Alumina-supported vanadyl complexes as catalysts for the C–H bond activation of cyclohexene with *tert*-butylhydroperoxide

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Abstract

Alumina-supported vanadyl complexes with ligands of ethylenediamine (en); [VO(en)$_2$]SO$_4$-Al$_2$O$_3$2-alum; tetramethylethylenediamine (TMED); [VO(TMED)$_2$]SO$_4$-Al$_2$O$_3$3-alum; bipyridine (bpy); [VO(bpy)$_2$]SO$_4$-Al$_2$O$_3$4-alum; 1,10-phenantroline (phen); [VO(phen)$_2$]SO$_4$-Al$_2$O$_3$5-alum; acetylacetonato (acac); [VO(acac)$_2$]-Al$_2$O$_3$; 6-alum; *N,N′*-ethylenebis(salicylideneiminato) (salen); [VO(salen)]-Al$_2$O$_3$7-alum; *N,N′*-phenylenebis(salicylideneiminato) (salophen); [VO(salophen)]-Al$_2$O$_3$8-alum; catalyzed the oxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP). The major products of the reaction were 2-cyclohexene-1-one. The influence of solvent and time for the oxidation reaction has been studied. The selectivity of the 2-cyclohexene-1-(*tert*-butylperoxy) varied with reaction time. Alumina-supported vanadyl catalysts with the nitrogen donor ligands show significantly higher catalytic activity than oxygen donor ligands at the same surface coverage. [VO(bpy)$_2$](SO$_4$)-Al$_2$O$_3$ shows significantly higher catalytic activity than other alumina supported vanandyl complexes. These catalysts can also be reused in the oxidation of cyclohexene for several times.
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1. Introduction

Heterogenized vanadium catalysts have found wide commercial application as oxidation catalysts, *e.g*., for the selective oxidation of *o*-xylene to phthalic anhydride, ammoxidation of alkyl aromatics, selective catalytic reduction (SCR) of NO$_x$ with NH$_3$, and controlling the oxidation of SO$_2$ to SO$_3$ during SCR [1–5]. Furthermore, supported vanadium catalysts are active in the oxidative dehydrogenation of alkanes to olefins, oxidative of butane to maleic anhydride, and the selective oxidation of methanol to formaldehyde or methyl formate [6,7]. In addition, vanadium catalysts are generally known as a poison for fluid catalytic cracking (FCC) catalysts by destroying the Brönsted acid sites and the structure of the ultra stable zeolite Y (USY), [8–10].

A prerequisite for understanding the behavior of supported vanadium catalysts is a through knowledge of their surface chemistry and reactivity as a function of the type and composition of the supports and of the environmental conditions. Despite numerous-mostly qualitative-characterization studies, many fundamental questions concerning the oxidation states and coordination geometries of surface vanadia species still remain unanswered, and this has been the subject of a recent review [11].

In this study, we synthesized several VO^{2+} complexes of various ligands of ethylenediamine, tetramethylethylenediamine, bipyridine, 1,10-phenantroline, acetylacetonato, *N,N′*-ethylenebis (salicylideneiminato) and *N,N′*-phenylenebis(salicylideneiminato) supported on acidic

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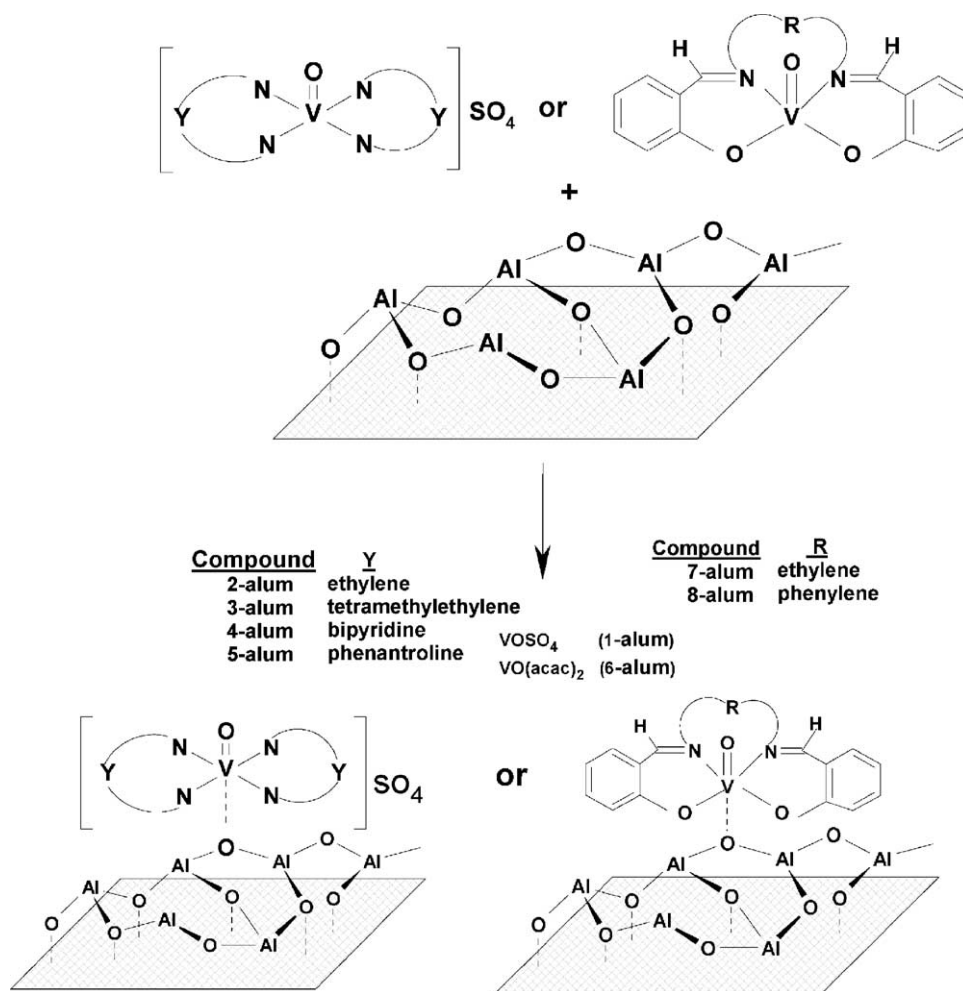
Scheme 1.

alumina (Scheme 1). These solids were then used as catalysts in cyclohexene oxidation reaction by TBHP.

2. Experimental

2.1. Materials and physical measurements

All the solvents were purchased from Merck (pro analysi) and were distilled and dried using molecular sieves (Linda 4 Å). Vanadyl sulfate pentahydrate, VO(acac)$_2$, ethylenediamine (en), tetramethylethylenediamine (TMED), bipyridine (bpy), 1,10-phenantroline (phen), 1,2-phenylenediamine, salicylaldehyde, and *tert*-butlhydroperoxide (solution 80% in di-*tert*-butylperoxide) were obtained from Merck Co. Cyclohexene was distilled under nitrogen and stored over molecular sieves (4 Å). Cyclohexanone was used as an internal standard for the quantitative analysis of the product using gas chromatography. Reference samples of cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one (Aldrich) were distilled and stored in the refrigerator. Acidic alumina was purchased from Merck (Art. No. 1078, aluminum oxide

90 active acidic, 0.063–0.200 mm). It was activated at 500 °C for 8 h before use.

Elemental analyses were obtained from Carlo ERBA Model EA 1108 analyzer. The vanadium contents of the samples were measured by Atomic Absorption Spectrophotometer (AAS-Perkin-Elmer 4100-1319) using a flame approach. The products were analyzed by GC-MS, using a Philips Pu 4400 Chromatograph (capillary column: DB5MS, 30 m), Varian 3400 Chromatograph (15 m capillary column of HP-5; FID) coupled with a QP Finnegan MAT INCOF 50, 70 eV. DRS spectra were taken with a Varian Cary 5 UV–vis-NIR spectrometer at room temperature.

2.2. Preparation of heterogeneous catalysts

2.2.1. Preparation of VOSO$_4$-Al$_2$O$_3$ (1-alum)

Acidic alumina (6 g) was added to a well-stirred solution of vanadyl sulfate pentahydrate (1 g) in methanol (50 ml). The mixture was then heated at 40 °C for 24 h. The light blue solid was filtered and washed with methanol and dried at 50 °C under vacuum. The resulting light blue powder was

stored in a lightly closed bottle and used without reactivation. The concentration of vanadium determined by AAS was $0.014\,mmol\,g^{-1}$.

2.2.2. Preparation of [VO(en)$_2$](SO$_4$)-Al$_2$O$_3$ (2-alum)

Ethylenediamine (4.5 mmol) was dissolved in 50 ml of ethanol, and the solution was stirred. To this solution was added vanadyl sulfate pentahydrate (2.25 mmol) dissolved in 25 ml of ethanol. The color of the solution changed to green. The mixture was then heated at 40 °C for 4 h. Upon cooling the solution, a green solid was obtained which was filtered, washed with chloroform, and dried in vacuum and purified by recrystallization from ethanol. Anal. Calcd for $C_4H_{16}N_4O_5SV$: V, 17.98; C, 16.96; H, 5.69; N, 19.78%. Found: V, 17.88; C, 16.82, H, 5.59; N, 19.83%. A solution of the [VO(en)$_2$](SO$_4$) in CH$_3$OH was added to a suspension of Al$_2$O$_3$ in CH$_3$OH. The resulting suspension was stirred at 40 °C for 8 h. The green solid was filtered, and washed with CH$_3$OH. The [VO(en)$_2$](SO$_4$)-Al$_2$O$_3$ catalyst was dried at 60 °C under vacuum overnight prior to use.

2.2.3. Preparation of [VO(TMED)$_2$](SO$_4$)-Al$_2$O$_3$ (3-alum)

This compound was prepared by a method similar to that for [VO(en)$_2$]SO$_4$ except that tetramethylethylenediamine was used instead of ethylenediamine. Anal. Calcd for $C_{12}H_{32}N_4O_5SV$: V, 12.88; C, 36.45; H, 8.16; N, 14.17%. Found: V, 12.76; C, 36.35, H, 8.07; N, 14.22%. The [VO(TMED)$_2$](SO$_4$) in CH$_3$OH was added to a suspension of acidic alumina in CH$_3$OH. The suspension was heated at 40 °C for 8 h. The green solid was filtered, washed with methanol. The [VO(TMED)$_2$](SO$_4$)-Al$_2$O$_3$ catalyst was dried at 60 °C under vacuum overnight prior to use.

2.2.4. Preparation of [VO(bpy)$_2$](SO$_4$)-Al$_2$O$_3$ (4-alum) and [VO(phen)$_2$](SO$_4$)-Al$_2$O$_3$ (5-alum)

This compound was prepared by a method similar to that for [VO(en)$_2$]SO$_4$] except that bipyridine or phenantroline was used instead of ethylenediamine. Anal. Calcd for $C_{20}H_{16}N_4O_5SV$: V, 10.72; C, 50.53; H, 3.39; N, 11.79%. Found: V, 10.68; C, 50.42, H, 3.34; N, 11.82%. Anal. Calcd for $C_{24}H_{16}N_4O_5SV$: V, 9.73; C, 55.07; H, 3.08; N, 10.70%. Found: V, 9.67; C, 54.12, H, 2.98; N, 10.81%. Acidic alumina was stirred with [VO(bpy)$_2$](SO$_4$) or [VO(phen)$_2$](SO$_4$)-Al$_2$O$_3$ in CH$_3$OH and after 40 °C for 8 h, the solid color changed to light green. It was then washed with CH$_3$OH and dried at 60 °C under vacuum.

2.2.5. Preparation of [VO(acac)$_2$]-Al$_2$O$_3$ (6-alum)

Acidic alumina was added to a well stirred solution of [VO(acac)$_2$] (from Merck) in methanol. The mixture was then heated at 40 °C for 8 h. The light green solid was filtered, washed with methanol and dried at 60 °C under vacuum overnight prior to use.

2.2.6. Preparation of [VO(salen)]-Al$_2$O$_3$ (7-alum) and [VO(salophen)]-Al$_2$O$_3$ (8-alum)

The Schiff-base was obtained by condensation of the appropriate diamine and salicylaldehyde [12–16]. Ligands were recrystallized from ethanol at least once before metalation. The vanadyl Schiff-base complexes were prepared under ambient condition. To a hot solution of Schiff-base ligand (2 mmol) in a mixed solvents (chloroform 15 ml/ethanol 15 ml), a hot solution of VO(acac)$_2$ (2 mmol) in methanol (15 ml) was added. The mixture was heated and a few drops of triethylamine were added. The reaction mixture was refluxed for 30 min. The colored solution concentrated and cooled to yield crystals. Analytical data and physical properties for vanadyl complexes are similar to their complexes were prepared by literature methods [17–19]. Acidic alumina was stirred with [VO(salen)] or [VO(salophen)] in CH$_3$Cl and after 40 °C for 8 h, the solid colour changed to light green. It was then washed with CH$_3$Cl and dried at 60 °C under vacuum.

2.2.7. Oxidation of cyclohexene; general procedure

A mixture of 1.0 g catalyst, 25 ml solvent and 10 mmol cyclohexene was stirred under nitrogen atmosphere in a 50 ml round bottom flask equipped with a condenser and a dropping funnel at room temperature for 30 min. Then 16 mmol of TBHP (solution 80% in di-*tert*-butylperoxide) was added. The resulting mixture was then refluxed for 8 h under N$_2$ atmosphere. After filtration and washing with solvent, the filtrate was concentrated and then subjected to GC analysis.

3. Results and discussion

3.1. Synthesis of neat complexes

Elemental analyses indicate that all of the vanadyl complexes are monomeric species formed by coordination of 1 mol of the vanadyl ion (VO^{2+}) and 2 mol of bidentate diamine (en, TMED, bpy, phen) or 1 mol of tetradentate Schiff-base (salen, slaophen) ligands. The vanadyl Schiff-base complexes are insoluble in water but soluble in most organic solvents. Infrared and UV–vis spectral analyses indicate that coordination of diamine groups on the vanadyl produce a less electrophilic metal-oxo center (Table 1). Green vanadyl complexes have V=O stretching frequencies in the range 976–993 cm^{-1}, which are characteristic of monomeric five coordinate structures [20].

3.2. Heterogenisation of complexes

The heterogenisation of homogenous catalysts is a field of continuing interest. Although some of homogeneous transition metal complexes exhibit remarkable catalytic properties (activities and selectivity), they are unsuitable to separate intact, from the reaction medium making their reuse difficult and contaminating the reaction products. Thus, the hetero-

genisation is always a toxicological and environmental challenge; moreover, it has an economical significance unless the activities of the homogeneous catalysts are exceptionally high. We have done the heterogenisation by supporting the catalysts on acidic alumina. Acidic alumina was chosen because neither of neutral nor basic alumina did adsorb the complex on its surface. The adsorbing tendency of the acidic alumina might arise from the presence of oxygen groups on the surfaces, which are able coordinate to the metal ion center (Scheme 1). This hypothesis was further confirmed when we observed that the complex with three bidentate ligands cannot be adsorbed on the acidic alumina surface [21c].

Vanadium contents of the alumina-supported catalysts were estimated by dissolving the known amount of the catalyst in concentrated HCl and from these solutions, vanadium contents were estimated by atomic absorption spectrometer (AAS). The concentration of vanadium was $0.014 \, mol \, g^{-1}$.

The IR bands of all catalysts are weak due to their low concentration of the complex on alumina. The IR spectra of supported complexes are essentially similar to that of the neat complexes (Table 1). The adsorbing tendency of the acidic alumina might arise from the presence of oxygen groups on the surface in order to coordinate to the metal ion center (Scheme 1).

The DRS spectra of alumina-supported vanadyl complexes are characterized by ligand field transitions, and their energies are dependent on the coordination environment. In the d↔d region the alumina-supported vanadyl catalysts are characterized by a week absorption band and a shoulder (Table 1). Both transitions are typical for V^{4+} in pseudooctahedral coordination. The DRS spectra for alumina-supported vanadyl complexes are quite similar to the reported for several reference compounds of V^{4+} [13–16]. The observation of pseudooctahedrally coordinated V^{4+} by DRS, point toward the presence of a distorted octahedral structure with one coordination vacancy along the other axial position. The latter vacancy is most probably filled by additional lattice oxygen, which completes the coordination sphere. A pictorial representation is given in Scheme 1.

3.3. Catalytic activity

We have recently reported the activation of C−H bond with TBHP and H_2O_2 in the presence of exchanged zeolite NaY with transition metal elements, alumina-supported and zeolite-encapsulation of metal complexes [21]. We showed that some complexes of Mn (II) included in zeolite Y, catalyzed the oxygen transfer from TBHP to cyclohexene and concluded that such simple systems mimic the behavior of cytochrome P-450 type oxidation systems [21b]. We also showed the [Mn(haacac)]-Al_2O_3; (haacac = bis(2-hydroxyanil)acetylacetone], catalyzed cyclohexene oxidation with the highest reactivity and selectivity and 2-cyclohexene-1-one was formed as the main product [21d], and we showed a simple catalyst system of alumina supported Mn (II) complexes with a number of bidentate ligands of N, N; N, O and O, O donors atoms in the oxidation of cyclohexene [21c]. Since, alumina-supported metal systems exhibit catalytic activity in a wide ranging of the industrially important processes and have been extensively studied, we decided to investigate the effect of vanadyl complexes with different chelates of N, N; N, O and O, O donor atoms, supported on acidic alumina in the oxidation of cyclohexene with TBHP.

Results of Table 2 show the catalytic activity of homogeneous catalysts. Comparing between neat and alumina supported complexes as catalyst evidence that alumina-supported catalysts gave higher conversion of cyclohexene than their corresponding neat complexes. The higher activity of supported complexes is because of site isolation of the complexes.

The selectivity and activity results of these alumina-supported catalysts on the oxidation of cyclohexene with

Table 1
Chemical composition, DRS absorption, UV–vis[a] and IR stretching frequencies of neat and alumina-supported vanadyl complexes

Sample	C (%)	H (%)	N (%)	V (%)	C/N	C/V	$^{v}V=O^{b}$ (cm^{-1})	d↔d (cm^{-1})
1	–	–	–	–	–	–	999	794, 658(sh)
1-Alum	–	–	–	1.76 (1.93)	–	–	991	798, 662(sh)
2	16.82 (16.96)	5.59 (5.69)	19.83 (19.78)	17.88 (17.98)	0.85 (0.86)	0.94 (0.95)	987	618, 558(sh)
2-Alum	1.76 (1.81)	1.09 (1.12)	2.20 (2.23)	2.17 (2.06)	0.80 (0.81)	0.81 (0.88)	985	623, 563(sh)
3	36.35 (36.45)	8.07 (8.16)	14.22 (14.17)	12.76 (12.88)	2.56 (2.57)	2.85 (2.83)	981	614, 554(sh)
3-Alum	5.06 (5.19)	1.60 (1.67)	2.16 (2.09)	1.78 (1.89)	2.34 (2.48)	2.84 (2.75)	978	625, 565(sh)
4	50.42 (50.53)	3.34 (3.39)	11.82 (11.79)	10.68 (10.72)	4.27 (4.29)	4.72 (4.71)	981	570, 510(sh)
4-Alum	8.30 (8.41)	0.98 (1.07)	2.02 (2.12)	1.84 (1.83)	4.11 (4.17)	4.52 (4.61)	978	575, 515(sh)
5	54.12 (55.07)	2.98 (3.08)	10.81 (10.70)	9.67 (9.73)	5.01 (5.14)	5.60 (5.66)	973	566, 505(sh)
5-Alum	9.79 (9.87)	0.91 (1.07)	2.06 (1.95)	1.66 (1.79)	4.76 (5.07)	5.89 (5.51)	971	569, 515(sh)
6	45.13 (45.29)	5.22 (5.32)	–	19.10 (19.21)	–	2.36 (2.35)	935	658.8, 591(sh)
6-Alum	4.30 (4.54)	0.96 (1.04)	–	1.76 (1.93)	–	2.44 (2.35)	934	693, 601(sh)
7	57.67 (57.51)	4.23 (4.15)	8.41 (8.56)	15.29 (15.13)	6.86 (6.72)	3.77 (3.80)	979	580.2, 443(sh)
7-Alum	7.06 (7.11)	1.03 (1.09)	1.05 (1.13)	2.01 (2.11)	6.72 (6.67)	3.52 (3.50)	978	586.4, 451(sh)
8	62.89 (63.01)	3.75 (3.70)	7.50 (7.37)	13.18 (13.36)	8.39 (8.55)	4.77 (4.75)	970	546, 436(sh)
8-Alum	8.67 (8.71)	1.02 (1.14)	1.07 (1.12)	1.90 (1.96)	8.12 (8.23)	4.56 (4.58)	968	553, 441(sh)

[a] In methanol solutions at 25 °C.
[b] Infrared spectra measured as KBr pellets. Estimated values are given in parentheses.

Table 2
Oxidation of cyclohexene with TBHP catalyzed by vanadyl complexes in CH_3CN

Catalyst	Conversion (%)	Selectivity (%)			
		Peroxide[a]	Epoxy[b]	Alcohol[c]	Ketone[d]
1	38.4	3.9	25.6	19.0	51.5
2	54.7	4.5	35.3	16.1	44.1
3	53.5	5.6	38.5	15.4	40.5
4	83.9	6.1	56.9	13.2	23.8
5	80.2	7.2	53.2	12.1	27.5
6	37.1	3.2	29.5	20.2	47.1
7	47.2	3.7	52.5	12.0	31.8
8	49.6	5.2	59.2	12.3	23.3

Solvent=10 ml; catalyst = 1.02×10^{-5} mol; duration=8 h, at reflux; cyclohexene=1 ml; TBHP = 2 ml.
[a] 1-(*tert*-butylperoxy)-2-cyclohexene.
[b] Cyclohexene oxide.
[c] 2-Cyclohexene-1-ol.
[d] 2-Cyclohexene-1-one.

TBHP are given in Tables 3–6. At the end of the reaction, the catalyst was separated by filtration, thoroughly washed with solvent and reused under similar conditions. Although the analysis of the recovered catalysts by Atomic Absorption Spectroscopy showed no reduction in the amount of vanadium ion, they showed a slightly lower catalytic activity (3%) (Table 3).

The effect of VO^{2+} complexes supported on alumina was studied on the oxidation of cyclohexene with TBHP in CH_2Cl_2 and the results are shown in Table 3. As shown in Fig. 1, only allylic oxidation has occurred with the formation of 2-cyclohexene-1-o1, 2-cyclohexene-1-one and 1-(*tert*-butylperoxy)-2-cyclohexene. Oxidation with the same oxidant in the presence of $VO(SO_4)$-Al_2O_3 was 26.5% (Table 3). The increase of conversion from 26.5 to 94.1% compared to $VOSO_4$-Al_2O_3 with $[VO(bpy)_2](SO_4)$-Al_2O_3 indicates that the existence of ligand has increased the activ-

Table 3
Oxidation of cyclohexene with TBHP catalyzed by vanadyl complexes on alumina in CH_2Cl_2

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide[a]	Alcohol[b]	Ketone[c]
1-Alum	26.5	6.1	37.2	56.7
2-Alum	53.2	18.6	31.2	50.2
3-Alum	51.5	19.2	32.1	48.7
4-Alum	94.1	5.6	11.7	82.7
4-Alum[d]	93.1	5.2	11.6	83.2
4-Alum[e]	91.3	5.2	11.3	83.5
4-Alum[f]	91.1	5.2	11.1	83.7
5-Alum	86.4	6.4	12.6	81.0
6-Alum	46.3	19.8	33.2	47.0
7-Alum	80.2	8.6	14.7	76.7
8-Alum	85.2	8.1	13.6	78.3

[a] 1-(*tert*-Butylperoxy)-2-cyclohexene.
[b] 2-Cyclohexene-1-ol.
[c] 2-Cyclohexene-1-one.
[d] First reuse.
[e] Second reuse.
[f] Third reuse.

Table 4
Oxidation of cyclohexene with TBHP catalyzed by vanadyl complexes on alumina in $CHCl_3$

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide[a]	Alcohol[b]	Ketone[c]
1-Alum	25.1	6.4	38.1	55.5
2-Alum	52.5	18.9	32.3	48.8
3-Alum	49.6	19.3	33.5	47.2
4-Alum	89.6	5.7	12.1	82.2
4-Alum[d]	89.1	5.6	11.8	82.6
4-Alum[e]	88.3	5.3	11.6	83.1
4-Alum[f]	86.8	5.1	11.2	83.7
5-Alum	84.1	6.6	13.4	80.0
6-Alum	43.5	20.1	34.6	45.3
7-Alum	79.1	8.7	14.9	76.4
8-Alum	84.1	8.5	13.8	77.7

[a] 1-(*tert*-Butylperoxy)-2-cyclohexene.
[b] 2-Cyclohexene-1-ol.
[c] 2-Cyclohexene-1-one.
[d] First reuse.
[e] Second reuse.
[f] Third reuse.

Table 5
Oxidation of cyclohexene with TBHP catalyzed by vanadyl complexes on alumina in CH_3CN

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide[a]	Alcohol[b]	Ketone[c]
1-Alum	18.3	10.7	40.2	49.1
2-Alum	36.5	24.5	43.6	31.9
3-Alum	31.2	26.7	41.5	31.8
4-Alum	69.2	11.7	16.5	71.8
4-Alum[d]	68.4	11.5	16.1	72.4
4-Alum[e]	67.2	11.2	15.7	73.1
4-Alum[f]	66.1	10.9	15.3	73.8
5-Alum	59.6	12.6	19.6	67.8
6-Alum	27.6	27.2	38.5	34.3
7-Alum	58.6	16.1	19.2	64.7
8-Alum	52.4	16.9	18.8	64.3

[a] 1-(*tert*-Butylperoxy)-2-cyclohexene.
[b] 2-Cyclohexene-1-ol.
[c] 2-Cyclohexene-1-one.
[d] First reuse.
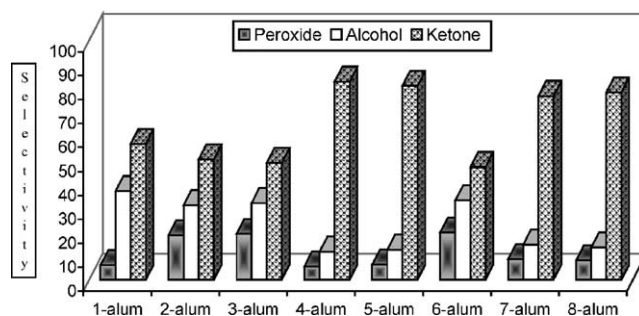[e] Second reuse.
[f] Third reuse.

Fig. 1. Oxidation products distribution on alumina in dichloromethane with vanadyl complexes/TBHP.

Table 6
Oxidation of cyclohexene with TBHP catalyzed by vanadyl complexes on alumina in cyclohexene

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide[a]	Alcohol[b]	Ketone[c]
1-Alum	29.8	4.5	31.2	64.3
2-Alum	57.4	11.2	28.2	60.6
3-Alum	56.3	11.8	29.1	59.1
4-Alum	95.2	4.1	10.1	85.8
4-Alum[d]	95.1	4.0	10.0	86.0
4-Alum[e]	94.8	3.9	9.8	86.3
4-Alum[f]	94.6	3.8	9.6	86.6
5-Alum	88.9	4.2	9.3	86.5
6-Alum	48.5	13.2	28.4	58.4
7-Alum	86.2	7.1	12.6	80.3
8-Alum	90.1	7.2	13.1	79.7

[a] 1-(*tert*-Butylperoxy)-2-cyclohexene.
[b] 2-Cyclohexene-1-ol.
[c] 2-Cyclohexene-1-one.
[d] First reuse.
[e] Second reuse.
[f] Third reuse.

ity of the catalyst by a factor 3.55. From the results indicated in Table 3, it is evident that cyclohexene-2-one is selectivity formed in the presence of all catalysts.

The trend observed in Tables 2–6 could be explained by the donor ability of ligands (en, TMED, bpy, phen, salen, salophen) available in the complex catalyst. As Wang et al. have pointed out recently, the key point in the conversion of cyclohexen to the products is the reduction of L-M^{n+} to L-$M^{(n-1)+}$. This reduction to L-$M^{(n-1)+}$ is facilitated with the ligands available around the metal cation [22].

The formation of the allylic oxidation products, 2-cyclohexene-1-one and 2-cyclohexene-1-ol shows the preferential attack of the activated C-H bond over the C=C bond. The formation of 1-(*tert*-butylperoxy)-2-cyclohexene shows the presence of radical reactions [23]. That TBHP as oxidant promotes the allylic oxidation pathway and epoxidation is minimized, especially under the highly acidic properties of alumina-supported with transition metal ions and complexes, has been observed by us and others [21c,24] (Fig. 2).

Table 7 gives the effect of time on product distribution. By increasing time, while conversion percentage and 2-cyclohexene-1-one, the yield of 2-cyclohexene-1-ol and 1-
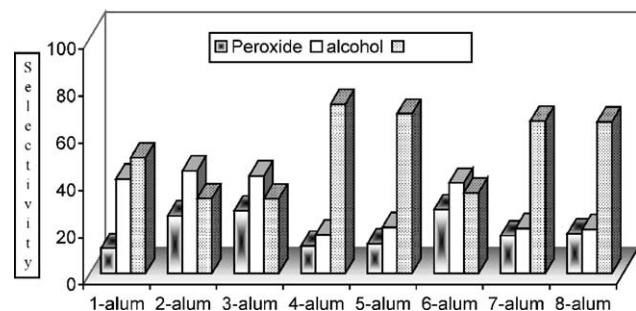

Fig. 2. Oxidation products distribution on alumina in acetonitrile with vanadyl complexes/TBHP.

Table 7
Effect of time oxidation of cyclohexene with TBHP catalyzed by [VO(bpy)$_2$](SO$_4$)-Al$_2$O$_3$ in CH$_3$CN

Time (h)	Conversion (%)	Selectivity (%)		
		Peroxide[a]	Alcohol[b]	Ketone[c]
2	42.9	20.2	24.7	55.1
4	51.8	18.5	22.1	59.4
6	60.6	14.7	19.6	65.7
8	69.2	11.7	16.5	71.8
10	71.9	10.9	13.7	75.4
12	82.3	10.1	10.8	79.1

[a] 1-(*tert*-Butylperoxy)-2-cyclohexene.
[b] 2-Cyclohexene-1-ol.
[c] 2-Cyclohexene-1-one.

(*tert*-butylperoxy)-2-cyclohexene decreases at the presence of [VO(bpy)$_2$](SO$_4$)-Al$_2$O$_3$/CH$_3$CN.

3.4. Effect of solvent

The effect of various solvents for the oxidation of cyclohxene with alumina-supported vanadyl complexes as catalyst was also studied. The oxidation reactions were carried out in protic and aprotic solvents. The results are given in Tables 3–6. In all the oxidation reaction, 2-cyclohexene-1-one was formed as the major product. The selectivity for 2-cyclohexene-1-one formation was 82% while the selectivity for 2-cyclohexene-1-ol and 1-(*tert*-butylperoxy)-2-cyclohexene was less than 18% for [VO(bpy)$_2$]SO$_4$-Al$_2$O$_3$ catalyst in CH$_2$Cl$_2$ (Table 3). When the reaction was carried out in acetonitrite as solvent, the conversion percentages decrease by a factor of 1.36 (Table 5). This might be attributed to the donor number of acentonitrile (14.1) and therefore, its higher ability to occupy the vacant spaces around the vanadium center and prevent the approaching of oxidant molecules toward the catalyst center. In dichloromethane and chloroform, the yields of 2-cyclohexene-1-ol and 2-cyclohexene-1-one were higher and lower yield of the peroxy species was obtained as compared to the other solvents.

4. Conclusion

In this study, we have used a simple catalysis system of alumina-supported vanandyl complexes with a number of bidentate (N, N; O, O) and tetradentate Schiff-base (NNOO) ligands in the oxidation of cyclohexene. Oxidation of allylic site was resulted with TBHP as oxidant. The high percentage yield of reactions especially in the presence of alumina-supported vanandyl bipyridine complex seems promising. The extension of the method to different olefines is currently under investigation in our laboratory.

References

[1] M.S. Wainwright, N.R. Foster, Catal. Rev. Sci. Eng. 19 (1979) 211.
[2] V. Nikolov, D. Klssurski, A. Anastasov, Catal. Rev. Sci. Eng. 33 (1991) 1.

[3] M. Sanai, A. Anderson, J. Mol. Catal. 59 (1990) 233.

[4] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.

[5] J. Svachula, L.J. Alemany, P. Feriazzo, E. Tronconi, F. Bregani, Ind. Eng. Chem. Res. 32 (1993) 826.

[6] W. Harding, K.E. Birkeland, H.H. Kung, Catal. Lett. 28 (1994) 1.

[7] P. Forzatti, E. Tronconi, G. Busca, P. Tittarelli, Catal. Today 1 (1987) 209.

[8] G.M. Woltermann, J.S. Magee, S.D. Griffith, Stud. Surf. Sci. Catal. 76 (1993) 105.

[9] S.J. Yang, Y.W. Chen, C. Li, Appl. Catal. A: Gen. 115 (1994) 59.

[10] C.A. Trujillo, P.P. Knops-Gerrits, L.A. Orieda, P.A. Jacobs, J. Catal. 168 (1997) 1.

[11] I.E. Wachs, B.M. Weckhuysen, Appl. Catal. A: Gen. 157 (1997) 67.

[12] H. Schiff, Ann. Chem. Suppl. 3 (1864) 43.

[13] E.N. Jacobsen, in: E.N. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, vol. 12, Pergamon, Oxford, UK, 1995, p. 12.

[14] L.F. Lindroy, The Chemistry of Macrocyclic Ligand Complexes, Cambridge University Press, Cambridge, UK, 1989.

[15] A. Böttcher, M.W. Grinstaff, J.A. Labinger, H.B. Gray, J. Mol. Catal. A 113 (1996) 191.

[16] D.M. Boghaei, S. Mohebi, J. Mol. Catal. A: Chem. 179 (2002) 41.

[17] C.J. Chang, J.A. Labinger, H.B. Gray, Inorg. Chem. 36 (1997) 5927.

[18] J.A. Bonaides, C.J. Carrano, J. Am. Chem. Soc. 108 (1986) 4088.

[19] E. Tsuchida, K. Yamamoto, K. Oyaizu, N. Iwasaki, F.C. Anson, Inorg. Chem. 33 (1994) 1056.

[20] D.M. Boghaei, S. Mohebi, J. Mol. Catal. A: Chem. 179 (2002) 41.

[21] (a) M. Salavati-Niasari, F. Farzaneh, M. Ghandi, J. Mol. Catal. A: Chem. 175 (2001) 105;
(b) M. Salavati-Niasari, F. Farzaneh, M. Ghandi, L. Turkian, J. Mol. Catal. A Chem. 157 (2000) 183;
(c) M. Salavati-Niasari, F. Farzaneh, M. Ghandi, J. Mol. Catal. A: Chem. 186 (2002) 101;
(d) M. Salavati-Niasari, H. Banitaba, J. Mol. Catal. A: Chem. 201 (2003) 43;
(e) M. Salavati-Niasari, J. Hasanalian, H. Najafian, J. Mol. Catal. A: Chem 209 (2004) 204;
(f) M. Salavati-Niasari, H. Najafian, J. Chem. Res. 9 (2003) 586;
(g) M. Salavati-Niasari, J. Mol. Catal. A 217 (2004) 87.

[22] M. Wang, C.J. Hao, Y.P. Wang, S.B. Li, J. Mol. Catal. 147 (1999) 173.

[23] D. Koola, J.K. Kochi, J. Org. Chem. (1987) 4545.

[24] A.H. Gemeay, M.A. Salem, I.A. Salem, Colloids Surf. 117 (1996) 245.