Oxyfunctionalization of Alkanes with H_2O_2 catalysed by Vanadium Silicates

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Vanadium silicate molecular sieves can catalyse the oxyfunctionalization of alkanes to corresponding alcohols, aldehydes and ketones; they are able to oxidise the primary carbon atom as well.

The introduction of oxygen containing functional groups in alkanes proceeds with low selectivities over most homogeneous and heterogeneous catalysts. The catalysts used in alkene oxidation are ineffective for alkanes.[1,2] Many transition metal complexes, on the other hand, are very effective in C–C bond cleavage leading to complete oxidation to respective acids.[2] Oxyfunctionalization with high selectivities was reported from natural and synthetic metalloporphyrin systems.[3,4] The use of zeolite and molecular sieve based catalysts in oxidation reactions is assuming a lot of importance in recent times. Titanium silicates exhibiting a pentasil structure (both TS-1 and TS-2), particularly, have been found to catalyse the oxidation of a variety of organic substrates with an aqueous solution of H_2O_2 and are found to be very selective in the oxidation of alkanes.[5–7]

Recently, we have prepared vanadium silicate molecular sieves with vanadium in framework positions.[8,9] These are found to be active in the hydroxylation (benzene to phenol, phenol to hydroquinone and catechol[10]) and simultaneous oxidation and hydroxylation (toluene to benzyl alcohol, benzaldehyde and cresols; aniline to nitrobenzene, azoxybenzene and hydroxy anilines[11]) reactions. We now report here that these vanadium silicate molecular sieves can oxidise unactivated alkanes under mild conditions with aqueous hydrogen peroxide. Unlike titanium silicates, vanadium analogues are able to oxidise the primary carbon atoms of alkanes to corresponding alcohols and aldehydes.

The hydrothermal crystallization of vanadium silicates with MEL structure was carried out using the following molar compositions: $SiO_2 : 0.2\ TBA\text{–}OH : X\ VO_2 : 30\ H_2O$.†

Details of the synthesis of vanadium silicates of different Si : V ratios and their characterisation are given elsewhere.[8,9] In general, the samples were characterised by X-ray diffrac-

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† *Abbreviations used*: MEL = Mobil Eleven, earlier nomenclature, ZSM-11; TBA = tetrabutyl ammonium (template for synthesis).

Table 1 Oxidation of alkanes over vanadium silicate molecular sieves[a]

Reactant	Turnover[b]	H_2O_2 selectivity[c]	Product distribution (wt.%)[d]									Product selectivity[f]
			1-ol	2-ol	3-ol	4-ol	1-al	2-one	3-one	4-one	Others[e]	
n-Hexane	1198	57.1	3.7	9.2	8.2	—	7.2	26.3	25.0	—	21.4	79.5
n-Heptane	1030	50.1	3.1	6.8	5.8	2.1	4.2	25.1	21.7	7.0	24.2	75.8
n-Octane	821	43.4	4.6	5.9	4.6	3.8	3.2	21.7	18.0	13.8	24.4	75.6
Cyclohexane	706	32.7			33.3[g]				60.7[h]		6.0	94.0

[a] Reaction conditions: catalyst = 0.1 g (Si : V = 78); alkane = 5 g; temp. = 373 K; alkane : H_2O_2 (mole ratio) = 3; solvent = acetonitrile; reaction duration = 8 h. [b] Moles of alkane converted per mole of vanadium. [c] H_2O_2 utilized for monofunctional product formation. [d] 1-ol = alcoh-1-ol; 2-ol = alcoh-2-ol; 3-ol = alcoh-3-ol; 4-ol = alcoh-4-ol; 1-al = 1-aldehyde; 2-one = ket-2-one; 3-one = ket-3-one and 4-one = ket-4-one of corresponding alkanes. [e] Mostly oxygenates with more than one functional group and lactones. [f] (Alcohols, aldehyde and ketones/alkane reacted) × 100. [g] Cyclohexanol. [h] Cyclohexanone.

tion (XRD), IR, electron spin resonance (ESR), scanning electron microscopy (SEM), NMR and adsorption techniques. A linear increase in the unit cell parameters (XRD), the intensity of 965 cm^{-1} (IR) band and the integrated intensity of ESR peaks with increasing vanadium content and a chemical shift to δ −573 observed in ^{51}V MAS–NMR spectrum,[12] strongly suggested the presence of vanadium in the framework position of the MEL structure.[8,9] One such well characterised vanadium silicate with Si : V ratio of 78 was used in this study.

The catalytic reactions were carried out in a stirred autoclave (Parr Instrument, USA) of 300 ml capacity at a temperature of 373 K under autogeneous pressure. Typically; 0.1 g of the catalyst, 2.53 g of 26% aqueous H_2O_2 (alkane–H_2O_2 = 3 moles) and 5 g of alkane were mixed in 25 ml of acetonitrile (solvent) and the reaction was carried out for 8 h. After the completion of the reaction, 25 ml of acetone was added to the products. The products were then separated from the catalyst and analysed by GC (HP 5880) using a capillary (crosslinked methylsilicone gum) column and flame ionization detector (FID).

The results of the oxidation of linear saturated hydrocarbons, *viz*., n-hexane, n-heptane, and n-octane and cyclohexane are summarised in Table 1. The major products of the reaction are corresponding alcohols, aldehydes and ketones. Small quantities of other products with more than one functional group (*e.g.* dihydroxyalkanes) and lactones were also detected. The interesting observation is the formation of primary alcohols and aldehydes. The product distribution shows that the activation of carbon atom at the second position is preferred to others and follows the order 2 > 3 > 4 > 1. Similar results have been reported in this reaction by using titanium silicates,[5–7] but then they are inactive in the oxidation of the primary C–H bonds. The ability of the vanadium silicates to activate the primary carbon atom is also demonstrated in the oxidation of other organic substrates. For example, toluene is oxidised to benzyl alcohol, benzaldehyde and cresols in presence of H_2O_2 at 353 K, with an H_2O_2 selectivity of *ca*. 50% (Table 2). In addition, a higher aldehyde and ketones to alcohol ratio in the product distribution (Table 1) indicates a greater oxidation ability of vanadium silicates compared to titanium silicates in this reaction.

Table 1 also compares the oxidation conversions of the linear alkanes and cyclohexane. The oxidation turnover of n-hexane and n-heptane is found to be over 1000 and that of n-octane and cyclohexane is only marginally lower. On titanium silicates, similar activity and slighlty higher H_2O_2 selectivity have been reported.[6,7] However, Tatsmal *et al.* have observed a large difference in oxidation turnovers between n-hexane and cyclohexane (or 2-methyl-3-methylpentane) over titanium silicate catalyst (under low turnover conditions of <10) and attributed this to substrate shape selectivity.[5] The oxidation conversion and H_2O_2 selectivity decreased in the order, n-hexane > n-heptane > n-octane > cyclohexane (Table 1). This order is consistent with the observed large decrease in diffusivity of these alkanes in zeolites with increase in chain length and molecular size.[13]

Table 2 Oxidation of toluene over vanadium silicate molecular sieves[a]

Conversion (wt.%)	H_2O_2[b] selectivity	Benzyl alcohol	Benzaldehyde	*o*-Cresol	*p*-Cresol	Others
11.7	49.5	7.7	52.2	19.7	17.1	3.7

[a] Reaction conditions: catalyst = 0.1 g; toluene = 1 g; temp. = 353 K; alkane : H_2O_2 (mole ratio) = 3; solvent = acetonitrile; reaction duration = 12 h. [b] H_2O_2 utilized in the formation of benzyl alcohol, benzaldehyde and cresols.

Investigation of the extent of oxidation with time revealed that the ratio of aldehyde (ketones) to alcohol increased with time. This suggests that the aldehyes and ketones are secondary products from respective primary and secondary alcohols. After 8 h, the product distribution levelled off to the values given in Table 1.

A test reaction with silicalite-2 or vanadium impregnated silicalite-2 as catalysts resulted in 3 to 4% n-hexane conversion with less than 25% selectivity to desired products. We believe that the oxyfunctionalization of alkanes is selectively effected only by those vanadium species which are in the framework positions as in the case of titanium silicates.

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