

# Vanadium-containing ordered mesoporous silicates: Does the silica source really affect the catalytic activity, structural stability, and nature of vanadium sites in V-MCM-41?

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## Abstract

A series of vanadium-substituted mesoporous materials were synthesized hydrothermally with the use of two commonly used silica sources, fumed silica and tetra ethyl orthosilicate. The extent of mesopore structural ordering was confirmed from X-ray diffraction, N<sub>2</sub> physisorption, SEM, and TEM, and the presence and nature of vanadium species inside the framework of the MCM-41 matrix was confirmed in detail with the use of various characterization techniques like FT-IR, <sup>29</sup>Si MAS NMR, DRUV-vis, EPR, <sup>51</sup>V MAS NMR, and Raman analysis. It is deduced from the above characterization techniques that, regardless of the silica source, vanadium is incorporated into the silica framework and thereby increases the structural ordering and wall thickness of the mesoporous material. Thermal and hydrothermal studies performed over the V-MCM-41 catalysts show that the Si–O–Si inorganic backbone from a fumed silica source is more resistant to severe thermal treatments and hydrolysis than the tetraethyl orthosilicate-synthesized catalysts. Spectroscopic characterization reveals the existence of easily accessible isolated tetrahedral vanadium sites on V-MCM-41 catalyst prepared from fumed silica catalyst, whereas the sample obtained from a tetraethyl orthosilicate silica source shows vanadium in more disordered sites. Catalytic results show that both catalysts display excellent activity toward the epoxidation reaction of bulkier olefins, and the exceptional activity of the fumed silica catalyst may arise from the more isolated tetrahedral sites and the complementary textural characteristics, which may facilitate the easy access of substrate to the isolated framework metal sites.

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## 1. Introduction

MCM-41, a typical member of the M41S family of mesoporous molecular silicates, had attracted considerable attention as a catalyst support for the processing of bulkier molecules, because of its large surface area (~1000 m<sup>2</sup>/g), uniform pore size (15–100 Å), and high-density surface silanol sites [1]. Numerous studies had been devoted after its discovery to surface modification in order to increase its structural stability and thereby to utilize its unique property in

various fields such as separation science, host-guest chemistry, optoelectronics, etc. [2–4]. Even though it is an attractive candidate, pure siliceous MCM-41 shows limited applications in various organic transformations, and hence modification of this material by the introduction of various active metal sites is necessary for its utility in catalysis. Thus the isomorphous replacement of silicon with transition metals or postsynthesis metal modification (impregnation/grafting) helps to create well-defined heterogeneous catalysts for designed applications [4,5]. However, there is considerable debate over the stability of metal-containing mesoporous materials prepared by various routes, and in a more generalized way it is argued that the isomorphously substituted metal species on the silicate framework would not leach easily un-

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der reaction conditions and hence exist as true heterogeneous catalysts!

Apart from Ti-MCM-41, one of the well-studied metal-containing mesoporous materials is V-MCM-41, because of its catalytic potential for selective oxidation reactions with aqueous  $\text{H}_2\text{O}_2$ /TBHP as oxidants [6–9]. Even though Reddy et al. [6] had first successfully synthesized vanadium-substituted MCM-41, a detailed characterization of these materials was carried out independently by Tuel et al. [10] and Luan et al. [11], and they concluded from their studies that (i) vanadium centers in the as-synthesized and calcined forms of V-MCM-41 had the same coordination state, and no direct chemical bonding was formed with the silicate frame work, and (ii) vanadium occurs simultaneously in two forms on the support surfaces, as framework and extraframework species. Even after a decade, there is still much research in this area, and arguments continue over the assignment of various bands for these mesoporous materials; hence concluding evidence is still needed to identify the exact species formed. Apart from these discrepancies, the stability/heterogeneity of vanadium-containing materials under severe reaction reactions is highly limited, and hence careful and detailed investigations are needed to account for the observed catalytic activity behavior [12,13]. Usually hydrothermal and thereby structural stability are the two important factors that determine the applicability of any mesoporous material in liquid-phase oxidation reactions. Actually the solid wall surfaces between the mesopores are too delicate to withstand severe reaction conditions, and hence a rapid disorder in mesoporosity is observed after drastic reaction conditions, which may enhance the leaching of framework substituted metal species to the reaction mixture and thereby limit its further usability. Hence it is of paramount importance to devote more attention to modification of the surface of the mesoporous materials for its wide applicability and reusability.

It is known that increased hydrothermal stability of mesoporous materials is related to an increase in the degree of silicate condensation, and hence control of the pH of the gel mixtures had been efficiently utilized in the synthesis of high-quality mesoporous materials [14]. Alternatively, prolonged stirring time plus hydrothermal treatments at higher temperatures ( $>150^\circ\text{C}$ ) are also employed to increase the stability of the mesoporous materials. However, the latter method suffers from numerous drawbacks, like the dissolution/decomposition of the micelles and further possible phase transformations due to the increased tail motion of the surfactants. Hence it is reasonable that the cooking parameters had a prominent effect on the structural perfection, percentage of metal incorporation, and stability. Even though vanadosilicates are the subject of a greater percentage of the literature reports on M-MCM-41 materials, thorough and systematic investigations of the stability and nature of vanadium sites are scarce, and hence the present study was undertaken to probe in detail the effect of silica sources in the synthesis of V-MCM-41 materials. Since it is known that the

activity and selectivity of vanadium-containing materials are very sensitive to the nature and coordination of vanadium ions, it is crucial to verify whether the silica source had a role in the nature of vanadium sites and in their further structural stability [7].

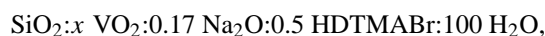
In the present work, we investigated in detail the nature of vanadium species formed on different silica sources (fumed silica and tetraethyl orthosilicate), in order to (i) uncover the structural property/stability difference in Si-MCM-41 and V-MCM-41 materials under different silica precursors and, (ii) determine whether the silica source had a role in the incorporation and nature of vanadium species in V-MCM-41 materials. The stability and heterogeneity of the developed materials were further verified in the epoxidation reaction of cyclooctene, through a series of heterogeneity studies.

## 2. Experimental

Vanadium-incorporated molecular sieves and pure siliceous MCM-41 were synthesized hydrothermally in the temperature range of  $100^\circ\text{C}$ , with vanadyl sulfate ( $\text{VO}_2\cdot 3\text{H}_2\text{O}$ ; Aldrich) as the vanadium source and fumed silica ( $\text{SiO}_2$ , 99.8%; Aldrich) and tetraethyl orthosilicate (TEOS, 98%; Aldrich) as the silica source.

### 2.1. Synthesis procedure

Vanadium-incorporated mesoporous materials were synthesized by a one-pot synthesis procedure with the use of a gel composition of



where HDTMABr is hexadecyl trimethyl ammonium bromide and  $x$  varies from 0.025 to 0.012. Typically, an aqueous solution of HDTMABr and vanadyl sulfate was added slowly to a vigorously stirred solution mixture of fumed silica/TEOS in alkaline condition. The mixture was stirred at room temperature for 5 h and then subsequently autoclaved at  $100^\circ\text{C}$  for 4 days. For comparison purposes, respective silica polymorphs are also prepared by the same method, but without the addition of vanadyl sulfate. The solid material obtained was then filtered and washed well with copious amounts of water, until the filtrate showed a neutral pH, and then dried at  $80^\circ\text{C}$  for 3 h. The surfactant occluded inside the pores of the mesoporous material was removed by calcination at  $540^\circ\text{C}$  for 6 h, at a heating ramp of  $1^\circ\text{C}/\text{min}$ , as the mesostructure of the materials is seriously affected at higher heating temperature rates. To evaluate the hydrophobicity of the material, both VMS and VMT samples ( $\text{Si}/\text{V} = 55$ ) were silylated under a nitrogen atmosphere with dimethyl dichloro silane (Aldrich) as the silylating agent. For that, 1 g of dimethyl dichloro silane in dry toluene was added dropwise to a stirred solution mixture of calcined V-MCM-41 sample (1 g) in 50 ml toluene. The solution was then allowed to reflux for 6 h, and finally the materials were filtered,

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