

Abstract

Isomorphous substitution of Al or Si in zeolites/molecular sieves with transition metals having redox properties leads to oxidation activity combined with shape selective properties. Ferrisilicates and titanium silicates are two such systems which have been synthesized and their catalytic applications explored. Vanadium incorporated molecular sieves are a new class of materials which can also catalyze various oxidation reactions selectively. They have interesting catalytic properties in ammoxidation of xylenes and propane, oxidative dehydrogenation of propane, oxyfunctionalization of alkanes and hydroxylation of aromatics. This thesis describes, in detail, the synthesis, characterization and catalytic properties of vanadium silicate molecular sieves with MEL structure. The major objectives of the work are 1) to synthesize vanadium silicate molecular sieves, 2) to characterize the structural environment of the vanadium in them and 3) to study the physico-chemical and catalytic properties. Vanadium silicate molecular sieves with MEL structure have been prepared with different Si/V ratios (40-300). Tetraethyl orthosilicate and a vanadium salt were used as ingredients and tetrabutyl ammonium hydroxide as templating agent. Three different sources of vanadium with different oxidation states viz. VCl_3 (III), $VOSO_4$ (IV) and NH_4VO_3 (V) were tested in the synthesis of vanadium silicates. The gels containing $VOSO_4$ and NH_4VO_3 were clear solutions that with VCl_3 was slightly turbid. The chemical analysis of the sample showed that only a part of the vanadium was retained in the samples after hydrothermal crystallization. The amount of the vanadium retained in the sample depends on the source of vanadium and is approximately 60, 50 and 25 % for VCl_3 , $VOSO_4$ and NH_4VO_3 , respectively. The oxidation activity of vanadium silicates prepared using $VOSO_4$ as vanadium source was found to be high. Hence, further detailed studies on the synthesis, characterization and activity of vanadium silicates were carried out using $VOSO_4$ as vanadium source. The effect of various synthesis parameters such as temperature, organic additive, Si/V ratios and water content on the crystallization kinetics of vanadium silicates are presented in Chapter II. An increase in Si/V molar ratio in the reaction mixture enhanced the rate of crystallization. $SiO_2/TBA-OH$ molar ratio of 5 was found to be optimum in the synthesis of vanadium silicates. An increase in the pH of mother liquor with crystallization was observed. This indicates the incorporation of probably both V and Si in the framework. The apparent activation energies for nucleation and crystallization were calculated to be 53.80 kJ mol⁻¹ and 56.54 kJ mol⁻¹, respectively. Physico-chemical characterization of V-silicates was carried out using XRD, spectroscopic (IR/FTIR, ESR, MAS NMR, UV-VIS) and adsorption techniques (Chapter III). The unit cell parameters of VS-2 samples increased uniformly and regularly with the vanadium content in the samples. On steaming the samples, a reduction in the unit cell parameters was observed. An absorption band at around 965 cm⁻¹ was observed in the IR spectra of VS-2 samples. This band is absent in the IR spectra of pure silicalite-2 and vanadium impregnated silicalite-2 samples. It has been proposed that the vanadium ions are probably coordinated at defect sites where the concentration of the Si-OH groups is likely to be high. A broad IR absorption band at 3532 cm⁻¹ (due to hydrogen bonded hydroxyl groups) was observed in all VS-2 samples. There is a correlation between the integrated intensity of this band (3532 cm⁻¹) and the vanadium content of the sample. This observation supports the model proposed for vanadium silicates. The characterization of the surface acidity of the VS-2 samples has been carried out using ammonia and pyridine adsorption. The FTIR spectra on the desorption of ammonia shows two distinct bands at 1680 and 1450 cm⁻¹ due to ammonium ions (ν_s and ν_{as} of NH_4^+ , respectively). The spectra of pyridine adsorption showed a weak band at 1547 cm⁻¹ due to pyridinium ions. This indicates the presence of Bronsted acid sites. However, the intensity of these bands decreased drastically on evacuation above 373 K indicating that these Bronsted acid sites are weak in nature. These bands are absent in pure silicalite-2 and are probably related to V-OH species of VS-2. This is in agreement with the sodium exchange behavior of the samples. The ESR spectra of the as-synthesized vanadium silicates have well resolved anisotropic 8-line hyperfine splitting. The hyperfine splitting at room temperature indicates atomically dispersed vanadium in the sample. The 'g' values and hyperfine coupling constants ($g_{\parallel} = 1.932$; $g_{\perp} = 1.981$; $A_{\parallel} = 185$ G and $A_{\perp} = 72$ G) are notably different from those observed for VO_2^+ exchanged into ZSM-5. They are assigned to V^{4+} at framework positions. A linear increase in the ESR signal intensities with vanadium content (of as-synthesized samples) and corresponding parallel increase in unit cell volume (calcined samples) strongly supports the presence of vanadium at framework positions. After calcination no ESR signal was observed indicating complete oxidation of V^{4+} to V^{5+} . After reducing in H_2 as well as after using in catalytic reaction the spectra reappeared. This shows the reversibility of $V^{4+} \leftrightarrow V^{5+}$ transition. The 51V MAS-NMR spectra of VS-2 samples reveal that the nature of vanadium strongly depends on the source of vanadium utilized during the synthesis. The 51V NMR spectrum of VS-2 prepared using $VOSO_4$ as source shows a main signal at -573 ppm (relative to $VOC13$). The observed line width at half height (approximately 50 ppm) is much narrower than that reported (around 250 ppm) for supported vanadium oxide catalysts. This is similar to those observed in monomeric vanadates with vanadium ions in distorted tetrahedral coordination. The absence of

an absorption band around -300 ppm shows that no V₂O₅ like phase and clustered vanadium are present. The UV-VIS spectrum of VS-2 shows an absorption band at 310 nm, which also indicate distorted tetrahedral environment for V⁵⁺ ions. Adsorption of n-hexane and cyclohexane also show the absence of occluded amorphous material. A possible environment of vanadium in VS-2 has been proposed consistent with our results. Vanadium silicates are found to have interesting catalytic properties in various oxidation reactions. They are active in the oxidation of alkanes, benzene, phenol, alkyl aromatics, aniline and sulfides (Chapter IV). Vanadium silicate-2 (VS-2) molecular sieves in the presence of dilute hydrogen peroxide oxidized alkanes (n-hexane, n-heptane, n-octane and cyclohexane) to corresponding alcohols and carbonyl compounds. They are also able to activate the primary C-H bond of the n-alkanes giving primary alcohols and aldehydes. However, the activation of the carbon atom at the second position is preferred to others and follows the order 2 > 3 > 4 > 1. The oxidation conversions and H₂O₂ selectivities decreased in the order n-hexane > n-heptane > n-octane > cyclohexane. This order is consistent with the large decrease in diffusivities with increase in chain length and molecular size of the paraffin molecules. Solvents have considerable influence in the oxyfunctionalization of alkanes. Acetonitrile is found to be the most effective solvent with highest selectivity to the monosubstituted products. The activity and selectivity seems to be related to the polarity of the solvent and decreased in the order: acetonitrile > methanol > acetone. The formation of the radical type intermediate has been inferred from the ESR observations. A mechanism involving vanadium peroxy-radical which abstracts a H atom from the hydrocarbon molecule to give a carbon radical, which is further hydroxylated to alcohol is proposed. Vanadium silicates are active in the hydroxylation of benzene. The product distribution contains phenol and para-benzoquinone (PBQ). Formation of PBQ was also observed when titanium silicates were used as catalysts, but not when acidic zeolites were used. Hence, as in titanium silicates, in vanadium silicates also peroxy species may be involved in the hydroxylation. VS-2 is an efficient catalyst in hydroxylation of phenol to hydroquinone and catechol. Solvents have interesting influence in this reaction. Water is the most suitable solvent in which the activity is comparable to that of titanium silicates. The phenol conversions and H₂O₂ selectivity's decreased in the order water > acetonitrile > acetone. When acetone is the solvent, only hydroquinone along with small quantities of para benzoquinone were the products. No hydroxylated products of phenol are formed when methanol is used as a solvent. In the oxidation of alkyl aromatics, VS-2 is active in both the hydroxylation of aromatic nucleus as well as the oxidation of side chain alkyl groups. Benzyl alcohol, benzaldehyde and ortho- and para-cresols were the products in the oxidation of toluene. The formation of benzaldehyde as the major product shows their ability to oxidize side chain methyl groups more effectively. In contrast, on titanium silicates, only ring hydroxylation takes place giving cresols as products. VS-2 is active in oxidation of aniline. As with alkyl aromatics, both ring hydroxylation and oxidation of amino group are possible. However, product distribution depends on the solvent used. Hydroxy anilines are the products when acetonitrile is used as solvent. Nitrobenzene and azoxybenzenes are the products when water is used as solvent. Thus solvents have a profound influence on the conversion and selectivity. VS-2 is found to be the most effective catalyst in the oxidation of sulfides to sulfoxides and sulfones, among VS-2, TS-2, silicalite-2 and ZSM-11.