reaction is limited by the thermal stability and volatility of the organosilanes. On the other hand, the modification in a liquid solvent generally yields low quality self-assembled monolayers mainly because of the need to carefully control the amount of water in solution [7]. Furthermore, the porous structure can be damaged by the capillary forces of the liquid phase [3]. On the other hand, supercritical carbon dioxide ($scCO_2$) has received significant attention as an attractive medium to modify the surface of inorganic materials in the last decade [10]. The low viscosity, high diffusivity and very low surface tension of $scCO_2$ facilitate the transport of the silane agent to the internal surface of nanopores without structural damage [11]. The density of the fluid can be modified from gas-like to liquid-like with small changes in temperature and/or pressure that allow to control the surface coverage which is not always possible in liquid-phase processes [12]. On the other hand, $scCO_2$ is considered a green solvent because it is non-toxic, non-flammable, inexpensive, naturally abundant and relatively inert and has low critical temperature and pressure ($T_c = 304.15$ K, $P_c = 7.38$ MPa). Besides, CO_2 is readily separated from the material by simply reducing the pressure and this is a great advantage in comparison to the liquid methods. For all these reasons, the use of $scCO_2$ as an alternative to traditional organic solvents offers new possibilities for the development of more sustainable silylation processes.

Tripp and co-workers [13,14] analyzed by FTIR spectroscopy the interaction of $scCO_2$ with silica and the reaction of different organosilanes such as hexamethyldisilazane (HMDS), and octadecyltrichlorosilane (OTS) with the OH groups present on the surface of SiO_2 in $scCO_2$. They also reported that CO_2 weakly physisorbs on the silica surface with an interaction strength similar to that of carbon tetrachloride and extracts part of the water adsorbed on the silica, behaving quite differently from traditional non-aqueous solvents where generally the water is adsorbed to the silica from the organic solvent. On the other hand, Zhao and Lu showed that isolated hydroxyls and germinal groups, but no hydrogen bond hydroxyls, participated in the silylation reaction due to the formation of hydrophilic networks among themselves [15]. Therefore, the extraction of water from the surface by CO_2 may increase the number of isolated hydroxyls group improving the condensation reaction on the surface.

The silylation reaction in $scCO_2$ has previously been used to modify the surface of different materials, obtaining highly ordered and densely packed monolayers of a wide variety of silane precursors [12,16–23]. However, the surface modification of porous materials using aminosilanes in supercritical CO_2 has never been reported. One of the reasons is that CO_2 can react with primary and secondary amine groups to form insoluble carbamate salts through the formation of the zwitterionic intermediates, thus hindering the silylation reaction on the surface. On the other hand, the CO_2 reaction with tertiary amines requires the presence of water because the mechanism involves the base catalyzed hydration of CO_2. In general, the surface modification of porous silica with an amino group has been carried out widely in the literature by conventional methods for different applications. Modification with an amino group has been found to be very useful for catalysis, enzyme immobilization and sorption of metals, anions, organics and gases [2,3,24]. Furthermore, amine modified mesoporous silica has recently been proposed as a material for adsorption of CO_2 generated from the fossil fuel combustion in order to reduce its emissions into the atmosphere [25,26].

In this paper, we report, for the first time, the modification of the silica SBA-15 surface by silylation reaction with DMAPTS using $scCO_2$. We explore the possibility of grafting tertiary amines to the silica surface since the CO_2 reaction with tertiary amines only occurs when a significant amount of water is present [27]. Our results indicate that surface modification using $scCO_2$ is faster and that the load of silane in $scCO_2$ is larger in comparison to those of the conventional process.

2. Materials and methods

2.1. Materials

Tetraethylorthosilicate (TEOS, 99+% pure), poly(ethyleneglycol)–block–poly(propylene glycol)–block–poly(ethyleneglycol) (Mw = 5800) (PEO–PPO–PEO), (*N*,*N*-dimethylaminopropyl)trimethoxysilane (DMAPTS, 96% pure), ethanol (>99.5% pure) and toluene