Vanadium-substituted MCM-41 zeolites as catalysts for oxidation of alkanes with peroxides

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Alkanes are oxidized selectively to ketones using V-MCM-41 with isobutyraldehyde/dioxygen as the preferred oxidant in terms of product selectivity and catalyst stability and recycle.

Substitution of transition metals into the framework of molecular sieves has led to a burst of activity in the use of these compounds as 'stable' catalysts for the oxidation of hydrocarbons. Most frequently, hydrogen peroxide is used as oxidant, but the use of other peroxidic compounds and also molecular oxygen has been reported. A special challenge is the oxidation of alkanes due to their extremely low reactivity. Titanium-substituted silicalite-1, TS-1, was found active for the oxidation of alkanes with aqueous hydrogen peroxide.[1–3] Later the vanadium-substituted silicalite-2, VS-2, showed improved activity in similar reactions.[4–6] The larger pore Ti-β-silicalite[7] and V-MCM-41[8] were also claimed to be active in the oxidation of cyclododecane with H_2O_2. Finally, the more hydrophobic cobalt-substituted aluminophosphates, CoAlPOs were active in autooxidation of cycohexane and *p*-cresol with molecular oxygen.[9,10] Surprisingly, the use of larger pore molecular sieves in conjunction with bulky oxidants such as isobutyraldehyde/O_2 (IBA/O_2) and *tert*-butyl hydroperoxide (TBHP) for the oxidation of alkanes has yet to be reported. Therefore, we describe the use of the mesoporous, MCM-41, vanadium-substituted zeolite, V-MCM-41 as catalyst in selective oxidation of such alkanes with IBA/O_2 and TBHP as oxidants. Using IBA/O_2 as oxidant, we found that these catalysts were stable, recoverable and recyclable, and highly selective for the oxidation of alkanes to the corresponding ketones. A mechanistic scheme has been proposed to explain the results.

The V-MCM-41 (A) zeolite was prepared analogously to the procedure described for the titanium compound[11] using cetyltrimethylammonium bromide as a template and vanadyl acetylacetonate as the metal precursor.† An alternative synthesis was carried out by grafting a vanadium metallocene onto MCM-41 in an analogous procedure‡ described for Ti-MCM-41 yielding V-MCM-41 (B).[12] For comparison a vanadium-containing amorphous silicate xerogel, 5% V_2O_5–SiO_2, was prepared using the two-step sol–gel procedure as reported by us previously.[13]

Our initial attempts to oxidize alkanes with 30% aqueous hydrogen peroxide using V-MCM-41 failed to yield acceptable results. Besides significant non-productive decomposition of H_2O_2 even at room temperature, almost the entire vanadium content of the heterogenous catalyst was leached into solution and any catalytic activity could be associated with dissolved vanadium species. These experiments were followed by use of 70% TBHP as oxidant. Using cyclooctane as a model substrate and V-MCM-41 (A) as catalyst, Table 1, one observes that both cyclooctanone (major product) and cyclooctyl-*tert*-butyl peroxide (minor product) were formed. Catalytic efficiency was moderate (14 turnovers). The catalyst could be easily recycled by filtration and recalcination without any perceptible loss in activity or change in selectivity. The differently prepared catalyst, V-MCM-41 (B), was significantly less reactive. Other substrates such as adamantane and ethylbenzene gave a similar product distribution with the expected order of reactivity; in the former case there was of course mostly oxidation at the tertiary carbon atom with a 9.5 : 1 ratio based on the number of carbon–hydrogen bonds. Use was made of *cis*-1,2-dimethylcyclohexane as a probe for reaction stereoselectivity. Besides reaction at the secondary carbon atoms to yield dimethylcyclohexanone, reaction at the tertiary position yielded an approximately equal amount of *cis*- and *trans*-dimethylcyclohexanol clearly indicating a planar and probably radical type reaction transition state. The reaction of cyclooctene (ordinarily not susceptible to allylic oxidation) to form cyclooct-3-enyl-*tert*-butyl peroxide along with cyclooctene oxide appears to confirm the formation of an alkyl (allylic) radical intermediate. A control reaction with no substrate showed by UV–VIS measurements that 0.1% of the total vanadium was leached into solution. Addition of cyclooctane (1 mmol) and more TBHP (2 mmol) to the filtered solution, however, showed no detectable formation of oxidation products. Apparently, the catalytic reaction is truely heterogeneous.

Table 1 Oxidation of hydrocarbons by V-MCM-41 (A)/TBHP

Substrate	Products(s) (selectivity/ mol%)	Conversion/ mol%
Cyclooctane	Cyclooctanone (90) Cyclooctyl-*tert*-butyl peroxide (10)	22.6
Cyclooctane[a]	Cyclooctanone (88) Cyclooctyl-*tert*-butyl peroxide (12)	21.8
Cyclooctane[b]	Cyclooctanol (3) Cyclooctanone (88) Cyclooctyl-*tert*-butyl peroxide (12)	7.5
Adamantane	Adamantan-1-ol (76) Adamantan-2-one (16) 2-Adamantyl-*tert*-butyl peroxide (8)	40.3
cis-1,2-Dimethylcyclohexane	*cis*-1,2-Dimethylcyclohexanol (21) *trans*-1,2-Dimethylcyclohexanol (26) *Sec*-1,2-Dimethylcyclohexanone (56)	12.0
Ethylbenzene	Acetophenone (97) Ethyl(1-phenyl)-*tert*-butyl peroxide (3)	19.6
Cyclooctene	Cyclooctene oxide (64) Cyclooct-3-enyl-*tert*-butyl peroxide (36)	20.6

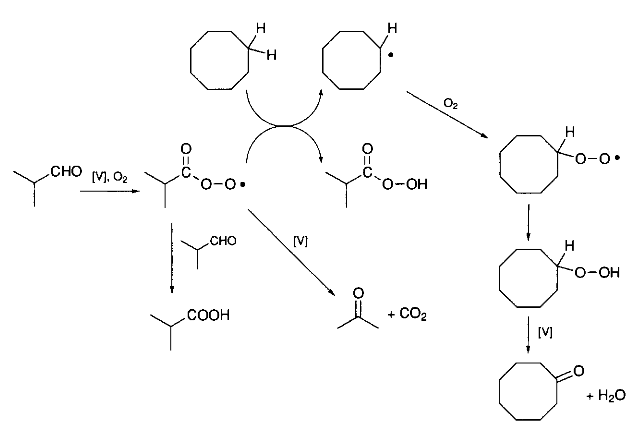
Reaction conditions: 100 mg V-MCM-41 (A) ([V] = 0.0167 mmol), [RH] = 1 mmol, [TBHP] = 2 mmol in 1 ml of acetone under Ar, T = 60 °C, t = 8 h. Conversion of TBHP was quantitative. Analysis by GLC. [a] V-MCM-41 (A) was regenerated and reused. [b] V-MCM-41 (B).

The inferior reaction selectivity along with the slight but measurable leaching of vanadium led us to search for a better oxidant system. We chose IBA/O_2 which is known to form, *in situ*, the anhydrous peracid, $Me_2CHC(O)OOH$, and/or acyl peroxo radical, $(CH_3)_2CHC(O)OO\cdot$. In a typical reaction using cyclooctane (1 mmol) as a model substrate, 100 mg catalyst (Si/V = 100, [V] = 0.016 mmol), isobutyraldehyde (2 mmol) under 1 atm O_2 at room temp., moderate catalytic activity was observed, however with very high reaction selectivity, Table 2. Significantly, cyclooctanone was the sole product. The order of catalyst activity was V-MCM-41 (A) > V-MCM-41 (B) > V_2O_5–SiO_2. The catalyst was easily recovered by filtration and regenerated by calcination. No leaching of vanadium into solution was measurable. Similar reactions with adamantane, cyclohexane and ethylbenzene yielded only ketone upon reaction at the secondary carbon atom. Use of *cis*-1,2-dimethylcyclohexane as a stereo-probe as above yielded equivalent amounts of *cis*- and *trans*-dimethylcyclohexanol again indicating a planar and radical type transition state. The tertiary/secondary C–H bond selectivity on a per bond basis for the oxidation of adamantane was 9, supporting this conclusion.

Table 2 Oxidation of hydrocarbons by V-MCM-41 (A)/IBA/O_2[a]

Substrate	Products(s) (selectivity/ mol %)	Conversion/ mol%
Cyclooctane	Cyclooctanone (100)	8.6
Cyclooctane[a]	Cyclooctanone (100)	3.9
Cyclooctane[b]	Cyclooctanone (100)	6.4
Cyclooctane[c]	Cyclooctanone (100)	9.2
Adamantane	Adamantan-1-ol (66) Adamantan-2-one (34)	15.2
cis-1,2-Dimethylcyclohexane	*cis*-1,2-Dimethylcyclohexanol (15) *trans*-1,2-Dimethylcyclohexanol (18) *sec*-1,2-Dimethylcyclohexanone (67)	6.2
Ethylbenzene	Acetophenone (100)	5.7
Cyclohexene	Cyclohexene oxide (7) Cyclohexenone (93)	55.0
Oct-1-ene	Oct-1-ene oxide (45) Oct-1-en-3-one (55)	6.2

Reaction conditions: 100 mg catalyst ([V] = 0.167 mmol), [RH] = 1 mmol, [aldehyde] = 2 mmol in 1 ml of acetone, T = 25 °C, t = 8 h. Conversion of IBA was quantitative. Analysis by GLC. [a] V_2O_5–SiO_2. [b] V-MCM-41 (B). [c] V-MCM-41 (A) was regenerated and reused.



Scheme 1 Proposed mechanistic scheme for the oxidation of cyclooctane to cyclooctane with IBA/O_2

Oxidation of alkenes yielded both β-unsaturated ketones (no alcohols) and epoxides.

The atypical formation of only ketone at secondary carbon alkanes warranted further explanation. To this end a competitive reaction between cyclooctane and cyclooctanol showed that the formation of cyclooctanone as the sole product could not be explained by fast oxidation of a cyclooctanol intermediate. In an additional experiment, a full mass balance was carried out for the cyclooctane oxidation in methyl isobutyl ketone (MIBK) as solvent. Thus, a reaction of 4 mmol cyclooctane, 8 mmol IBA under 1 atm of O_2 in the presence of 400 mg of V-MCM-41 (A) in 4 ml of MIBK yielded, as determined by GLC after 4 h at ambient temperatures, 3.8 mmol of cyclooctane, 0.2 mmol of cyclooctanone, 0.4 mmol of IBA, 6.6 mmol of isobutyric acid, 1.0 mmol of acetone and 0.9 mmol of CO_2 (determined as $BaCO_3$).

Combining all of the above results leads us to propose the reactions of Scheme 1. The IBA used is converted mainly to isobutyric acid. However, the intermediate acyl peroxo radical may be decomposed to acetone and CO_2. Similar decomposition of the alkyl peracid yields ketone as sole product and water. Oxidation at a tertiary carbon (not shown) yields alcohol in the usual manner. Finally, the synthetic utility of the V-MCM-41 and IBA/O_2 catalytic system may be optimized by continuous addition of IBA to the reaction. Thus, addition of ten portions of 2 mmol IBA over a 24 h period to a reaction mixture as outlined in Table 2 yielded 83% isolated cyclooctanone.

Footnotes

† V-MCM-41 (A) was prepared at ambient temperature by mixing a solution containing tetraethylorthosilicate (1 mole), ethanol (6.5 mole), isopropyl alcohol (1 mole), hexadecyltrimethylammonium bromide (0.27 mole) and vanadyl acetylacetonate (0.01 mole) to 65.3 ml of 0.3 M HCl. The resulting solution was homogenized, stirred for 2 h and aged for one day at room temp. The solution was filtered and the deep green crystals dried at 120 °C overnight, followed by calcination in air at 500 °C for 6 h, to yield an orange crystalline solid.

‡ V-MCM-41 (B) was prepared from 3.46 g of MCM-41 and 0.137 g (0.58 mmol) bis(cyclopentadienyl)vanadium dichloride by mixing these two components in chloroform followed by addition of 1 ml of triethylamine. The mixture was stirred overnight, then filtered and was washed with chloroform. The crystalline solid was deep red and turned orange after calcination at 500 °C for 6 h.

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