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One-step synthesis and structural characterization of mesoporous vanadosilicates and super-microporous vanadosilicates

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Abstract

This paper reports the one-step ambient-temperature synthesis of porous vanadosilicates by using tetraethyl orthosilicate as a silicon source, V_2O_5 powder as a vanadium source, and long-chain *n*-alkylamine (C_8–C_{12}) as a structure directing agent. The texture of the materials was characterized by powder X-ray diffraction, N_2 adsorption–desorption isotherms, transmission electron microscopy, and thermogravimetric and differential thermal analysis. The pore size of the vanadosilicates depended largely upon the chain length of *n*-alkylamine. The *n*-alkylamine with longer carbon chain was advantageous for the formation of the larger pores. The Si/V ratio was another key factor affecting pore size of the vanadosilicates. When *n*-dodecylamine was employed as a structure directing agent, only mesopore structure vanadosilicates were obtained. However, when *n*-decylamine was used, the pore diameter of the vanadosilicates underwent a change from mesoporous scale to super-microporous scale through changing the Si/V molar ratio. The vanadosilicates exhibit a large BET specific surface area and a good thermal stability. The Si/V molar ratios of both mesoporous and super-microporous vanadosilicates with the relatively uniform pore channels could be reached 10.0 or even below. The vanadosilicates with a Si/V ratio in the range of 8.5–12 synthesized by using either *n*-dodecylamine or *n*-decylamine have a high thermal stability beyond 823 K. The nature of vanadyl species in the vanadosilicates was investigated with the use of several characterization techniques. It was determined by Raman, H_2-TPR and ESR that both V^VO_x and $V^{IV}O_x$ species were coexisted in the calcined vanadosilicates. The V^VO_x species occurred mainly in a form of monomeric tetrahedral vanadyl species on the pore wall, having one V=O bond and three bridging V—O—Si bonds linked with the framework. The V^{4+} centers were in an isolated octahedrally-coordinated $V^{IV}O_x$ mode. It was interesting to find that only a small part of $V^{IV}O_x$ species existed in the as-synthesized vanadosilicates, while a large part of $V^{IV}O_x$ species were formed upon calcination in air.

Keywords: Vanadosilicates; Mesoporous; Super-microporous; One-step synthesis; Pore structure; Vanadyl species

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1. Introduction

According to the definition accepted by IUPAC (the International Union of Pure and Applied Chemistry) [1], porous materials are classified into three categories based on their pore diameters (D): microporous ($D < 2$ nm), mesoporous ($2\text{ nm} < D < 50$ nm) and macroporous ($D > 50$ nm). Zeolites are crystalline microporous materials (microporous molecular sieves) that are the most widely used catalysts in industry. They possess unique properties with respect to both activity and shape selectivity [2]. However, the presence of micropores limits the catalytic performance of zeolites in the processing of long-chain and bulky hydrocarbons because of the severe restriction to the diffusion of the larger molecules in micropore channels. New synthesis routes have been undertaken to enlarge the pore size of molecular sieves and thus to extend their use in catalytic reactions of bulky molecules. In 1992, researchers at Mobil Research & Development Corporation reported the

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synthesis of mesoporous molecular sieves of the M41S family [3,4]. Such materials exhibit a large surface area beyond 1000 m^2/g, a very narrow pore size distribution in the mesoporous range, and high-density surface silanol sites. Since then, other varieties of mesoporous materials with a pore diameter typically in the range of 2.5–15 nm, such as HMS, MSU, SBA series, FSM-16 and KIT-1, have been largely reported [5–9]. Nevertheless, it should be pointed out that the pores having a size within such a range (2.5–15 nm) may be too large to be charged with useful size/shape-based separation and shape-selective catalytic reactions, and it has been suggested that the porous materials with pores in the super-microporous (pore diameter 1.0–2.0 nm) range may be better to use for such tasks. The synthesis of the super-microporous solids is believed to be a highly significant work since such materials bridge the gap between microporous and mesoporous materials. The synthesis of crystalline aluminosilicates such as PCH materials [10] and UTD-1 [11], the preparation of silica–metal oxide sol pillared clays [12], and the tailoring the pore-opening size of MCM-41 materials [13] are among the somewhat few significant examples at approaching the pore-diameter range of 1.0–2.0 nm. Most recently, some templated silica-base porous materials and silica-pillared niobic acid with uniform pore channels in this size domain have also been reported [14–21].

Heteroatom-modified microporous and mesoporous silica matrix have been of great significance because of their unique structures and potential applications in catalysis. The established importance of vanadium compounds as oxidation catalysts has made the introduction of vanadium into the porous silica matrix particularly desirable. Vanadium-containing porous silicates, including microporous and mesoporous materials, were reported to have excellent catalytic activity for the partial oxidation of organic compounds [22–24]. However, it should be pointed out that vanadium-containing microporous molecular sieves are inert for the oxidation of the larger organic molecules due to the narrow channels of the catalysts, while vanadium-containing mesoporous silica such as V-MCM-41 and V-MCM-48 are of interest in view of their likely catalytic properties and capability of being able to introduce bulky molecules into the mesoporous channels. So far, the direct-hydrothermal-synthesis route (denoted as DHT) for mesoporous vanadosilicates has been extensively studied and mainly used [25–29]. On the other hand, the conventional impregnation method could produce vanadium species on the surface of the siliceous materials and the dispersed vanadium species thus could be accessed by the reactant molecules involved in catalytic reactions. However, this method cannot ensure that the vanadium species are effectively introduced into the pore wall of the mesoporous silica. Moreover, the pore structure of the mesoporous silica may be destroyed to some extent and some “bulk-like” V_2O_5 also appears by the impregnation method [30]. The introduction of vanadium to mesoporous framework by a grafting method using an organic vanadium compound has also been reported [31]. However, the vanadium centers introduced by this way are thermally unstable, and their catalytic functions seem limited [32]. Mou et al. prepared a vanadium-immobilized catalyst, which was rather active and selective for the benzene hydroxylation reaction since the active vanadium sites were well isolated and anchored on the support [33]. Yonemitsu et al. developed a template-cation-exchange (TIE) route, in which the metal was introduced to mesoporous silica matrix by exchange of the template cations in as-synthesized sample with the metal ions in solution [34]. By this method, vanadium has been recently incorporated to the pore-wall surface of MCM-41 without leading to the collapse of the mesoporous structure [35]. By DHT way, vanadium was mainly incorporated inside the framework of MCM-41 [36]. Most recently, vanadyl species have been incorporated into MCM-48 by an anion-exchange route, in which the negatively charged ions contained in the channels of the as-synthesized MCM-48 are exchanged with VO_4^{3-} ions in Na_3VO_4 solution [37].

It should be noted that most preparation methods reported for mesoporous and microporous vanadosilicates suffer from a common problem, that is, the synthesis process is diverse and complicated, and time-consuming. Only several papers have presented the simple methods such as the room-temperature-synthesis routs developed by Sayari [38] and Pinnavaia [39], respectively. On the other hand, the vanadium content in the products is not sufficiently high, and the reported Si/V molar ratio is generally higher than 15. In addition, Na^+ ions, SO_4^{2-} ions and Cl^- ions are usually involved in the synthesis processes due to employing $VOSO_4 \cdot 5H_2O$ or Na_3VO_4 as a vanadium source or using HCl solution to adjust pH value of the reaction system, making the washing of the corresponding products very difficult. The existence of S and Cl element in catalyst is generally disadvantageous to catalytic reaction because these elements lead easily to the deactivation of the catalyst.

In this paper, we report a simple and novel route for the preparation of mesoporous vanadosilicates with the relatively uniform pore channels. In the preparing process, no Na^+ ions, SO_4^{2-} ions and Cl^- ions are introduced into the reaction system. The Si/V molar ratio in the obtained materials may reach 10 or even low. More interestingly, the super-mesoporous vanadosilicates or microporous vanadosilicates can be synthesized, respectively, through changing preparation conditions based on the same procedure. The nature of vanadyl species in the porous vanadosilicates is also investigated.

2. Experimental

2.1. Preparation

The porous vanadosilicates were prepared at ambient-temperature by employing tetraethyl orthosilicate (TEOS) as a silicon source and vanadium pentaoxide (V_2O_5)