

Structure and Applications of Isolated VO_x on H-MFI Zeolite for the Conversion of CH₄ and C₂H₆

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Introduction

The synthesis and structure/functional characterization of well-defined and single-site VO_x structures within spatially-constrained environments remain formidable but important challenges. Conventional aqueous methods fail to exchange high-valent cations because of the size and charge of V(V) isopolyanions at pH values consistent with zeolite stability; these methods form instead vanadate oligomers at external zeolite surfaces [1-2]. An alternate approach exploits vapor phase exchange of volatile VOCl₃ species, which can access intrazeolitic exchange sites via diffusion of gaseous species at modest temperatures. Here, we report the synthesis of isolated single-site VO_x species in H-ZSM5 using these methods and describe complementary methods for the detailed characterization of their local structure.

Catalyst Preparation

Vapor phase exchange was carried out in a glass sublimation cell. H-ZSM5 (Si/Al_f = 13.4) was dried under vacuum (< 0.13 Pa) at 573 K for 1 h, then transferred to a N₂ atmosphere where VOCl₃ (0-5 wt.%) was injected by syringe into the cell [3]. The cell was re-evacuated and sealed; it was then heated to 473 K after which the contents were removed and hydrolyzed at 473 K in flowing 20% O₂/He saturated with H₂O (0.5 kPa).

Results and Discussion

Zeolite materials, after sublimation with VOCl₃ and hydrolysis (as described above), were investigated to assess the extent of Si-O_fH-Al exchange. No change in framework Al (Al_f) content was observed for V/Al_f ratios of 0-0.5 as determined by ²⁷Al and ²⁹Si MAS NMR (Bruker AV-500, 14 kHz rotation), and <10% of Al_f were removed at 0.5-1 V/Al_f. Infrared spectra were measured (Mattson 10000) in the hydroxyl region; the decrease in hydroxyl band intensity (~3600 cm⁻¹ for acidic hydroxyls) was proportional to V/Al_f ratios up to stoichiometric loadings (Δ(OH)/V = 0.9 ± 0.2). The amount of residual hydroxyls in V-ZSM5 was also measured by isotopic exchange with D₂; the resulting HD and H₂ formed were measured using on-line mass spectrometry (MKS Minilab) to quantify the remaining zeolite hydroxyl content. The maximum in HD formation decreased in temperature from 791 K to 700 K in V-ZSM5 samples, indicating that vanadium catalyzes D₂ dissociation and subsequent HD recombination reactions. The concentration of hydroxyls also decreased linearly with V loading ((Δ(OH)/V = 1.1 ± 0.2); confirming the one-to-one exchange ratio of vanadium with Si-O_fH-Al, as found with infrared spectroscopy.

Two structures are consistent with this hydroxyl exchange stoichiometry: a VO₂⁺ monomer and a V₂O₄²⁺ dimer. The Si-O_fVOCl₂-Al species, formed by reaction of VOCl₃ with zeolitic Si-O_fH-Al, is hydrolyzed to form Si-O_fOV(OH)₂-Al. The hydroxyl vanadium species then react either intramolecularly to form VO₂⁺ anchored to the framework via linking oxygen atom(s) or

intermolecularly with another Si-O_fOV(OH)₂-Al to form V₂O₄²⁺. Trimeric and larger VO_x species are unlikely to form due to the low density of proximate Al_f in these zeolites.

Raman spectra were also measured (Figure 1) on V-ZSM5 samples. Spectra for samples with V/Al_f less than 0.4 show one intense peak near 1070 cm⁻¹ that increases in intensity with V content, and weaker bands near 1010 cm⁻¹ assigned to V-O-Si stretches. At higher loadings, a second intense peak near 1044 cm⁻¹ is also observed, suggesting that two VO_x species are present. Assignments were confirmed by optimizing structures and simulating vibrational spectra using density functional theory (Gaussian-03, B3LYP/6-31G(d)). Raman spectra were also measured in 20% O₂/He saturated with H₂O; H₂O interacts only with accessible vanadium atoms and disrupts V-O bonding. Raman bands at 1070 and 1044 cm⁻¹ disappeared immediately upon exposure to H₂O, and weaker bands near 1000 cm⁻¹ were observed, indicating that all VO_x species are isolated and accessible. V-ZSM5 materials were regenerated upon removal of H₂O. Scattering contributions from both vanadium structures were also observed in X-ray absorption spectra. The fraction of vanadium atoms present as dimers was 0.36 as determined from the simulation of EXAFS with V/Al_f near unity.

Oxidative C₂H₆ dehydrogenation (ODH) rates and selectivities were measured at 673 K on these samples. ODH rates and ethene selectivities increased with increasing V content; these materials were much more active than V-silicalite. Below 0.4 V/Al_f, turnover rates were 8 ± 1 × 10⁻⁴ s⁻¹; a step increase in reactivity occurred at higher loadings (13 ± 1 × 10⁻⁴ s⁻¹), indicating that bridging oxygen in dimeric structures, present at high loadings, and strained V-O-Al bonding in dimers lead to more reactive structures, consistent with the more reducible nature of these dimers. V-ZSM5 materials were also active for the non-oxidative conversion of CH₄ at 973 K. Forward rates were 0.9 × 10⁻⁴ mol C₆H₆ (g-atom Mo)⁻¹ s⁻¹ with 68% selectivity to C₂H₄ products. Pre-reduction/carburization in C₂H₄ increased forward rates to 6 × 10⁻⁴ mol C₆H₆ (g-atom Mo)⁻¹ s⁻¹.

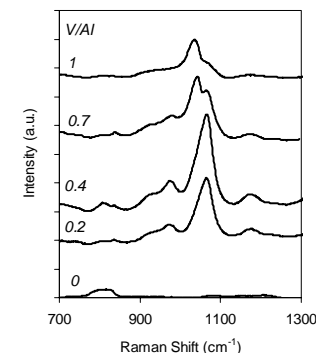


Figure 1. Raman spectra of V-ZSM5 with different V/Al_f (0- 1) loadings.

Significance

The study describes a general method to prepare isolated metal-oxo species within medium-pore zeolites and to establish their structure complementary spectroscopic and chemical techniques. Isolated and catalytically interesting materials were synthesized by anchoring VO_x monomers and dimers onto cationic exchange positions up to stoichiometric loadings.

References

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