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Heterogenized vanadyl cations over modified silica surfaces: A comprehensive understanding toward the structural property and catalytic activity difference over mesoporous and amorphous silica supports

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Abstract

Using a postsynthesis grafting method, 3-aminopropyltriethoxysilane (3-APTS) was functionalized over silica gel and mesoporous silica materials like SBA-15 and MCM-41. Vanadyl cations were then immobilized over the functionalized amino groups of the silica samples and used as a catalyst in the liquid-phase oxidation reaction of cyclohexane. Elemental analysis, PXRD, TEM, N_2 adsorption–desorption isotherms, FTIR, ^{13}C and ^{29}Si MAS NMR, UV–vis, and EPR techniques were used to characterize the developed materials. Characterization results suggest that the percentage of 3-APTS grafting depends on the number of isolated and geminal silanol sites of the support material, the solvents used during the grafting reactions, and the sample pretreatment conditions. We found that using toluene as the dispersing medium and Si-MCM-41 as a support provides the maximum amount of amine functionalization, and thereby the highest percentage of vanadium immobilization. Catalytic activity and metal leaching studies show that vanadium-immobilized mesoporous solids are more active and stable than the silica gel-functionalized vanadium catalyst and a framework-substituted V-MCM-41 catalyst. The enhanced activity and stability of the immobilized vanadium catalysts compared with the V-MCM-41 and silica gel samples are attributed to the active metal site isolations, as well as to the spatial restrictions imparted from the concave silica surfaces of the mesoporous solids rather than the convex silica surfaces of the silica gel sample.

Keywords: Mesoporous solids; Silica gel; 3-APTS; Vanadium; Oxidation

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1. Introduction

Mesoporous silica materials like SBA-15 and MCM-41 with high surface area, uniform pore size, and high thermal stability are of considerable research interest in shape-selective heterogeneous catalysis, adsorption, separation, ion exchange, and hosts for various kinds of molecules [1–5]. The ability to control and to tune the pore size, morphology, and surface silanols has increased their applications dramatically [6,7]. However, a major drawback of these materials lies in their inherent inert nature toward various organic transformations, and hence surface modifications are necessary to make then more suitable, especially in the field of catalysis. Thus, the incorporation of transition metals into the framework of mesoporous materials is a novel technique for introducing active metal sites and thereby extends its applicability in heterogeneous catalysis, where the zeolite catalyst cannot perform [3,4]. However, these framework-substituted materials have serious drawbacks due to their low metal content and lower activity (because many of the active sites are well buried inside the pore channels), and the gradual decrease in catalytic activity after each cycle. Thus, the heterogenization of useful homogeneous catalysts on mesoporous solids is an area of research interest that is expanding due to considerable refinements in synthesis procedures. This technique provides potential advantages over its homogeneous counterparts, including easy separation of the catalyst and enhanced activity [8–12]. In previous work, various metal complexes were occluded inside the pores of the mesoporous support (using, e.g., a "ship in a bottle" technique) or grafted to

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the internal silanol sites; the activity of the catalysts was questionable due to leaching of the confined metal complexes under drastic liquid-phase reaction conditions [13]. However, the immobilization of homogeneous metal catalysts by strong chemical bonding to organo-modified mesoporous materials enhances their potential in two ways, by making them truly heterogeneous and by increasing activity.

Surface modifications over mesoporous materials are generally performed by two common ways: a postsynthesis method and a direct co-condensation method. Compared with postsynthesis grafting methods, which use a two-step synthesis procedure, the direct method allows preparation of nanoporous organic–inorganic hybrid materials in a limited time. However, the resultant materials usually show less structural ordering, and the organosilane precursor must be chosen carefully to avoid phase separations and Si–C bond cleavages during both synthesis and the surfactant removal process. On the other hand, the postsynthesis methods have the following advantages: (i) The structure of the resultant mesoporous materials is ordered after the grafting reactions; (ii) the functional groups can be chosen according to the requirements; and (iii) the obtained materials show higher hydrothermal stability. Even though the literature displays a wide spectrum of organo-tethered mesoporous materials with active functionalities, thiol (–SH) and amine ($-NH_2$) terminated mesoporous materials receive more attention than the other active pendant groups (–Cl, –OH, $(-PPh_3)_3$) for the immobilization of various traditionally used active homogeneous catalysts [5,6,9]. Recently, we demonstrated the immobilization of $(VO)^{2+}$ on an amino-terminated organosilane MCM-41, considering the point that harder transition metal ions form stable complexes with ligands with harder donor sites. Characterization of the fresh and spent catalyst after the naphthalene oxidation reaction showed that this significantly affects the structural and morphological features of the MCM-41 support [14]. Consequently, an attempt was made to extend the same procedures over the large-pore hexagonally ordered SBA-15 and on a silica gel sample to gain better insight into the changes occurring on the surface during the silylation process and to facilitate the design of a specific support for grafting and subsequent complexation procedures.

The present paper deals with the immobilization of $(VO)^{2+}$ species on an amino propyl-modified SBA-15/MCM-41/silica gel sample. Although the literature contains several reports over amine-functionalized mesoporous materials, a proper comparison or a comprehensive understanding of the structural changes and the binding nature of aminopropyl groups over SBA-15, MCM-41, and silica gel surfaces during postsynthesis modifications is highly limited. Thus, this work probes in detail the affect of solvents used for grafting of the aminopropyl groups, the effect of amino groups anchored toward the structural stability of the mesoporous silicas and the nature of vanadium species formed over SBA-15/MCM-41/silica gel surfaces. The obtained materials are then used as catalyst in the liquid-phase oxidation of cyclohexane using aqueous H_2O_2 as an oxidant and were compared with a hydrothermally synthesized V-MCM-41 sample.

2. Experimental

2.1. Materials

The following reagents were used for the synthesis of pristine SBA-15, MCM-41, and organo-modified mesoporous materials: tetraethyl orthosilicate (TEOS, Aldrich), silica gel (Loba Chemie, $S_{BET} = 444\ m^2\,g^{-1}$), pluronic 123 (P123, BASF), cetyl trimethyl ammonium bromide (CTMABr, Aldrich), 3-aminopropyltriethoxysilane (3-APTS, Lancanster) and vanadyl sulphate ($VOSO_4{\cdot}3H_2O$, Aldrich). All chemicals were used as received.

2.1.1. Synthesis of siliceous mesoporous materials (Si-SBA-15 and Si-MCM-41)

Siliceous SBA-15 was synthesized according to the procedure reported by Zhao et al. [2]. In a typical synthesis procedure, 2 g of P123 surfactant was stirred with 20 ml of deionized water at 35 °C. The mixture was stirred until the surfactant gets dissolved, followed by the addition of 30 g of 2 M HCl solution. The stirring was allowed to run for another 30 min, after which 4.5 g of TEOS was added dropwise to the stirred solution mixture. The mixture was then stirred for 24 h at 35 °C, transferred in an autoclave, and heated for another 48 h at 100 °C. The solid material obtained was then filtered, washed with water (5 times), and calcined at 540 °C for 6 h at a heating ramp of 1 °C/min to remove the occluded polymeric surfactants.

Gel with a molar composition of SiO_2:0.39 Na_2O:0.48 CTMABr:0.29 H_2SO_4:100 H_2O was used for the synthesis of siliceous MCM-41 [14]. The gel mixture was stirred for 2 h under ambient conditions and finally transferred into a Teflon-lined autoclave and kept at 100 °C for 72 h. The solid material thus obtained was then filtered, washed well with copious amounts of water until the filtrate showed a neutral pH, then air-dried. The surfactant inside the pores of the mesoporous material was removed by calcination as described above.

2.1.2. Functionalization of 3-aminopropyltriethoxysilane over mesoporous silica/silica gel (NH_2-SBA-15/ NH_2-MCM-41/NH_2-SG)

Before functionalization, the support silica materials were dehydrated at 150 °C for 3 h to remove the physisorbed water molecules. Postsynthesis modification of the mesoporous material was done by refluxing 1 g of the silica sample with 2.2 mmol of 3-aminopropyltriethoxysilane in 50 ml of dry toluene. The mixture was then allowed to run for 6 h at 100 °C. Finally, the material was filtered, washed with toluene, Soxhlet-extracted using a mixture of diethyl ether (100 ml) and dichloromethane (100 ml) for 24 h. and dried under vacuum. To evaluate the influence of solvents during grafting reactions, the grafting process was repeated using such solvents as dichloromethane, acetone, and chloroform.