JOURNAL OF CATALYSIS **141**, 604–611 (1993)

Studies on Crystalline Microporous Vanadium Silicates

III. Selective Oxidation of *n*-Alkanes and Cyclohexane over VS-2

P. R. HARI PRASAD RAO, A. V. RAMASWAMY, AND P. RATNASAMY

National Chemical Laboratory, Pune-411 008, India

Received September 30, 1992; revised December 15, 1992

The oxyfunctionalization of *n*-alkanes (C6, C7, and C8) and cyclohexane over vanadium silicates (VS-2) with Si/V = 79, 122, and 161 in presence of aqueous H_2O_2 yields corresponding alcohols and carbonyl compounds at 373 K. Unlike titanium silicates, VS-2 is able to activate the primary carbon atoms of *n*-alkanes, giving rise to primary alcohols and aldehydes in addition to secondary alcohols and ketones. The latter are, however, the preferred products of oxidation. The oxidative conversions and the H_2O_2 selectivities decreased in the order, *n* C6 > *n* C7 > *n* C8 > cyclohexane, consistent with the decrease in the diffusivity of these alkanes in the zeolites. Solvents have considerable influence on the conversion, CH_3CN being the most suitable. The formation of a radical-type intermediate has been confirmed by ESR spectral observations. A possible mechanism for the oxidation through a peroxo radical intermediate has been proposed. © 1993 Academic Press, Inc.

INTRODUCTION

The presence of transition metals in the framework of a zeolite lattice can impart oxidation activity which can be combined with shape selective properties of the molecular sieve. Titanium silicate molecular sieves, both TS-1 and TS-2, have been studied extensively in such applications and are used industrially in the hydroxylation of phenol (*1–4*). Vanadium-incorporated molecular sieves are a new class of materials which can also catalyze various oxidation reactions selectively. They are reported to have superior catalytic activity in the ammoxidation of propane and xylenes (*5*, *6*), oxidation of butadiene to furan (*7*), and oxidative dehydrogenation of propane to propylene (*8*). The nature of vanadium and its environment in the molecular sieve, however, are not clear, although they are reported to be extremely well dispersed.

Oxyfunctionalization of alkanes with high selectivities on natural and synthetic metalloporphyrin systems, and on vanadium (V) oxo peroxo complexes are well documented (*9–11*). Recently, we have reported the synthesis of vanadium silicate molecular sieves with MEL structure, which show interesting oxidation properties (*12–14*). They are able to oxidize unactivated alkanes under mild conditions with aqueous hydrogen peroxide. In a preliminary communication, we had reported that unlike titanium silicates, the vanadium analogs are able to oxidize even the primary carbon atoms of alkanes to the corresponding alcohols and aldehydes (*15*). We report, in this paper, our detailed studies on the catalytic activity of VS-2 (vanadium silicates with MEL structure) in the oxyfunctionalization of alkanes. The influence of various reaction parameters on the activity and selectivity of this catalyst and a possible mechanism of the oxidation reaction are presented.

EXPERIMENTAL

The hydrothermal crystallization of vanadium silicates with MEL structure was carried out using the molar compositions

$$SiO_2 : 0.2\ \text{TBA-OH} : X\ VO_2 : 30\ H_2O,$$

where $X = 0.03–0.01$ and TBA-OH = tetrabutyl ammonium hydroxide. Details of the synthesis of vanadium silicates of different Si/V ratios and their characterization are

0021-9517/93 $5.00

reported elsewhere (*12–14*). The samples were characterized by XRD, IR, ESR, SEM, NMR, and adsorption techniques. A linear increase in the unit cell parameters (XRD), an increase in the intensity of 965 cm^{-1} (IR) band, and the integrated intensity of ESR peaks with increasing vanadium content and a chemical shift to −573 ppm observed in ^{51}V MAS-NMR spectrum strongly suggested the presence of vanadium in framework positions of the MEL structure (*14*). The calcined samples were treated with 1 *N* ammonium acetate and calcined at 753 K in air for 6 h before using them in the catalytic reactions. Three such samples with Si/V ratios of 79, 122, and 161 have been used along with the vanadium-free silicalite-2 sample. For comparison an Al-ZSM-11 (Si/Al = 82), a titanium silicate sample (TS-2, Si/Ti = 77) and a vanadium-impregnated silicalite-2 sample (Si/V = 75) have been used in this study. They were prepared as per published procedures (*16*, *17*).

The oxidation of alkanes was carried out in a stirred autoclave (Parr Instrument, USA) of 300 ml capacity at 373 K under autogenous pressure. Typically, 0.1 g of the catalyst, 2.53 g of 26% (wt%) aqueous H_2O_2 (alkane/H_2O_2 = 3 mol) and 5 g of alkane were mixed in 25 ml of acetonitrile (solvent) and the reaction was carried out for 8 h. Under these conditions the reaction occurs in the liquid phase. After the completion of the reaction, 25 ml of acetone was added to the products, which were then separated from the catalyst by filtration and analyzed by GC (HP 5880) using a capillary (cross-linked methylsilicone gum) column and flame ionization detector. The identity of the products was confirmed by GC mass spectroscopy (Shimadzu GCMS-QP2000A) using standard compounds. The influence of various parameters such as the temperature, alkane-to-H_2O_2 (mol) ratio, the vanadium content, and solvents (acetonitrile, acetone, and methanol) on the activity and product selectivity have been studied.

RESULTS AND DISCUSSION

Activity of Different Catalysts

A comparison of the activity of VS-2, silicalite-2, Al-ZSM-11, vanadium-impregnated silicalite-2, and titanium silicate (TS-2) (all crystalline samples with MEL structure) in the oxidation of *n*-hexane is given in Table 1. The major products of the reaction are 2- and 3- hexanols and hex-

TABLE 1

Oxidation of *n*-Hexane on Different Molecular Sieve Catalysts[a]

Catalyst[b]	Conversion (mol%)	H_2O_2 selectivity[c]	Product distribution (mol%)[d]							Product selectivity[f]
			1-ol	2-ol	3-ol	1-al	2-one	3-one	Others[e]	
VS-2	14.6	57.1	3.7	9.2	8.2	7.2	26.3	25.0	21.4	79.5
S-2	3.6	4.4	—	9.5	9.5	—	4.7	7.1	69.2	30.8
ZSM-11	2.8	5.2	—	3.8	4.7	—	14.4	13.9	63.2	36.8
V impreg.S-2	3.5	3.6	—	8.0	12.0	—	4.0	4.0	72.0	28.0
TS-2	15.9	58.6	—	19.1	17.6	—	23.7	23.0	16.6	83.4

[a] Reaction conditions: catalyst (g) = 0.1; *n*-hexane (g) = 5; temperature (K) = 373; *n*-hexane/H_2O_2 (mole ratio) = 3; solvent = acetonitrile; reaction duration = 8 h.

[b] VS-2: Si/V = 79; S-2: Si/Al = >2000; ZSM-11: Si/Al = 82; V impregnated S-2: Si/V = 80; TS-2: Si/Ti = 77.

[c] H_2O_2 utilized for monofunctional product formation.

[d] 1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanal; 2-one and 3-one = 2 and 3 hexanone.

[e] Oxygenates with more than one functional group and lactones, methyl cyclopentane, and unidentified olegomeric material.

[f] (alcohols, aldehyde, and ketones/alkane reacted) × 100, mole/mole.

anones. In addition, 1-hexanol and 1-hexanal were also detected on VS-2. Small quantities of other products with more than one functional group (e.g., dihydroxyalkanes) and lactones were also detected but were not analyzed in detail. The results show that the most active catalysts are TS-2 and VS-2, which are also the most selective for the formation of monofunctional compounds. On all the other samples (not containing V or Ti in framework positions), including vanadium impregnated silicalite-2 sample, both the activity and the selectivity are very low. Between TS-2 and VS-2, the oxyfunctionalization of the primary carbon atoms leading to the formation of primary alcohols and aldehydes is observed only with the vanadium silicate. We have also observed that in addition to VS-2, other vanadium silicates such as VS-1 (with MFI structure) and V-NCL-1 (the vanadium silicate analogue of NCL-1, a novel large-pore molecular sieve, recently synthesized by us (*18*)) also exhibit this unique catalytic property of oxyfunctionalizing the primary carbon atom in alkanes and in the side-chain alkyl groups of aromatics. Toulene, for example, yields benzyl alcohol and benzaldehyde in addition to cresols (*15*).

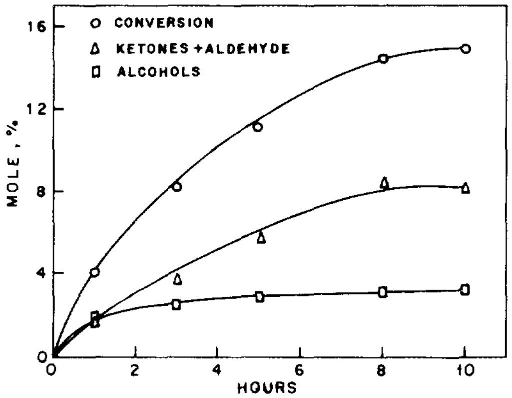


Fig. 1. Oxidation of *n*-hexane over VS-2 (Si/V = 79) in aqueous H_2O_2 at 373 K. Other conditions are given under Table 1.

An examination of the product distribution shows that the activation of the carbon atom at the second position is preferred to others and the activation follows the order, 2C > 3C > 1C on vanadium silicates. Similar activities for TS-1 and TS-2 in the oxidation of *n*-hexane, but with no activation of the primary C-H have been reported (*2, 19, 20*). Investigation of the oxidation kinetics revealed that the ratio of (aldehyde + ketones) to alcohol increased with time as shown in Fig. 1. This suggests that the aldehydes and ketones are secondary products from the corresponding primary and secondary alcohols. After 8 h, the product distribution levelled off. A higher (aldehyde + ketone)-to-alcohol ratio in the product distribution in the case of VS-2 compared to TS-2 (2.77 and 1.27, respectively, Table 1) indicates a greater oxidation ability of the vanadium silicates compared to titanium silicates in the secondary oxidation reaction.

Oxidation of Various Hydrocarbons

In addition to *n*-hexane, the oxidation of *n*-heptane, *n*-octane, and cyclohexane has been studied on a VS-2 sample, with Si/V = 79 at 373 K (Table 2). The results are similar to those observed in the case of *n*-hexane. The oxyfunctionalization of the secondary carbon atom is preferred even though significant quantities of primary alcohols and aldehydes are formed with both C7 and C8 substrates. The product distribution is in the order, 2C > 3C > 4C > 1C. No regio selectivity has been observed in these cases. Oxidation of cyclohexane, on the other hand, leads to cyclohexanol and cyclohexanone with very small concentration of oxygenates with more than one functional group. The product selectivity is, therefore, considerably higher than observed in the oxidation of *n*-alkanes. However, the oxidative conversions and the H_2O_2 selectivities decreased in the order n-C6 > n-C7 > n-C8 > cyclohexane (Table 2). This order is consistent with the observed large decrease in the diffusivity of these alkanes in zeolites with increasing chain length and molecular size (*21*).

TABLE 2

Oxidation of Alkanes over Vanadium Silicate Molecular Sieves[a]

Reactant	Conversion (mol%)[b]	H_2O_2 selectivity[c]	Product distribution (mol%)[d]									Product selectivity[f]
			1-ol	2-ol	3-ol	4-ol	1-al	2-one	3-one	4-one	Others[e]	
n-Hexane	14.6	57.1	3.7	9.2	8.2	—	7.2	26.3	25.0	—	21.4	79.5
n-Heptane	14.3	50.1	3.1	6.8	5.8	2.1	4.2	25.1	21.7	7.0	24.2	75.8
n-Octane	12.8	43.4	4.6	5.9	4.6	3.8	3.2	21.7	18.0	13.8	24.4	75.6
Cyclohexane	8.4	32.7	33.3[g]					60.7[h]			6.0	94.0

[a] Reaction conditions: catalyst (g) = 0.1 (Si/V = 79); alkane (g) = 5; temperature (K) = 373; alkane/H_2O_2 (mole ratio) = 3; solvent = acetonitrile; reaction duration = 8 h.

[b] Moles of alkane converted/total no. of moles of alkane × 100.

[c] H_2O_2 utilized for monofunctional product formation.

[d] 1-ol = 1-alcohol; 2-ol = 2-alcohol; 3-ol = 3-alcohol; 4-ol = 4-alcohol 1-al = 1-aldehyde; 2-one = 2-ketone; 3-one = 3-ketone and 4-one = 4-ketone of corresponding alkanes.

[e] Mostly oxygenates with more than one functional group and lactones.

[f] (Alcohols, aldehyde, and ketones/alkane reacted) × 100, mole/mole.

[g] Cyclohexanol

[h] Cyclohexanone.

Influence of Solvent

The effect of solvent on the oxidation of n-hexane in the presence of VS-2 (Si/V = 79) has been studied by employing other less-polar solvents than acetonitrile. In methanol and acetone, the conversions are lower, i.e., 9.1 and 5.4 mol%, respectively (Table 3). Acetonitrile is found to be the most effective solvent with the highest selectivity to monosubstituted products. The activity and H_2O_2 selectivity is related to the polarity of the solvent and decreased in the order, acetonitrile > methanol > ace-

TABLE 3

Influence of Solvent on n-Hexane Oxidation over Vanadium Silicate Molecular Sieves[a]

Solvent	Conversion (mol%)[b]	H_2O_2 selectivity[c]	Product distribution (mol%)[d]							Product selectivity[f]
			1-ol	2-ol	3-ol	1-al	2-one	3-one	Others[e]	
Acetonitrile	14.6	57.1	3.7	9.2	8.2	7.2	26.3	25.0	21.4	79.5
Methanol	9.1	30.3	3.0	11.9	10.9	4.9	18.8	18.8	31.7	68.3
Acetone	5.4	18.9	1.8	9.3	9.3	1.9	22.2	24.1	31.4	68.6
Aetonitrile + Acetone (1 : 1)	8.4	29.1	3.6	8.3	8.3	3.7	21.4	22.6	32.1	67.9
Aetonitrile + Acetone (4 : 1)	11.8	42.6	4.2	8.5	9.3	3.4	22.9	22.9	28.8	71.2

[a] Reaction conditions: catalyst (g) = 0.1 (Si/V = 79); n-hexane(g) = 5; temperature (K) = 373; alkane/H_2O_2 (mole ratio) = 3; reaction duration = 8 h.

[b] Moles of hexane converted/total no. of moles of hexane × 100.

[c] H_2O_2 utilized for monofunctional product formation.

[d] 1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanal; 2-one and 3-one = 2 and 3 hexanone.

[e] Mostly oxygenates with more than one functional group and lactones

[f] (Alcohols, aldehyde, and ketones/alkane reacted) × 100, mole/mole.

tone. The product distribution, however, in both methanol and acetone is similar to that in acetonitrile solvent. A change of solvent from the nonpolar acetone to mixtures of acetone and acetonitrile and then finally to the more polar acetonitrile increases both the conversion and H_2O_2 selectivity (Table 3). On titanium silicate, on the other hand, the rates are not influenced by the polarity of the solvents (*20*). Indeed, in nonpolar solvents such as acetone, fairly high conversions (of the order of 20 to 25 mol%) and high H_2O_2 selectivities have been reported both on TS-1 and TS-2 samples (*2, 20*). Moreover, a changeover to more polar solvents retarded the rate of oxidation on titanium silicates (*20*).

Influence of Vanadium Content

The oxidation of *n*-hexane was carried out over three VS-2 samples with different vanadium contents (Si/V = 79, 122, and 161, respectively) under identical conditions. The results are given in Table 4. As expected, the conversion and selectivity of the samples increased with vanadium content. However, the increase in the activity is not linearly proportional to the vanadium content of the samples. The alcohol-to-(aldehyde + ketone) ratio is higher on the two low-vanadium-containing samples, showing that the secondary oxidation from alcohol to aldehydes and ketones is slower on these samples. The higher vanadium in the sample with Si/V = 79 leads to a more extensive secondary oxidation. Interestingly, the oxyfunctionalization of the primary carbon atom is enhanced at higher vanadium content as seen from increasing concentration of (1-ol and 1-al) in the product with increasing vanadium content in the catalyst.

Influence of n-Hexane to H_2O_2 Ratio

While maintaining the concentration of *n*-hexane constant (0.058 mol), the concentration of hydrogen peroxide in the reaction mixture was varied during the oxidation of *n*-hexane. The results are given in Table 5. Conversion, as expected, increases with increasing H_2O_2 content. The selectivity for alcohols, ketones, and aldehydes decreases marginally (80.4 to 75.7%) due to the formation of polyoxygenated products. The H_2O_2 selectivity also decreases at higher H_2O_2 concentrations due to the formation of polyoxygenated compounds and greater loss of H_2O_2 by decomposition into $H_2O + O_2$.

Influence of Temperature

Conversion increases with temperature. On a given VS-2 sample (Si/V = 79), the

TABLE 4

Influence of Vanadium Content on Oxidation of *n*-Hexane over Vanadium Silicate Molecular Sieves[a]

Si/V ratio	Conversion (mol%)[b]	H_2O_2 selectivity[c]	Product distribution (mol%)[d]							Product selectivity[f]
			1-ol	2-ol	3-ol	1-al	2-one	3-one	Others[e]	
79	14.6	57.1	3.7	9.2	8.2	7.2	26.3	25.0	21.4	79.5
122	10.0	36.6	5.0	10.0	11.1	3.0	21.1	24.1	25.7	74.3
161	7.0	24.6	4.2	8.6	10.1	2.8	20.0	24.3	30.0	70.0

[a] Reaction conditions: catalyst (g) = 0.1; *n*-hexane(g) = 5; temperature (K) = 373; solvent = acetonitrile; reaction duration = 8 h.

[b] Moles of hexane converted/total no. of moles of hexane × 100.

[c] H_2O_2 utilized for monofunctional product formation.

[d] 1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanal; 2-one and 3-one = 2 and 3 hexanone.

[e] Mostly oxygenates with more than one functional group and lactones.

[f] (Alcohols, aldehyde, and ketones/alkane reacted) × 100, mole/mole.

TABLE 5

Effect of H_2O_2 Concentration on Oxidation of *n*-Hexane over Vanadium Silicate Molecular Sieves[a]

Hexane/H_2O_2 mole ratio	Conversion (mol%)[b]	H_2O_2 selectivity[c]	Product distribution (mol%)[d]							Product selectivity[f]
			1-ol	2-ol	3-ol	1-al	2-one	3-one	Others[e]	
1.5	23.0	42.2	3.4	7.5	6.2	8.4	26.7	23.0	24.3	75.7
3.0	14.6	57.1	3.7	9.2	8.2	7.2	26.3	25.0	21.4	79.5
4.5	10.2	61.7	5.9	9.8	10.8	4.9	25.5	23.5	19.6	80.4

[a] Reaction conditions: catalyst (g) = 0.1 (Si/V = 79); *n*-hexane(g) = 5; solvent = acetonitrile; reaction duration = 8 h.

[b] Moles of hexane converted/total no. of moles of hexane × 100.

[c] H_2O_2 utilized for monofunctional product formation.

[d] 1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanal; 2-one and 3-one = 2 and 3 hexanone.

[e] Mostly oxygenates with more than one functional group and lactones.

[f] (Alcohols, aldehyde, and ketones/alkane reacted) × 100, mole/mole.

observed conversions of *n*-hexane at 353, 373, and 393 K are 9.0, 14.6, and 16.8 mol%, respectively (Table 6). Beyond 373 K, the selectivity for monoxoygenated products decreases. A marginal decrease in H_2O_2 selectivity was also observed. In the product distribution, the $\frac{2}{3}$ ratio (2-substituted/ 3-substituted products) decreased from 1.4 to 1.0 with an increase in reaction temperature.

Mechanism of Oxidation

In the liquid-phase oxidations using H_2O_2 or other peroxides as oxidants, peroxo compounds are likely intermediates (*11, 22*). The same may not be true when O_2 is used as oxidant. Vanadium(V) peroxo complexes in nonprotic solvents are also known to be effective oxidants of olefins (to epoxides), aromatics (to phenols) and alkanes (to alcohols and ketones) (*11*). Their reactivity was attributed to a peroxo radical V^{4+}–O–O* species (generated from peracid-like forms, which adds to double bonds/aromatic nuclei and abstracts hydrogen from alkanes to give a carbon radical intermediate (*11*)). The peroxo complexes are derived from the reaction of the $V{=}O$

TABLE 6

Effect of Temperature on Oxidation of *n*-Hexane over Vanadium Silicate Molecular Sieves[a]

Temperature	Conversion (mol%)[b]	H_2O_2 selectivity[c]	Product distribution (mol%)[d]							Product selectivity[f]
			1-ol	2-ol	3-ol	1-al	2-one	3-one	Others[e]	
353	9.0	35.8	2.3	8.3	7.2	2.2	32.2	22.2	25.6	74.3
373	14.6	57.1	3.7	9.2	8.2	7.2	26.3	25.0	21.4	79.5
393	16.8	56.4	6.0	11.3	11.3	3.5	19.0	19.1	29.7	70.3

[a] Reaction conditions: catalyst (g) = 0.1 (Si/V = 79); *n*-hexane(g) = 5; alkane/H_2O_2 (mole ratio) = 3; solvent = acetonitrile; reaction duration = 8 h.

[b] Moles of hexane converted/total no. of moles of hexane × 100.

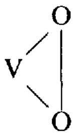
[c] H_2O_2 utilized for monofunctional product formation.

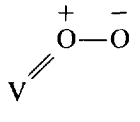
[d] 1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanal; 2-one and 3-one = 2 and 3 hexanone.

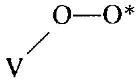
[e] Mostly oxygenates with more than one functional group and lactones.

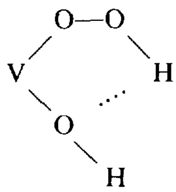
[f] (Alcohols, aldehyde, and ketones/alkane reacted) × 100, mole/mole.

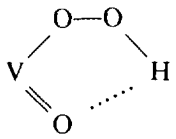
groups with H_2O_2 and may be represented as:


a

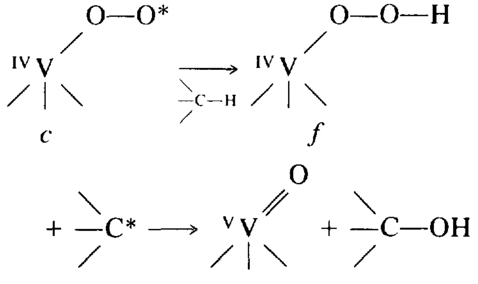

b


c


d


e

In homogeneous liquid phase reactions, the oxidation is usually carried out in nonprotic solvents such as CH_3CN, the reaction rate being retarded in protic solvents like CH_3OH. Protic solvents probably inhibit the formation of intramolecular hydrogen bonds. In our studies (also in the liquid phase), the formation of a radical species was detected (an ESR signal with g = 1.987), when VS-2 was added to a mixture of *n*-octane and H_2O_2. This signal was not observed in the absence of VS-2. The intensity of the signal increased up to 30 min and then decreased. The formation of the radical and its subsequent decay by reaction with the alkane molecules may be envisaged to proceed as given below:



In this scheme, a hydrogen atom of the alkane is abstracted by the diradical, *c*, to give an intermediate carbon radical. The latter combines with a hydroxyl radical coming from V^{4+}–O–O–H (species *f*) to give an alcohol molecule and the V^{5+} oxo complex (*g*). Peroxo species like *c* may be generated by the rearrangement of the intramolecularly hydrogen-bonded oxo-hydroperoxide species like *e* (*11*). Only isolated V^{5+} species are probably involved in the formation of such peroxo moieties and, hence, it is not surprising that the vanadium impregnated silicalite sample (which probably contains vanadium clusters) are inactive in this reaction.

CONCLUSIONS

Our studies on selective oxidation of *n*-hexane, *n*-heptane, *n*-octane, and cyclohexane in the presence of H_2O_2 on VS-2 can be summarized as follows:

1. Like titanium silicates (TS-1 and TS-2), vanadium silicates are active in the oxyfunctionalization of hydrocarbons yielding alcohols, which undergo further oxidation to carbonyl compounds.
2. Unlike titanium silicates, the vanadium silicates are also able to activate the primary C–H bond of the *n*-alkanes giving primary alcohols.
3. Solvents have considerable influence on the activity. Nonprotic solvents enhance the rate of reactions. Amongst the nonprotic solvents, more polar solvents such as CH_3CN are more effective.
4. The formation of a radical-type intermediate has been inferred from ESR observations. A mechanism involving a peroxo vanadium radical which abstracts a H atom from the hydrocarbon molecule to give a carbon radical which is further hydroxylated to the alcohol is proposed. Only isolated vanadium ions (which exist in VS-2 samples) are probably involved in the oxidation reaction.

ACKNOWLEDGMENTS

This work was partly funded by UNDP. One of us (PRH) thanks the CSIR, New Delhi for a research fellowship.

REFERENCES

1. Notari, B., *Stud. Surf. Sci. Catal.* **37,** 413 (1987); **60,** 343 (1991).

2. Huybrechts, D. C., Bruyerker, L. D., and Jacobs, P. A., *Nature* **345,** 240 (1990).
3. Thangaraj, A., Sivasanker, S., and Ratnasamy, P., *J. Catal.* **131,** 394 (1991).
4. Reddy, J. S., Sivasanker, S., and Ratnasamy, P., *J. Mol. Catal.* **71,** 373 (1992).
5. Miyamoto, A., Iwamoto, Y., Mtsuda, H., and Inui, T., *Stud. Surf. Sci. Catal.* **49,** 1233 (1989).
6. Cavani, F., Trifiro, F., Habersberger, K., and Tvaruzkova, Z., *Zeolites* **8,** 12 (1988).
7. Tvaruzkova, Z., Centi, G., Jiru, P., and Trifirò, F., *Appl. Catal.* **19,** 307 (1985).
8. Zatorski, L. W., Centi, G., Neito, J. L., Trifirò, F., Bellussi, G., and Fattore, V., *Stud. Surf. Sci. Catal.* **49,** 1243 (1989).
9. Meunier, B., *Bull. Soc. Chim. Fr.*, 578 (1986).
10. Herron, N., and Tolman, C. A., *J. Am. Chem. Soc.* **109,** 2837 (1987).
11. Mimoun, H., Saussine, L., Daire, E., Postel, M., Fischer, J., and Weiss, R., *J. Am. Chem. Soc.* **105,** 3101 (1983).
12. Hari Prasad Rao, P. R., Ramaswamy, A. V., and Ratnasamy, P., *J. Catal.* **137,** 225 (1992).
13. Hari Prasad Rao, P. R., and Ramaswamy, A. V., *Appl. Catal.* A: General, **93,** 123 (1993).
14. Hari Prasad Rao, P. R., Belhekar, A. A., Hegde, S. G., Ramaswamy, A. V., and Ratnasamy, P., *J. Catal.* **141,** 595 (1993).
15. Hari Prasad Rao, P. R., and Ramaswamy, A. V., *J. Chem. Soc. Chem. Commun.*, 1245 (1992).
16. Kokotailo, G. T., Chu, P., Lawton, S. L., and Meier, W. M., *Nature* **272,** 437 (1978).
17. Reddy, J. S., Kumar, R., and Ratnasamy, P., *Appl. Catal.* **58,** L1 (1990).
18. Kumar, R., Reddy, K. R., Raj, A., and Ratnasamy, P., *9th Int. Zeolite Conf.*, Montreal, Canada, July, 1992, Paper A-6.
19. Tatsmui, T., Nakamura, M., Negishi S., and Tominaga, H., *J. Chem. Soc. Chem. Commun.* 476 (1990).
20. Reddy, J. S., Sivasanker, S., and Ratnasamy, P., *J. Mol. Catal.* **70,** 335 (1991).
21. Weisz, P. B., *Stud. Surf. Sci. Catal.* **7,** 3 (1980).
22. Talsi, E. P., Chinakov, V. D., Babenko, V. P., and Zamaraev, K. I., *React. Kinet. Catal. Lett.* **44,** 257 (1991).