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Novel alkoxysilane pentacoordinate O=V(IV) complexes as supported catalysts for cyclohexane oxidation with dioxygen

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ABSTRACT

A variety of newly synthesized and well characterized alkoxysilane pentacoordinate Oxovanadium(IV) complexes, VO[Sal(PMeOSi)DPTA] **3[a]**, VO[Cl-Sal(PMeOSi)DPTA] **3[b]**, VO[Sal(PMeOSi)DETA] **6[a]** and VO[Cl-Sal(PMeOSi)DETA] **6[b]**, (Sal = salicylaldehyde, DPTA = bis(aminopropyl)amine, DETA = diaminoethylamine), have been anchored by covalent bond into the surface of SiO_2 and/or Al_2O_3 via silicon-alkoxide route by a condensation process as supported catalysts. These solid supported catalysts (abbreviated as catalysts A to H) showed high catalytic efficiency in the selective oxidation reaction of cyclohexane using molecular oxygen under relatively mild condition in a micro-batch reactor. The Catalyst C (SiO_2/**3[a]** complex) system exhibits best activity, overall yield 38.5% (TONs, *ca.* 5.0×10^3) as well as high selectivity 98% (cyclohexanol 74%, cyclohexanone 24%). Notably, cyclohexane shows significantly improved yield 44.0%, by the addition of pyrazinecarboxylic acid as a co-catalyst. The TGA indicates these catalysts are stable up to maximum reaction temperature, *ca.* 473 K and ICP analysis shows there is negligible vanadium loss from the supported catalyst after the reaction, allowing further use of the V-catalyst. The various factors influences (*i.e.* temperature, O_2 pressure, reaction time, catalyst amount) were also investigated in the systematic way, to optimize the reaction processes. The impact of radical traps and detection of intermediate peroxy radical were also investigated to establish a radical mechanism.

1. Introduction

The vanadium complexes have attracted interest owing to their potential roles in several types of catalytic reactions and biological activities with industrial significance [1–6]. In particular, the pentacoordinate vanadium complexes have been well known for a long time to undergo reversible coordination of the N_3O_2-ligands in a solution [7,8]. On the other hand, heterogenized V-complexes have been found to act as efficient catalysts for various types of reactions, as well [9,10]. Previously, we have also successfully applied some heterogenized Schiff-base V-complexes for the oxidation reactions of alkanes [11] but, although promising, the use of these vanadium metal complexes as supported catalyst still constitutes an underdeveloped field of research. Several types of supporting materials (*i.e.* SiO_2, MCM-41, SBA-15) have been used for the immobilization purpose of the metal complexes. This was mainly achieved by the formation of covalent bond between support material matrixes with –OH and alkoxysilanes via –Cl, $–NH_2$, –CN and –SH groups [12–15]. The main drawback of these processes are (i) leaching of metal because it is added at the last step of reaction and (ii) possibly the breaking of original structure and (iii) difficulties to characterize the original structure of the metal complex on the supported matrix.

In view of relevance, we have selected cyclohexane as substrate and its partially oxidized products (cyclohexanol and cyclohexanone) for the production of adipic acid and caprolactum, which are further used in the manufacturing of nylon-6,6′, nylon-6, urethane foams, polyamide-6 and lubricating additives [16–18]. Normally, cobalt naphthenate or cobalt acetate have been used for the industrial oxidation reaction, with O_2, at above 150 °C, and only a low conversion (*ca.* 4%) is achieved to obtain a high selectivity (*ca.* 85%) towards a mixture of cyclohexanone and cyclohexanol [19,20]. Thus, commercial cyclohexane oxidation uses inherently inefficient methodology that necessitates repeated recycling of feedstock. The alternative use of peroxides is expensive and is also accompanied by the formation of by-products [21]. The establishment of a greener, more effective and selective cyclohexane oxidation system with atmospheric oxygen is therefore a current need. Many heterogeneous catalysts have been developed for this reaction and generally these catalysts are either oxides or metal cations [22].

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The system activity is mainly dependent on the correct choice of the solvent, which is determined by the polarity of the medium and the size of the substrate that needs to be adsorbed at the catalytic surface [23,24]. Sometimes promoters or co-reactants like acetaldehyde, cyclohexanone, cyclohexanol and azo-bis isobutyronitrile, pyrazinecarboxylic acid, etc. are also added to reduce the induction period and to increase the conversion [25]. Among other oxidation catalysts, heteropolyoxometalates compounds also show high catalytic activity towards the alkanes oxidation [26].

Hence, the main purpose of this current study is to provide newly synthesized and well characterized alkoxysilane of N_3O_2 ligands (*i.e.* **2[b]**, **5[a]**, **5[b]**) with Oxovanadium(IV) complexes (*i.e.* **3[a]**, **3[b]**, **6[a]** and **6[b]**). These silica and/or alumina anchored V-complexes catalysts have been applied for the selective gas–liquid phase oxidation reaction of cyclohexane (with molecular oxygen) without adding any additives and solvents in batch process under optimized conditions.

2. Experimental

2.1. General materials and procedure

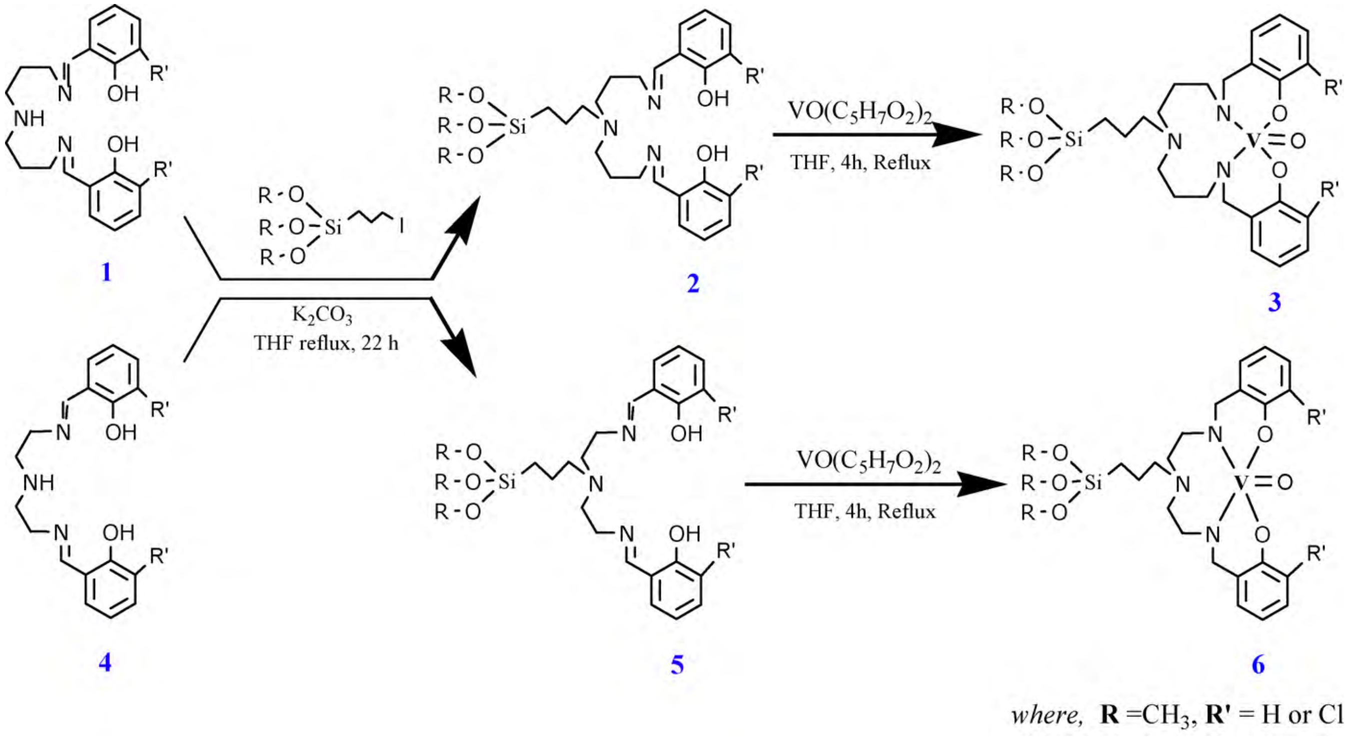
All the reactions and manipulations were performed under an atmosphere of dinitrogen using standard Schlenk techniques. All the solvents were purified by standard procedures and freshly distilled immediately prior to use. The chemicals, *i.e.* bis(aminopropyl)amine, potassium carbonate, 2,2-diaminoethylamine (all from Acros), salicylaldehyde, 5-chlorosalicylaldehyde, 3-iodopropyl trimethoxysilane, pyrizine carboxylic acid, silica gel, alumina, acetonitrile, bromotrichloromethane, diphenylamine, triphenylphosphane (all Sigma), bis(acetylacetonate)oxovanadium, tetra hydro furan, cyclohexane (all Mark), ethanol, *n*-pentane, picolinic acid, 2-pyrazinecarboxylic acid, 3-amino-2-pyrazinecarboxylic acid and 2,6-pyrizinedicarboxylic acid, 5-hydroxy-2-pyrazinecarboxylic acid, 5-methyl-2-pyrazinecarboxylic acid, toluene (all from Janssen) were used as received from supplier.

The NMR spectra (^1H, ^{13}C and ^{15}N) were recorded on a Bruker ARX400 NMR spectrometer at ambient temperature; δ values are in ppm relative to $SiMe_4$. Coupling constants are in Hz; abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = complex multiplets; br = broad, dd = doublet or doublets, dm = doublet of multiplets. Infrared spectra (4000–400 cm^{-1}) were recorded on a Unicam (Research Series) FT-IR spectrometer in transmission mode using KBr pellets; wavenumbers are in cm^{-1}; abbreviations: vs = very strong, s = strong, m = medium, w = weak, br = broad. The C, H, N elemental analyses were carried out by Fisons EA-1108. Gas chromatography was carried out with a FISONS GC-8000 series gas chromatograph equipped with a FID detector and a DB-WAX capillary column (length: 60 m; internal diameter: 0.32 mm). FAB-mass spectra were obtained on a Trio-2000 Fisons spectrometer by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca.* 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI, GC–MS analyses were performed by using this spectrometer with a coupled gas chromatograph Carlo Erba Instruments, Auto/HRGC/MS. Thermogravimetric analysis of the solid catalyst was performed by TA Instruments Q50. Vanadium concentrations of fresh and filtrates after the catalytic experiments were determined by AAS analysis on a Perkin-Elmer 41000ZL spectrometer. Morphology of the solid supported catalysts was analyzed by scanning electron microscopy (FEI Quanta 400), equipped with an EDS detector (EDAX).

2.2. Metal complex synthesis and characterization

2.2.1. Synthesis of ligand, *2[a]*

The ligand, bis(salicylidenimino-3-propyl)amine with 3-iodopropyl trimethoxysilane **2[a]** (Scheme 1), was prepared and characterized as described earlier [27]. Anal. calcd. for $C_{26}H_{39}N_3O_5Si$: C, 62.15; H, 7.77; N, 8.37. Found: C, 62.11; H, 7.72; N, 8.15. FT-IR (KBr pellet, cm^{-1}): ν = 3045 and 2940 [s, ν(C–H)]; 1629 and 1542 [s, ν (C=C), s, ν (N=C)]; 1160 [s, ν (Si–O)]; 1092 [s, ν (C–N)]. ^1H NMR (δ, $CDCl_3$): δ = 0.62 (m, 2H, Si–CH_2), 1.54 (m, 2H, CH_2), 1.81 (m, 4H, CH_2), 2.40 (m, 6H, CH_2N), 3.55 (m, 4H, CH_2N;



Scheme 1. Synthesis of trialkoxysilane pentacoordinate Oxovanadium(IV) complexes.

9H, CH_3O), 6.56–7.35 (m, CH, ring), 8.22 (s, 2H, HC=N), 9.82 (s, 2H, C–OH). $^{13-}$C NMR (δ, $CDCl_3$): $\delta = 7.4$, 20.6, 29.0 and 50.9 (s, C–H_2), 51.8, 57.3, 57.8 (s, O–CH_3), 117.3, 118.8, 119.2, 131.6 and 132.4 (s, C–H, ring), 161.7 and 165.3 (s, N=C). ^{15}N NMR (δ, $CDCl_3$): $\delta = 82.7$ (s, imines) and 343.2 (s, amine). FAB$^+$-MS: $m/z = 502$ [$(M+H)^+$, 25], 364 [M–$(CH_2Si(OCH_3)_3)^+$, 13], 120 [(Si(O $CH_3)_3$), 100].

2.2.2. Synthesis ligand, **2[b]**

The ligand **2[b]** (Scheme 1) was prepared with 5-chlorosalicylaldehyde instead of salicylaldehyde as similar procedure **2[a]** ligand, a solution of **1** (2.0 g, 3.5×10^{-3} mol) and equimolar amount of 3-iodoprpyle-trimethoxysilane (1.0 g, 3.5×10^{-3} mol) with K_2CO_3 (0.97 g, 7.0×10^{-3} mol) in MeCN (50 mL). The reaction mixture was heated and refluxed for 22 h. After the reaction, the product was filtered and washed three times with *n*-pentane and dried under *vacuo* obtained, 2.7 g, 92% yield of ligand **2[b]** (orange colour). Anal. calcd. for $Cl_2C_{26}H_{37}N_3O_5Si$: C, 54.64; H, 6.48; N, 7.63. Found: C, 53.08; H, 6.12; N, 7.15. FT-IR (KBr pellet, cm^{-1}): $\nu = 3040$ [s, ν(C–H)]; 2933 [s, ν(C–H)]; 1620 and 1541 [s, ν(C=C), s, ν(N=C)]; 1162 [s, ν(Si–OCH_3)]; 1082 [s, ν(C–N)]; 746 [s, ν(–Cl)]. ^{1}H NMR (δ, $CDCl_3$): $\delta = 0.51$ (m, 2H, Si–CH_2), 1.52 (m, 2H, CH_2), 1.88 (m, 4H, CH_2), 2.55 (m, 6H, N=CH_2), 3.61 (m, 4H, N=CH_2; 9H, CH_3O), 6.54–7.51 (m, 2H, –OH), 8.02 (s, 2H, HC=N), 9.82 (s, C–OH, ring). $^{13-}$C NMR (δ, $CDCl_3$): $\delta = 7.6$, 20.3, 23.1 and 60.2 (s, C–H_2), 51.4, 56.5, 57.0 (s, O–CH_3), 119.1, 118.3, 121.2, 128.6 and 130.8 (s, C–H, ring), 162.6 and 166.0 (s, N=C). ^{15}N NMR (δ, $CDCl_3$): $\delta = 82.8$ (s, imines), 345.6 (s, amine). FAB$^+$-MS: $m/z = 571$ [$(M+H)^+$, 27], 371 [M–$(CH_2Si(OCH_3)_3)^+$, 14], 121 [$(Si(OCH_3)_3)$, 99].

2.2.3. Synthesis ligands, **5[a]**

The ligand **5[a]** (Scheme 1) was prepared with 2,2-diaminoethylamine instead of bis(aminopropyl)amine as similar procedure **2[a]** ligand. A solution of ligand **4[a]** (3.24 g, 1.07×10^{-3} mol), and equimolar amount of 3-iodoprpyle-trimethoxysilane (3.02 g, 1.07×10^{-3} mol) in MeCN (50 mL) with K_2CO_3 (2.8 g, 2.03×10^{-3} mol) was heated and refluxed for 22 h. After the reaction, the solution was filtered and washed several times with *n*-pentane and dried under *vacuo* obtained, 5.5 g, 88% yield of ligand **5[a]** (orange colour product). Anal. calcd. for $C_{25}H_{37}N_3O_5Si$: C, 61.52; H, 7.59; N, 8.61. Found: C, 60.08; H, 7.32; N, 7.44. FT-IR (KBr pellet, cm^{-1}): $\nu = 3038$ [s, ν(C–H)]; 2929 [s, ν(C–H)]; 1618 and 1534 [s, ν(C=C), s, ν(N=C)]; 1160 [s, ν(Si–OCH_3)]; 1076 [s, ν(C–N)]. ^{1}H NMR (δ, $CDCl_3$): $\delta = 0.43$ (m, 2H, CH_2Si), 1.62 (m, 2H, CH_2), 2.21 (m, 2H, CH_2N), 2.63 (m, 4H, CH_2N), 3.59 (m, 4H, CH_2N; 9H, CH_3O), 6.01–7.53 (m, Ar + 2OH), 8.3 (m, HC=N). $^{13-}$C NMR (δ, $CDCl_3$): $\delta = 7.5$, 23.4, 53.5 and 59.7 (s, CH_2), 51.4, 56.5 (s, O–CH_3), 117.2, 118.5, 120.9, 124.6 and 129.6 (s, C–H, ring), 159.6 (–C=N) and 164.1 (–C–OH). ^{15}N NMR (δ, $CDCl_3$): $\delta = 82.4$ (s, imines), 344.8 (s, amine). FAB$^+$-MS: $m/z = 488$ [$(M+H)^+$, 27], 371 [M–$(CH_2Si(OCH_3)_3)^+$, 14], 121 [$(Si(OCH_3)_3)$, 99].

2.2.4. Synthesis ligands, **5[b]**

The ligand **5[b]** (Scheme 1) was prepared with 5-chlorosalicylaldehyde and 2,2-diaminoethylamine instead of salicylaldehyde and bis(aminopropyl)amine as similar procedure **2[a]** ligand. A solution of **4[b]** (2.0 g, 3.65×10^{-3} mol) and equimolar amount of 3-iodoprpyle-trimethoxysilane (1.06 g, 3.65×10^{-3} mol) with K_2CO_3 (1.01 g, 7.32×10^{-3} mol) in MeCN (50 mL) was heated and refluxed for 22 h. After the reaction, the mixture was filtered and washed several times with *n*-pentane and dried under *vacuo* obtained 2.75 g, 90% yield of ligand **5[b]** (orange colour product). Anal. calcd. for $Cl_2C_{25}H_{25}N_3O_5Si$: C, 54.89; H, 6.40; N, 7.68. Found: C, 54.40; H, 6.62; N, 7.25. FT-IR (KBr pellet, cm^{-1}): $\nu = 3038$ [s, ν(C–H)]; 2929 [s, ν(C–H)]; 1618 and 1534 [s, ν(C=C), s, ν(N=C)]; 1160 [s, ν(Si–OCH_3)]; 1076 [s, ν(C–N)]. ^{1}H NMR (δ, $CDCl_3$): $\delta = 0.43$ (m, 2H, CH_2Si), 1.62 (m, 2H, CH_2), 2.21 (m, 2H, CH_2N), 2.63 (m, 4H, CH_2N), 3.59 (m, 4H, CH_2N; s, 9H, CH_3O), 6.01–7.53 (m, Ar + 2OH), 8.2 (m, HC=N). $^{13-}$C NMR (δ, $CDCl_3$): $\delta = 7.5$, 23.4, 53.5 and 59.7 (s, C–H_2), 51.4, 56.5 (s, O–CH_3), 117.2, 118.5, 120.9, 124.6 and 129.6 (s, C–H, ring), 159.6 (–C=N) and 164.1 (–C–OH). ^{15}N NMR (δ, $CDCl_3$): $\delta = 82.4$ (s, imines), 344.8 (s, amine). FAB$^+$-MS: $m/z = 547$ [$(M+H)^+$, 27], 371 [M–$(CH_2Si(OCH_3)_3)^+$, 14], 121 [$(Si(OCH_3)_3)$, 99].

2.2.5. Synthesis complex, **3[a]**

To a solution of VO[(acac)$_2$] (1.16 g, 4.38×10^{-3} mol) in the THF (30 mL) was added, with constant starring, an equimolar amount of ligand **2[a]** (2.20 g, 4.38×10^{-3} mol) in THF (20 mL). The green mixture was heated and refluxed for 4 h (Scheme 1). The final solution was concentrated and upon addition of *n*-pentane a green solid precipitated. The solid was collected by the filtration, washed with *n*-pentane (3× 100 mL) and dried under *vacuo* to obtained, a new **3[a]** complex of vanadium (2.9 g, 87% yield, Scheme 1). It is soluble in methanol, ethanol, tetrahydrofuran but insoluble in ether. Anal. calcd. for $VC_{26}H_{37}N_3O_6Si$: C, 55.07; H, 6.53; N, 5.38. Found: C, 55.26; H, 6.32; N, 5.26. FT-IR (KBr pellet, cm^{-1}): $\nu = 3190$ [s, ν(C–H)]; 2921 [s, ν(C–H)]; 1623 and 1534 [s, ν(C=N) and s, ν(C=C)]; 1160 [s, ν(Si–OCH_3)]; 1076 [s, ν(C–N)], 933 and 635 [s, ν(V=O) and s, ν(V···O)]. EPR (CH_2Cl_2, at 25 °C): $g = 1.9982$, A|| and A⊥ (in $\times 10^{-4}\,cm^{-1}$) = 1.62 and 59.8. FAB$^+$-MS: $m/z = 567$ [$(M+H)^+$, 100], 405 [M–$(CH_2Si(OCH_3)_3)^+$, 14], 1 [$(Si(OCH_3)_3)$, 99].

2.2.6. Synthesis complex, **3[b]**

To a solution of VO[(acac)$_2$] (0.70 g, 2.63×10^{-3} mol) in THF (30 mL) was added, with constant starring, an equimolar amount of ligand **2[b]** (1.5 g, 2.63×10^{-3} mol) in THF (20 mL). An olive green mixture was obtained which was refluxed for 4 h. The final solution was concentrated and upon addition of *n*-pentane a green solid precipitated (Scheme 1). The solid was collected by the filtration, washed with *n*-pentane (3× 100 mL) and dried under *vacuo* to obtain a new **3[b]** complex of vanadium (1.91 g, 86% yield, Scheme 1). It is soluble in methanol, ethanol, tetrahydrofuran but insoluble in ether. Anal. calcd. for $VCl_2C_{26}H_{35}N_3O_6Si$: C, 49.09; H, 5.51; N, 6.61. Found: C, 49.21; H, 5.02; N, 6.26. FT-IR (KBr pellet, cm^{-1}): $\nu = 3145$ [s, ν(C–H)]; 2929 [s, ν(C–H)]; 1626 and 1540 [s, ν(C=N) and s, ν(C=C)]; 1153 [s, ν(Si–OCH_3)]; 1059 [s, ν(C–N)], 941 and 630 [s, ν(V=O) and s, ν(V···O)]. EPR (CH_2Cl_2, at 25 °C): $g = 1.9892$, A|| and A⊥ (in $\times 10^{-4}\,cm^{-1}$) = 164.1 and 58.5. FAB$^+$-MS: $m/z = 636$ [$(M+H)^+$, 100], 405 [M–$(CH_2Si(OCH_3)_3)^+$, 14], 121 [$(Si(OCH_3)_3)$, 99].

2.2.7. Synthesis complex, **6[a]**

To a solution of VO[(acac)$_2$] (0.81 g, 3.07×10^{-3} mol) in THF (30 mL) was added, with constant starring, an equimolar amount of ligand **5[a]** (1.65 g, 3.07×10^{-3} mol) in THF (20 mL). A dark green mixture was produced which was refluxed for 4 h (Scheme 1). The final solution was concentrated and upon addition of *n*-pentane a green solid was precipitated. It was collected by the filtration, washed with *n*-pentane (3× 100 mL) and dried under *vacuo* to obtain a new **6[a]** complex of vanadium (2.14 g, 85% yield, Scheme 1). It is soluble in methanol, ethanol, tetrahydrofuran but insoluble in ether. Anal. calcd. for $VC_{24}H_{33}N_3O_6Si$: C, 53.48; H, 6.13; N, 7.80 Found: C, 54.03; H, 5.99; N, 7.16. FT-IR (KBr pellet, cm^{-1}): $\nu = 3054$ [s, ν(C–H)]; 2933 [s, ν(C–H)]; 1600 and 1564 [s, ν(C=N) and s, ν(C=C)]; 1145 [s, ν(Si–OCH_3)]; 1055 [s, ν(C–N)], 936 and 633 [s, ν(V=O) and s, ν(V···O)]. EPR (CH_2Cl_2, at 25 °C): $g = 1.9863$, A|| and A⊥ (in $\times 10^{-4}\,cm^{-1}$) = 162.2 and 57.6. FAB$^+$-MS: $m/z = 538$ [$(M+H)^+$, 100], 405 [M–$(CH_2Si(OCH_3)_3)^+$, 14], 121 [$(Si(OCH_3)_3)$, 99].

2.2.8. Synthesis complex, **6[b]**

To a solution of VO[(acac)$_2$] (0.73 g, 2.74×10^{-3} mol) in THF (30 mL) was added, with constant starring, an equimolar amount of ligand **5[b]** (1.66 g, 2.74 × 10^{-3} mol) in THF (20 mL) to give a olive green mixture. It was refluxed for 4 h (Scheme 1). The solution was concentrated and upon addition of *n*-pentane yielded a green solid precipitate. The solid was collected by the filtration, washed with *n*-pentane (3× 100 mL) and dried under *vacuo* to obtained, a new **6[b]** complex of vanadium (2.1 g, 88% yield, Scheme 1). It is soluble in methanol, ethanol, tetrahydrofuran but insoluble in ether. Anal. calcd. for $VCl_2C_{24}H_{31}N_3O_6Si$: C, 47.41; H, 5.10; N, 6.91. Found: C, 46.99; H, 5.02; N, 6.65. FT-IR (KBr pellet, cm^{-1}): ν = 3050 [s, ν(C–H)]; 2940 [s, ν(C–H)]; 1643 and 1551 [s, ν(C=N) and s, ν(C=C)]; 1121 [s, ν(Si–OCH_3)]; 1044 [s, ν(C–N)], 945 and 629 [s, ν(V=O) and s, ν(V···O)]. EPR (CH_2Cl_2, at 25 °C): g = 1.8999, A|| and A⊥ (in ×10^{-4} cm^{-1}) = 161.0 and 59.2. FAB$^+$-MS: m/z = 608 [$(M+H)^+$, 100], 405 [$M-(CH_2Si(OCH_3)_3)^+$, 14], 121 [$(Si(OCH_3)_3)$, 99].

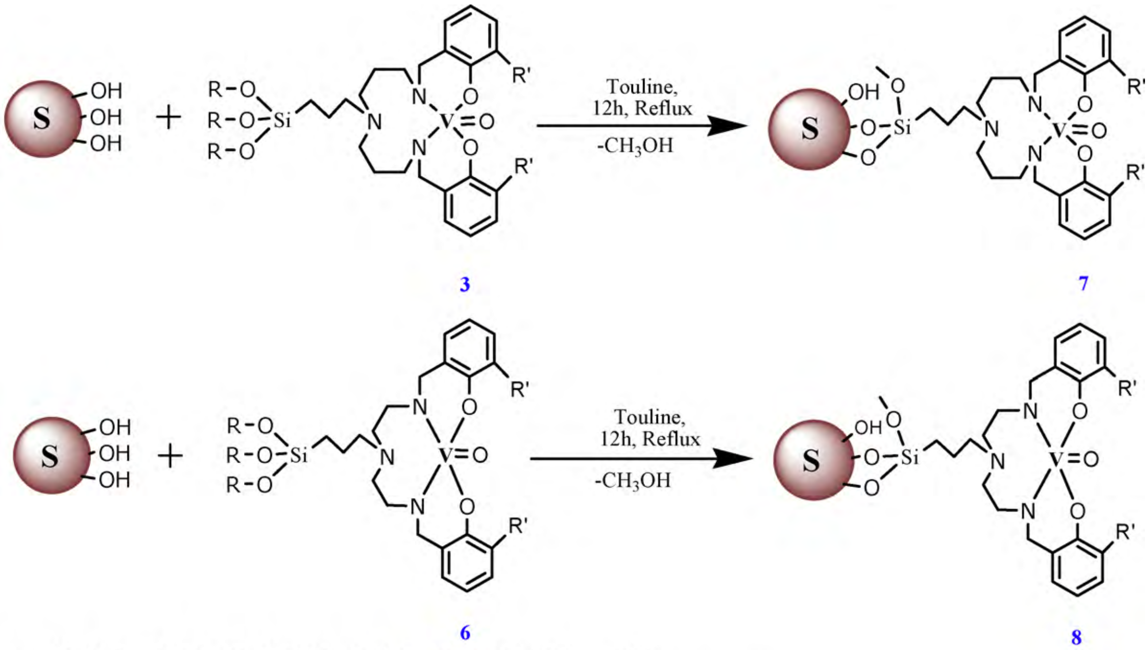
2.3. Supported catalysts preparation and characterization

In a surface modification process, we have used the wet-impregnation method [28] for immobilization of the vanadium Schiff-base complexes **3[a]**, **3[b]**, **6[a]** and **6[b]**, which are covalently bound on the surface (silanol group, –OH) of silica and or alumina [13,29]. Each of the above vanadium complexes **3[a]**, **3[b]**, **6[a]** and **6[b]** (50 mg) were separately dissolved in dry toluene (50 mL), the solution separately added to the SiO_2 (1000 mg) and or Al_2O_3 (1000 mg) for the preparation of supported catalysts. The mixtures were heated and refluxed for 12 h with the elimination of CH_3OH (Scheme 2). The functionalized SiO_2 and or Al_2O_3 with covalently anchored vanadium (IV) complexes were filtered-off, washed several times with methanol, and then dried at 40 °C for 4 h, in an oven. After drying we found that 45 mg of Catalyst A, 41 mg of Catalyst B, 44 mg of Catalyst C, 42 mg of Catalyst D, 45 mg of Catalyst E, 40 mg of Catalyst F, 43 mg of Catalyst G and 41 mg of Catalyst H, were separately loaded, per gram of functionalized SiO_2 and or Al_2O_3 as supported inorganic–organic catalysts. All the supported catalysts are olive green in colour.

Characterization: FT-IR (KBr pellet, cm^{-1}): for all the final supported catalysts (A to H) of vanadium (IV) complexes **3[a]**, **3[b]**, **6[a]** and **6[b]** are buried under those of the supports, one can observe a broad shoulder (at *ca.* 3300–3150 cm^{-1}) of the silica and alumina and strong [s, ν(V=O)] bands of V-complexes was also observed between 945 and 926 cm^{-1}. The other related bands of complexes are observed at ν = 3050–2935 [s, ν(C–H)]; 1655–1637 [s, ν(C=N)]; 1552–1533 [s, ν(C=C)]; 1080 [s, ν(Si–O)] (not clear). *TGA*: all the supported catalysts A–H, complexes are started to decompose between *ca.* 488 and 588 K. *SEM analysis*: morphological analysis (20,000× magnification) of the Catalyst C picture shows, bright spotted portion as V-complex and the presence of vanadium content (0.37%) was also confirmed by SEM/EDS detector. *EPR analysis*: for the catalysts samples A to H (at room temperature) eight line spectrum with range of g = 1.8999–1.9821 and range of A|| and A⊥ (in ×10^{-4} cm^{-1}) = 158.0–166.3 and 58.1–62.2, were obtained, respectively. *ICP analysis*: the catalysts A to H was measured in the range of 0.28–0.34 wt.% of vanadium on the surface of support.

2.4. Typical oxidation procedure and product analysis

In typical oxidation conditions, 3.0 mL (27.8 mmol) of neat cyclohexane and 30 mg of supported vanadium catalysts were charged in a micro-batch reactor (a cylindrical rocking type reactor, 40 mL capacity, provided with a pressure gauge and gas delivery inlet). The reaction mixture was stirred for 180–1800 min under oxygen pressure. At the end of the reactions, the supported catalysts were separated from the reaction mixture by filtration, using a filter paper, and washed three times with acetonitrile. The supported catalysts could be reactivated for further use by heating in an air oven at 40 °C for 6 h. The reaction products analysis was performed by GC as follows: 60 μL of cyclopentanone as internal standard and 1000 μL of final product were added and injected (0.5 μL), in a GC injector (at 240 °C, He used as carrier gas). The initial temperature was maintained at 100 °C for 1 min, then raised 10 °C/min up to 180 °C, and held at this temperature for 1 min. They were further confirmed by GC–MS analysis. After the oxidation reaction, the mixture was treated with the excess PPh_3 for the detection of alkyl hydroperoxide (*CyOOH*) and also analyzed



R = CH_3, **7[a]** and **8[a]** = R' = H, **7[b]** and **8[b]** = R' = Cl, *S* = SiO_2 or Al_2O_3
Catal. **A** = SiO_2/**7[a]**, Catal. **B** = Al_2O_3/**7[a]**, Catal. **C** = SiO_2/**7[b]**, Catal. **D** = Al_2O_3/**7[b]**,
Catal. **E** = SiO_2/**8[a]**, Catal. **F** = Al_2O_3/**8[a]**, Catal. **G** = SiO_2/**8[b]**, Catal. **H** = Al_2O_3/**8[b]**,

Scheme 2. Immobilization of trialkoxysilane pentacoordinate Oxovanadium(IV) complexes to the silica or alumina matrix as supported hybrid catalysts.

by GC. The turnover numbers (TONs) (moles of product per mole of catalyst) and yields (moles of product per mole of alkane) were estimated. *Caution!* The oxidation reactions (exothermic reactions) are potentially explosive and necessary care and safety reactions should be taken.

3. Results and discussion

The potentially active novel trimethoxysilyl pentacoordinated Schiff-base Oxovanadium(IV) complexes, V=O[Sal(*n*-propyltrimethoxysilyl)DPTA], V=O[Sal(PMeOSi)DPTA] **3[a]**, V=O[Cl-Sal(*n*-propyltrimethoxysilyl)DPTA], V=O[Cl-Sal(PMeOSi)DPTA] **3[b]**, V=O[Sal(*n*-propyltrimethoxysilyl)DETA], V=O[Sal(PMeOSi)DETA] **6[a]** and V=O[Cl-Sal(*n*-propyltrimethoxysilyl)DETA], V=O[Cl-Sal(PMeOSi)DETA] **6[b]** (Scheme 1), have been synthesized and well characterized by modern spectroscopic techniques. These are the first examples of the alkoxysilane ligands with Oxovanadium(IV) complexes in best of our knowledge. Only one article has been found with Schiff-base Co and Cu complexes with **2[a]** ligand [32]. These vanadium metal complexes have been covalently anchored into the functionalized silica and/or alumina surface via silicon-alkoxide route by the condensation process (elimination of CH_3OH) as supported inorganic–organic hybrid catalysts (supported catalysts A to H, see in Scheme 2). These supported catalysts with Oxovanadium(IV) complexes have been tested for the cyclohexane oxidation reaction with molecular oxygen (cheaper and freely available from air) under relatively mild condition in micro-batch reactor.

3.1. *V-complexes: synthesis and characterization*

Trimethoxysilyl pentacoordinate Schiff-base ligand with five-coordination **2[a]** was synthesized as according to Carré et al. [27] and ligands **2[b]**, **5[a]**, **5[b]** are included first time here. Two different amines 2,2′-bis(aminopropyl)amine(DPTA), 2,2′-bis(aminoethyl)amine (DPTA) have been used along with two different aldehydes, viz. salicylaldehyde (Sal), 5-chlorosalicylaldehyde (Cl-Sal). These ligands with donor sets of two phenolate oxygen, two Schiff-base nitrogen and another tertiary amine nitrogen atom have been reacted with the terminal iodo group of the 3-iodopropyl-trimethoxysilane as ligands **2[a]** yield 90%, **2[b]** yield 92%, **5[a]** yield 88% and **5[b]** yield 90%. The structures of all the ligands have been confirm by ^{1}H NMR, $^{13-}$C NMR, ^{15}N NMR, FAB-mass, elemental analysis and FT-IR spectra (see Section 2). The $V{=}O(C_5H_7O_2)_2$ was introduce at the last step of synthetic process [30], with the ligands **2[a]**, **2[b]**, **5[a]** and **5[b]** for the preparation of four trimethoxysilyl pentacoordinate Schiff-base V-complexes, **3[a]** yield 87%, **3[b]** yield 86%, **6[a]** yield 85% and **6[b]** yield 88% (Scheme 1).

The proposed formulation for these vanadium complexes have been supported by FAB-mass spectral data, FT-IR spectroscopy, EPR spectroscopy and elemental analysis. The mass spectrum of each V-complex is characterized by an intense molecular ion, which is the most abundant ion in the spectrum, as well as relatively abundant doubly charged parent molecular ions. No polymeric species were detected in any spectrum which suggests that either the complexes are monomeric or any polymers present were destroyed upon sublimation or upon electron impact.

The infrared spectra of all the ligands show a broad shoulder around 3400 ν(–OH) which was due to the –OH, which has been disappeared after the coordination with vanadium occurs. The typical Si–O lattice vibrations bonds was observed around 1160 ν(–Si–O). Appearance of a band at ν(1623–1643) associated to the C=N group confirms the presence of Schiff-base moiety, whereas the absence of bands in the region ν(1634–1651) associated with the N–H bond was also observed. The presence of main characteristic bands of the V=O unit is clearly reflected in the typical IR signals at 926–960 [s, ν(V=O)] and 630–635 [s, ν(V···O)]. It was further confirmed by the EPR spectra which show typical eight line spectrum of paramagnetic V=O(IV) monomeric species (^{51}V, $I = 7/2$) with characteristic g, A|| and A⊥ parameters.

3.2. *Supported V-catalysts: preparation and characterization*

The main target of our study was the preparation of supported vanadium complex catalysts, which had been obtained from a grafted reaction technique of the silanol groups (–OH) on surface of supports matrix (SiO_2 and Al_2O_3) with trimethoxy groups ($-OCH_3$) of Schiff-base Oxovanadium(IV) complexes **3[a]**, **3[b]**, **6[a]** and **6[b]**, by the condensation reaction (overnight reflux in toluene) and liberation of MeOH (Scheme 2) [13(a)]. These final supported catalysts are abbreviated as (SiO_2/**7[a]** as Catalyst A, Al_2O_3/**7[a]** as Catalyst B, SiO_2/**7[b]** as Catalyst C, Al_2O_3/**7[b]** as Catalyst D, SiO_2/**8[a]** as Catalyst E, Al_2O_3/**8[a]** as Catalyst F, SiO_2/**8[b]** as Catalyst G and Al_2O_3/**8[b]** as Catalyst H). As methoxysilane is sensitive towards moisture all the manipulations have been carried out under N_2. Any residual and excess of V-complexes in toluene were subsequently removed by the soxhlet thimble filled by the supported V-catalysts extraction.

The thermal stability of all the solid catalysts samples were analyzed by TGA (Fig. 1) showing only a 1% weight loss up to 523 K, below the maximum reaction temperature (448 K in entry 8 of Table 2). In FT-IR spectrum after the immobilization of V-complexes, a broad shoulder was appeared between; $\nu = 3620$ and 3375 and $\nu = 1620$ and 1010 in all the supported catalysts due to support effect (silica and alumina). The anchoring of V=O(IV) complex on the support was confirmed by the V=O bond between $\nu = 926$ and 960 in all the catalysts. The eight line of EPR results of solid supported catalysts also confirm the presence of vanadium (IV) oxidation state of complexes with typical *g* values and *a* parameters. The presence of vanadium on the supported catalysts were further confirmed by inductive couple plasma (ICP) analysis in fresh catalysts (0.28–0.34 wt.%) and after the oxidation reaction of used catalysts shows very little amount (~0.2 wt.%) of metal loss.

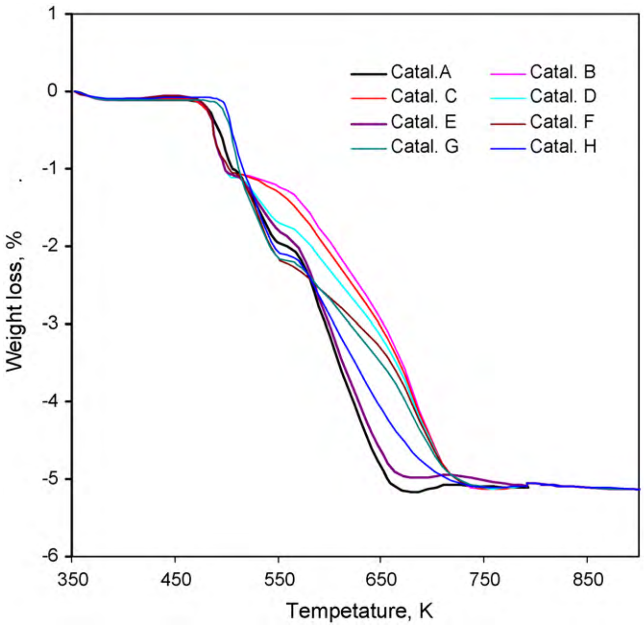


Fig. 1. TGA analysis results of supported catalysts A to H (trialkoxysilane pentacoordinate V=O(IV) complexes anchored with inorganic martial of solid supports).

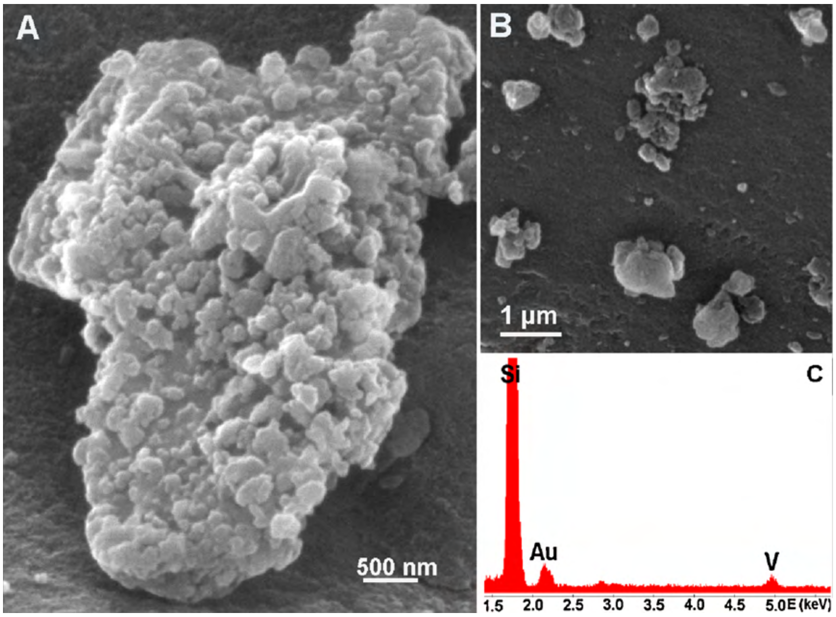


Fig. 2. Morphological study of Catalyst C complex, analyzed by scanning electron microscopy [image magnification, 5 nm (A), 1 μm (B) and by EDS detector (C)].

The above analytical evidences indicate the possible anchoring of V-complexes on the surface of support matrix. The morphological study of Catalyst C is shown by SEM results in Fig. 2A (500 nm magnification), the bright particles on the dark background on the surface of supported matrix, *i.e.* SiO_2 being assigned as the presence of the vanadium complex. The SEM-EDS detector analysis result clearly indicates the presence of vanadium metal percentage (Fig. 2C), as bunch of brighter particles on the SiO_2 matrix in Fig. 2B.

3.3. *Typical cyclohexane oxidation with molecular oxygen*

A series of SiO_2 and/or Al_2O_3 anchored trimethoxysilane pentacoordinate Oxovanadium(IV) complexes as supported catalysts (A, B, D, E, F, G and H) were applied for the selective oxidation reaction with neat cyclohexane and molecular oxygen (O_2) in a rocking type micro-batch reactor. The cyclohexane was converted by the chemical oxidation process, to cyclohexanol and cyclohexanone under relatively mild conditions, without adding any solvent or additive (Table 1 and Scheme 3).

Supported Catalyst C (SiO_2/**7[b]**), provides the most effective catalytic system, in a typical entry (entry 3, Tables 1 and 2) leading, after 720 min reaction time, to yields (moles of product per mole of C_6H_{12}) of $C_6H_{11}OH$ and $C_6H_{10}O$ of 28.5 and 9.4% (37.9% overall for these products), within a total 38.5% of C_6H_{12} yield, including a little amount of by-products (*i.e.* alkyl hydroperoxide, adipic acid, hexanolactone and other esters), for molecular oxygen, $p(O_2) = 10.1$ bar, at 423 K. Conducting a mass balance to this run, we obtain that 2.340 g of cyclohexene (27.82 mmol) reacts with 0.484 g of O_2 (15.13 mmol) producing 0.794 g of cyclohexanol (7.92 mmol), 0.256 g of cyclohexanone (2.61 mmol) and 0.019 g of by-products (0.17 mmol); 1.439 g of cyclohexane (17.10 mmol) and 0.316 g of O_2 (9.86 mmol) remain unreacted. The catalytic activity corresponds to a TON (estimated as number of moles of cyclohexanol plus cyclohexanone per mole V-complex loaded on support) of 5.0×10^3 and is higher than those of the other supported catalysts, A to H (Table 1). The increasing molar ratios of the *K*/*A oil* (under low temperature and pressure, Table 2) were suggested that the decompose of *CyOOH* intermediate in the reaction mixture and constantly alcohol was convert into ketone [16(c)]. This intermediate was completely decomposed, under deep oxidation condition (above 423 K or 10.1 bar). It was conformed by GC analysis when the reaction mixture was treated with the excess of PPh_3. We also observed not a big difference of *A*/*K oil* ratio between supported and unsupported C catalyst (Table 2, run **3[e]**). When the oxidation reaction carried out in the presence of the above V-catalyst,

Table 1
Oxyfunctionalization of cyclohexane with molecular oxygen catalyzed by Oxovanadium(IV) complexes supported on silica or alumina under solvent free conditions[a].

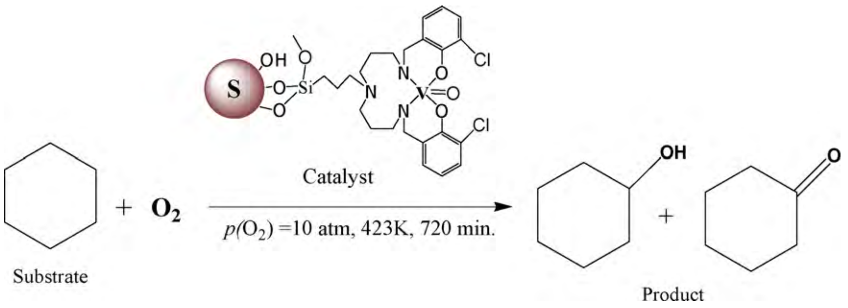
Entry	Catalysts	Yield (%)[b]			*A*/*K* Ratio	TON[c]
		$C_6H_{11}OH$ (*A*)	$C_6H_{10}O$ (*K*)	Overall[d]		
1.	SiO_2/**7[a]** (Catal. A)	20.3	7.0	30.3	2.9	3192
2.	Al_2O_3/**7[a]** (Catal. B)	19.5	6.9	28.6	2.8	3499
3.	SiO_2/**7[b]** (Catal. C)	28.5	9.4	38.5	3.0	5023
4.	Al_2O_3/**7[b]** (Catal. D)	23.6	8.1	33.7	2.9	4494
5.	SiO_2/**8[a]** (Catal. E)	20.8	8.0	29.8	2.6	3192
6.	Al_2O_3/**8[a]** (Catal. F)	17.4	7.1	26.4	2.5	3057
7.	SiO_2/**8[b]** (Catal. G)	23.5	9.2	34.1	2.6	4291
8.	Al_2O_3/**8[b]** (Catal. H)	21.9	8.9	31.8	2.5	4245

[a] Reaction conditions (unless stated otherwise): cyclohexane = 27.82 mmol, supported catalyst = 30 mg, temperature = 323 K, time = 720 min, $p(O_2) = 10.1$ bar (measured at 25 °C; 1 atm = 1.01 bar = 101 kPa).

[b] Percentage molar yield (moles of product/mole of alkane).

[c] Turnover number (mole of $C_6H_{11}OH + C_6H_{10}O$/mol V-complex immobilized on 30 mg of solid catalyst).

[d] $C_6H_{11}OH + C_6H_{10}O$ + by-products.



Scheme 3. Cyclohexane oxidation with O_2 in the presence of supported V-catalyst.

a strong smell at the end of the experiment indicated the formation of oxyfunctionalized product, which have been analyzed by GC and further confirmed by GC–MS techniques that allow to quantify the amounts of cyclohexanol (main product) and cyclohexanone (in lesser amount). As a result of chemical reaction, the colour of the supported catalysts changes to brown. After being used, the supported catalysts can be reactivated upon washing (three times) with acetone and drying in an air oven at 60 °C for 6 h, showing usually a comparable activity to that of the initial entry.

The unsupported vanadium complexes, **3[a]**, **3[b]**, **6[a]** and **6[b]**, do not lead to amounts of products significantly above those obtained in blank essays, which indicates that the V(IV)-species (covalently anchored pentacoordinated Oxovanadium(IV) complexes on SiO_2 or Al_2O_3) are more active than their parents. The effects of various factors such as reaction time, temperature, oxygen pressure, amount of catalyst, presence of a co-catalyst and radical traps on the catalytic activity and selectivity, were studied towards the optimization of the chemical reaction process. All the catalytic results are summarized in Tables 1–3, as well as in Figs. 3–6 for the case of the silica supported Catalyst C in Table 1, which provides the most reactive system.

The ideal condition for the cyclohexane in respect of reaction time was investigated by the most active supported Catalyst C (Table 1, entry 3 and Table 2, entries 1–5, Fig. 3) in the time range of 180–1800 min (under constant conditions: substrate = 27.8 mmol, temp. = 423 K, $p(O_2)$ = 10.1 bar and catalyst = 30 mg) and it was observed that the maximum yield (41.1%) towards the desired products, *i.e.* cyclohexanol (28.4%) and cyclohexanone (9.7%), reaches after 1800 min, but the best selectivity of alcohol (74%) and ketone (24%) were obtained after 720 min. Moreover, extending the reaction period above 720 min results in a detrimental effect on product selectivity particularly for cyclohexanol and little change in formation of cyclohexanone was observed (Fig. 3), concomitantly with an increment of the by-products formation.

We have investigated the best optimized reaction temperature for this system by using the range from 373 to 473 K (Table 1, entry 3, Table 2, entries 6–9 and Fig. 4), under constant reactions: substrate = 27.8 mmol, time = 720 min, $p(O_2)$ = 10.1 bar, catalyst = 30 mg. Although the overall yield, *ca.* 19.6%, of cyclohexane to desired product (*KA oil*) increases rather slowly up to 398 K, a rapid change occurs towards the overall yield, *ca.* 38.5% at 473 K, with good yield of cyclohexanol 28.5% and low yield of cyclohexanone 9.4%. The selectivity dependence on the temperature graph is also shown in Fig. 4 which indicates that the best selectivity, 74.1% towards cyclohexanol is achieved at *ca.* 423 K. However, the reaction temperature was not allowed to go beyond 473 K, due to the formation of an unidentified polymerized dark brown material.

Table 2
Effect of various factors on oxyfunctionalization of cyclohexane to cyclohexanol and cyclohexanone under solvent free conditions, catalyzed by supported Catalyst C with molecular oxygen[a].

Entry	Time (min)	Temp. (K)	$p(O)_2$[b] (bar)	n (catalyst) × 10^{-5}	Yield (%)[c]			Molar ratio A/K
				n (substrate) (mmol)	$C_6H_{11}OH$ (A)	$C_6H_{10}O$ (K)	Over-all[d]	
1	180	423	10.1	7.5	3.4	1.7	5.1	2.0
2	360	423	10.1	7.5	11.2	4.8	16.2	2.3
3	720	423	10.1	7.5	28.5	9.4	38.5	3.0[e]
4	1080	423	10.1	7.5	28.6	9.9	40.4	2.9
5	1800	423	10.1	7.5	28.4	9.7	41.1	2.9
6	720	373	10.1	7.5	4.3	2.3	6.6	1.9
7	720	398	10.1	7.5	13.4	5.9	19.6	2.3
8	720	448	10.1	7.5	30.8	10.2	42.6	3.0
9	720	473	10.1	7.5	33.0	11.0	46.0	3.0
10	720	423	5.1	7.5	9.2	4.2	13.4	2.2
11	720	423	15.2	7.5	32.7	10.7	44.2	3.1
12	720	423	25.3	7.5	32.0	10.6	46.1	3.0
13	720	423	10.1	2.5	7.8	3.9	11.9	2.0
14	720	423	10.1	5.0	15.4	6.8	22.6	3.0
15	720	423	10.1	9.9	31.1	10.0	42.8	3.1
16	720	423	10.1	12.4	31.6	9.8	44.5	3.2
17	720	423	10.1	7.5 + PCA[f]	34.8	10.8	49.1	3.2

[a] Reaction conditions (unless stated otherwise): supported Catalyst C = 2.1 × 10^{-3} mmol, cyclohexane = 27.8 mmol, temperature = 323 K, time = 720 min, $p(O_2)$ = 10.1 bar (measured at 25 °C; 1 atm = 1.01 bar = 101 kPa), micro-batch reactor = 40 mL capacity.

[b] Measured at 25 °C (1 atm = 1.01 bar = 101 kPa).

[c] Molar yield in percentage (moles of product per mole of substrate).

[d] Alcohol + ketone + by-product (total yield).

[e] 2.2% ratio, A/K obtained by unsupported V-complex catalyst (7.8 × 10^{-3} mmol).

[f] 2-Pyrazinecarboxylic acid.

Table 3
Effect of heteroaromatic carboxylic acids as co-catalysts on the cyclohexane oxidation with molecular oxygen catalyzed by supported Oxovanadium(IV) Catalyst C[a].

Entry	Co-catalyst	Time (min)	Yield (%)			Molar ratio *A*/*K*
			$C_6H_{11}OH$ (*A*)	$C_6H_{10}O$ (*K*)	Overall	
1.	PCA	180	4.7	2.2	7.2	2.1
		720	31.2	10.5	44.0	3.0
2.	DPCA	180	4.6	2.1	7.0	2.2
		720	29.7	9.4	42.5	3.1
3.	HPCA	180	4.6	2.0	7.0	2.3
		720	29.1	9.4	42.2	3.0
4.	MePCA	180	4.2	2.1	6.6	2.0
		720	28.6	9.3	41.4	3.1
5.	APCA	180	4.0	1.9	6.2	2.1
		720	27.6	8.6	40.7	3.2
6.	PA	180	3.7	1.8	5.7	2.0
		720	26.5	8.4	39.0	3.1

[a] Reaction conditions same as Table 1, for other conditions (see Section 2).

The effect of molecular oxygen (as oxidant) pressure, $p(O_2)$ on chemical reaction was investigated in the range from 5.1 to 25.3 bar (Table 1, entry 3, Table 2, entries 3 and 10 to 12, under constant conditions: substrate = 27.8 mmol, time = 720 min, temp. = 423 K, and catalyst = 30 mg). The increase of this pressure results in an enhancement of the yields of cyclohexane, *e.g.* upon changing $p(O_2)$ from 5.1 to 25.3 bar, the overall yield increases from 13.4 to 46.1%, what is consistent with the promotion of the solubility of this oxidant (oxygen gas) in the current system (Fig. 5). The selectivity towards alcohol also increases with $p(O_2)$, but only until 10.1 bar, while that for the ketone decreases with the increase of pressure due to the promotion of the relative amount of by-products. Hence, the use of O_2 pressures above *ca.* 25.3 bar is not advantageous in terms of selectivity.

The effect of supported Catalyst C amount on oxidation reaction was also investigated in the range from 10 to 50 mg (Table 1, entry 3, Table 2, entries 3 and 13 to 16, under constant conditions: substrate = 27.8 mmol, time = 720 min, temp. = 423 K and $p(O_2)$ = 10.1 bar). We have found that the overall yield, *ca.* 11.7–44.5% increases with the amount of Catalyst C, 10–50 mg up to a limit. Beyond 50 mg of catalyst, no appreciable further increase in the overall yield is observed (Fig. 6). The selectivity towards the major product, *i.e.* cyclohexanol, remains nearly invariant, *ca.* 71%, but the relative amount of by-products increases.

Some heteroaromatic acids, such as picolinic acid (PA), 2,6-pyrazinedicarboxylic acid (DPCA), 5-hydroxy-2-pyrazinecarboxylic acid (HPCA), 5-methyl-2-pyrazinecarboxylic acid (MePCA), 3-aminopyrazine-2-carboxylic acid (APCA) and 2-pyrazinecarboxylic acid (PCA) have been tested with two time intervals, *i.e.* 180 and 720 min, as possible co-catalysts (constant amount, 8.1×10^{-2} mmol, Table 3). The PCA was found to be the most effective one, promoting the yield of cyclohexane oxidation (overall yield increase from 38.5 to 44.0%, entry 3, Table 2, to entry 1, Table 3, respectively) to the corresponding alcohol and ketone. The above results of PCA (as co-catalyst) shows, it is necessary for this oxidation process to increase the yield of product significantly. The addition of more PCA (up to a PCA amount: supported Cata-

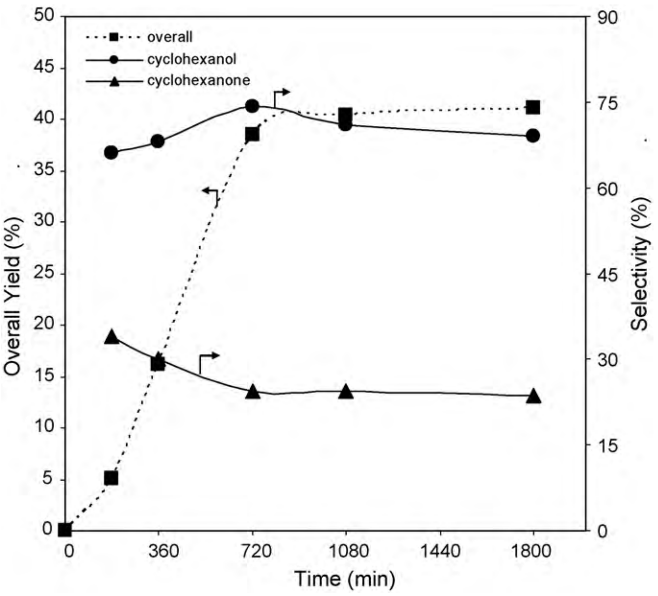


Fig. 3. Time-dependence of the overall yield and % selectivity in the course of catalytic cyclohexane oxidation catalyzed by supported Catalyst C and O_2 as an oxidant (reaction conditions: substrate = 27.82 mmol, catal. = 30 mg, *T* = 323 K, $p(O_2)$ = 1013 kPa).

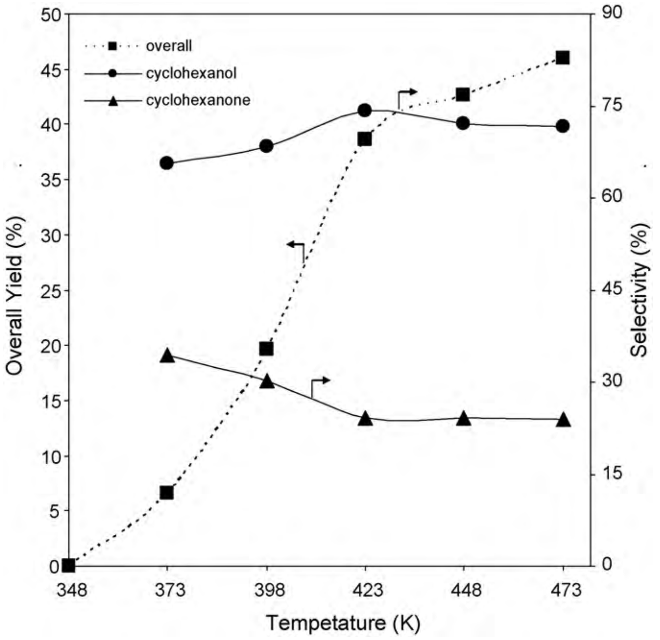


Fig. 4. Temperature-dependence of the overall yield and % selectivity of the products in the course of cyclohexane oxidation, catalyzed by supported Catalyst C and O_2 as an oxidant (reaction conditions: substrate = 27.82 mmol, catal. = 30 mg, *t* = 720 min, $p(O_2)$ = 1013 kPa).

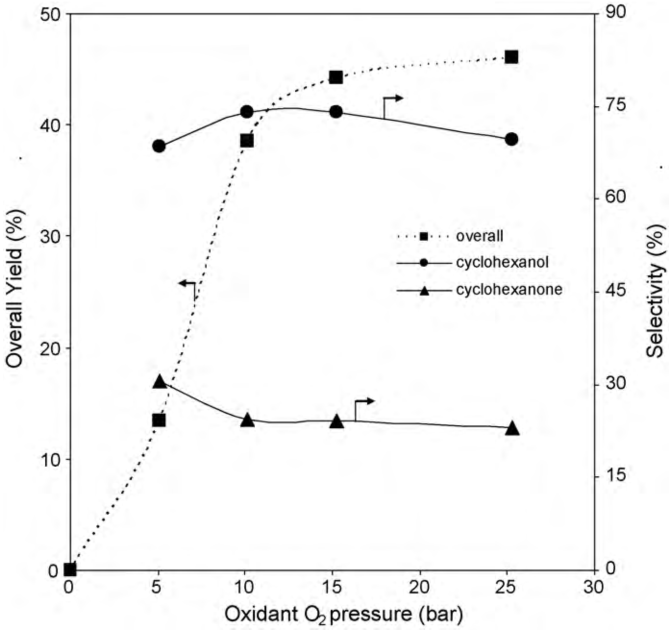


Fig. 5. Pressure-dependence of the overall yield and % selectivity of the products in the course of cyclohexane oxidation catalyzed by supported Catalyst C and O_2 as an oxidant (reaction conditions: substrate = 27.82 mmol, catal. = 30 mg, T = 323 K, t = 720 min).

lyst C molar ratio of 2:1) leads to a considerable yield growth for both cyclohexanol + cyclohexanone (overall yield reaches, *ca.* 49%, Table 2, entry 17). Shul'pin and co-workers have also observed same promoting effect for alkanes oxidation, when vanadate anions combine together with PCA/H_2O_2. They produces free radicals $HOO^•$ and create V(IV)-species, which are also responsible to from $HO^•$ radicals. These radicals are playing an important role to initiate the oxidation reactions of alkanes and cyclohexane [31]. Similar type of promoting effect with PCA was also observed by us for the oxyfunctionalization of cyclic and linear alkanes with dioxygen, catalyzed by supported V-species and Re-species [11(a–c),20(a)].

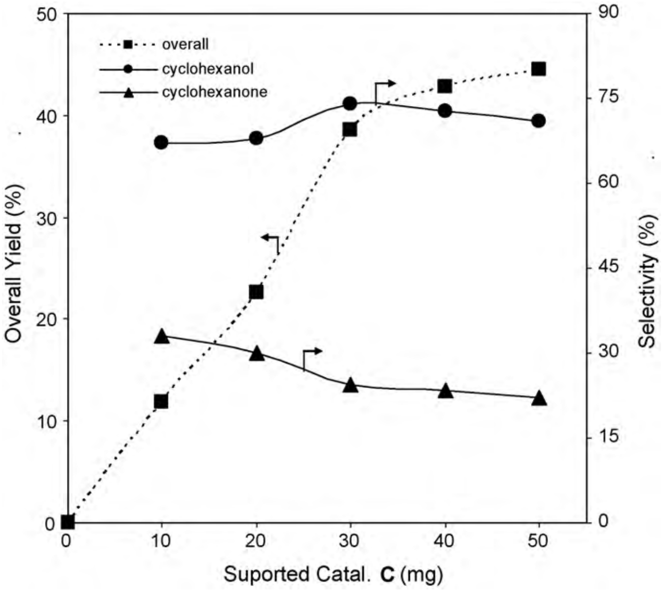


Fig. 6. Amount of supported Catalyst C dependence of the overall yield and % selectivity of the products in the course of cyclohexane oxidation with O_2 as an oxidant (reaction conditions: substrate = 27.82 mmol, T = 323 K, t = 720 min, $p(O_2)$ = 1013 kPa).

The catalyst can be reused or recycle for further oxidation batches by simple admission of more amount of O_2, even without isolating or reactivating the catalyst. Nevertheless, after being used, the catalyst can be reactivated (see Section 2), still displaying a considerable catalytic activity. Thus, following oxidation reaction (entry 3, Table 2) for 720 min, the catalyst was separated, reactivated and recycled leading under the same condition, to achieve overall *ca.* 23.8% (33.5% less from first run). The used Catalyst C was further applied for several more oxidation runs (each time for 720 min) and found after second run the overall conversion (see above) was not decreased significantly (less then ~3%) from 3rd to 6th runs. Finally, the used Catalyst C was considerably lost the catalytic activity after 6th runs (about total 72 h duration). It is suggested that metal loss should not be the main factor responsible for the observed decrease of the catalytic activity or the deposition on the catalyst surface of polymerized material of cyclohexane, which can also act as pore-blocking of support material of V-catalyst, should probably account for it.

The preservation of some catalytic activity is consistent with the ICP analysis of the supported catalyst that shows only little metal loss upon first time use. In fact, the freshly supported Catalyst C has 0.23 wt.% of vanadium whereas, after the reaction (entry 3, Table 2), a metal content of 0.21 wt.% (2nd time run) is still present but change original green into brown colour. Probably, it was due to contact of oxygen gas during oxidation reaction and also change the oxidation state of vanadium-IV to V of solid catalyst (confirm by silent line in EPR for vanadium-V state).

Molecular oxygen is a limiting reagent and the catalyst is still active at the end of oxidation reaction. In fact, after performing the oxidation of cyclohexane under same condition, entry 3, Table 2, the reactor was degassed, more oxygen was admitted until 10.1 bar pressure and the reaction was allowed to proceed for further 720 min. The overall yield then increased (~10%), relatively to the first entry, from 38.5 to 42.1%, showing that the same reaction system still presents a considerable catalytic activity after the consumption of O_2. It can be reused by the simple admission of more oxygen, even without isolating and reactivating of supported catalyst.

The involvement of a free-radical mechanism [32] is supported by the inhibition of the catalytic activity when performing the reactions in the presence of bromotrichloromethane or diphenylamine, *i.e.* carbon- and an oxygen-radical trap, respectively. When the reaction is carried out in the presence of the above liquid radical traps (under same condition, entry 3, Table 2), the amount of formed product (cyclohexanol and cyclohexanone) drops considerably. The uses of common solid radical traps were prevented in the view of their insolubility in the cyclohexane. Moreover, the addition of a free-radical initiator such as 2,2′-azo-bis(2-methylpropionitrile) reduces the induction period of the reaction and increases the conversion of cyclohexane products.

Hence, the cyclohexane (*CyH*) oxidation is proposed to proceed via the cyclohexyl radical ($Cy^•$) obtained by reaction of *CyH* with molecular O_2 upon homolytic C–H bond cleavage (slow induction period). H-atom abstraction from the *CyH* to form the alkyl hydroperoxide (*CyOOH*), whose homolytic decomposition to alkyloxy ($CyO^•$) (O–O bond cleavage) and $CyOO^•$ (O–H rupture) can be catalyzed by transition nature of our catalyst, *i.e.* V(IV) to V(V)–OH and V(V)–OH to V(IV) and formation of H_2O. The *CyOH* can then be formed by the H-abstraction from the *CyH* and $CyO^•$ radicals. The decomposition of the $CyOO^•$ to yield also $Cy(-H){=}O$, which also forms further *CyOH* thus in accord with the higher yield of the cyclohexanol relatively to the cyclohexanone. This type of radical mechanism is known to occur for metal catalysts with two metal oxidation states of comparable stability, like Co(II/III), Cu(I/II), Mn(IV/V) and Fe(II/III) [18(a),32(a,b),33], and this condition is fulfilled also in our case involving V(IV/V) oxidation systems. The oxidation states of fresh catalyst V(IV) eight line spectrum and used catalyst V(V), silent spectrum were also confirmed by the EPR.

The formation of intermediate radical (*CyOOH*) is confirmed by the increase of the detected amount of *CyOH* with concomitant decrease of that of *Cy(–H)=O*, if the final reaction solution, before the GC analysis, is treated with an excess of PPh_3 as indicated by Shul'pin [34]. The hydroperoxide still present is deoxygenated by PPh_3 to the alcohol *CyOH* (with formation of the phosphine oxide Ph_3PO) a reaction that replaces the *CyOOH* decomposition to both *CyOH* and *Cy(–H)=O* in the chromatograph. However the amount of *CyOOH* at the end of the reaction under our usual experimental oxidation (entry 3, Table 2) is relatively small since the variations in the yields of the *CyOH* and *Cy(–H)=O* upon the above treatment with PPh_3 are typically not higher than 11%.

4. Conclusions

In summary, we have successfully synthesized trimethoxysilane pentacoordinate Oxovanadium(IV) Schiff-base complexes, *i.e.* **3[a]**, **3[b]**, **6[a]** and **6[b]** and well characterized by modern instrumental techniques. These O=V(IV) complexes are anchored into silica or alumina matrix via covalent bond by the condensation process as new supported hybrid catalysts. Remarkable catalytic effects were observed when these supported V-catalysts act for cyclohexane oxidation with molecular oxygen (cheaper and greener oxidant, freely available in air) to cyclohexanol (the major product) and cyclohexanone in batch process. The silica supported chlorocomplex, V=O[Cl-Sal(PMeOSi)DPTA] **3[b]** as Catalyst C, provides the best catalytic system, overall 38.5% and high selectivity 98.4%, towards cyclohexanol (74%) and cyclohexanone (24.4%) products, reaching, under typical optimize conditions ($p(O_2) = 10.1$ bar at 423 K, 720 min reaction time). These supported V-catalysts provided remarkable high TONs, *ca.* 5.0×10^3.

The pyrazinecarboxylic acid shows most effective co-catalyst within those tested carboxylic acids; conversion increases significantly overall 38.5–44%. TGA analysis shows the all the supported catalysts are stable up to maximum oxidation reaction temperature up to 473 K. ICP indicates that the metal does not leach out extensively during a normal reaction condition, what allows its reutilization. A radical mechanism appears to occur since, when the reaction is carried out in the presence of the radical traps $CBrCl_3$ or Ph_2NH, the above products are formed only in very small amounts. The intermediate radicals (*CyOOH*) are also observed in the final reaction solution by use of PPh_3. These radical traps and formation of intermediate radical provide some supporting testimony in favour of a free-radical chain mechanism.

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