

Nafion[®]-supported vanadium oxidation catalysts: redox *versus* acid-catalysed ring opening of 2-substituted cycloalkanones by dioxygen

Leïla El Aakel^a, Franck Launay^{a,*}, Jean-Marie Brégeault^{a,*},
Ahmed Atlamsani^b

^a *Laboratoire des Systèmes Interfaciaux à l'Echelle Nanométrique, Université Pierre et Marie Curie/CNRS, case 196,
4 place Jussieu, 75252 Paris Cedex 05, France*

^b *Département de Chimie, Laboratoire de Chimie Physique Appliquée, Faculté des Sciences, Université Abdelmalek-Essaadi,
BP2121, 93000 Tétouan, Morocco*

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Abstract

[VO]²⁺-Exchanged Nafion[®] beads are efficient catalysts for the aerobic C–C bond cleavage of 2-hydroxycyclohexanone and 2-methylcyclohexanone in methanol and acetonitrile, respectively. Performances of the heterogeneous systems are similar to their homogeneous counterparts. However, diffusion limitations with these two substrates, especially for the higher vanadyl contents have led to the design of different mixed redox and acid solid catalysts. Blank tests using non-exchanged Nafion[®] in methanol show that primary and secondary α -hydroxyketones are easily converted to various methoxy derivatives which are prone to autoxidation. More selective oxidation occurs when both protons and vanadyl salts are involved. Bead size and the nature of the solvent used for the ion exchange are important. The leaching of the different solids is less for α -alkyl ketones in acetonitrile.

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1. Introduction

The oxidative cleavage of cyclic ketones and their substituted derivatives is the main pathway for the synthesis of diacids and keto-acids on both the laboratory and industrial scales [1,2]. The conversion of cyclohexanone or of cyclohexanol–cyclohexanone mixtures (KA oil) to adipic acid, one of the starting materials of Nylon[®] 6-6, is the most important application of this reaction [3]. Nitric acid is used as the oxidant in current processes, thereby leading to pollution by side-products such as NO_x and N₂O [4]. Similarly, laboratory-scale experiments based on stoichiometric oxidants like Pb(OAc)₄, NaIO₄, etc. [1,5] result in the formation of large amounts of solid toxic wastes which are not easily recyclable.

For these reasons, there is still a need for an active and selective catalyst working under environmentally friendly conditions. Alternatives using dioxygen [6,7] or hydrogen peroxide [8,9] have been proposed. More specifically, vanadium-based heteropolyacids H_{3+n}[PMo_{12-n}V_nO₄₀]·aq (hereafter HPA-*n*, where *n* = 2, 3, etc.) or copper(II) salts [2,10] were shown to be efficient catalyst precursors for the C–C bond cleavage of α -alkylcycloalkanones [6,7] and α -hydroxyketones [11] by dioxygen; promising results were also obtained with cyclohexanone [2,12,13]. The mechanistic investigations of these homogeneous systems are consistent with homolytic reactions involving V(IV and V) species [2,14]. However, solutions of HPA-*n* are complex and questions arise as to the nature of the vanadium species and the role of the Brønsted acidity of the heteropolyacids [2,14–16]. Mono- or dimeric vanadium species can give the same chemistry as the HPA-*n*, but with lower yields of diacids or keto-acids if the redox and acid properties are not tuned correctly [14]. It is known that the redox potential of the V(V)/V(IV) couple increases with acidity [12,17],

* Corresponding authors. Tel.: +33-1-44-27-55-23;
fax: +33-1-44-27-55-36.

E-mail addresses: flaunay@ccr.jussieu.fr (F. Launay),
brégeault@ccr.jussieu.fr (J.-M. Brégeault).

so the reactions should be better if carried out in acidic aqueous media, and strong acids dramatically accelerate the oxidation and favour the enolisation.

Simpler catalyst precursors like vanadyl salts can be used also for the ring opening of ketones by dioxygen in one-phase systems. However, $[\text{VO}]^{2+}$ -exchanged Nafion[®] would combine the advantages of both homogeneous and heterogeneous catalysts. Such perfluorosulfonic acid polymers [18,19] have been proposed successfully for many acid-catalysed processes (isomerisation, esterification, alkylation, hydrocarboxylation, etc.) [20–22]. Partially exchanged with transition metal ions or complexes, they are potential catalysts for the hydrogenation of alkenes [23–25], ethene dimerisation or co-polymerisation with carbon monoxide [26], the hydration of alkynes [27] or the cyclopropanation of alkenes [28,29]. Applications of these resistant polymers under oxidative conditions are less common. Most of the catalytic systems are based on reactions using hydrogen peroxide [30–32] or *tert*-butyl hydroperoxide [33] catalysed by Fe(II), Cr(III), Ce(IV), etc. and some others use dioxygen and carbon monoxide for the oxidative carbonylation of toluene to toluic acid [34]. In parallel, Nafion[®] membranes have been developed in order to control electrochemical reactions and especially in situ hydrogen peroxide generation from hydrogen/dioxygen mixtures [35]. Silica-based Nafion[®] composites exchanged with cationic platinum and palladium complexes were used recently as catalyst precursors for the chemical in situ production of hydrogen peroxide from H₂ and O₂ and the subsequent hydroxylation of benzene [36].

Nafion[®]-supported copper(II) oxidation catalysts combined with dioxygen were proposed previously for the oxidative cleavage of cycloalkanones. However, diffusion limitations and the formation of Cu...Cu pairs within the Nafion[®] beads [37,38] were shown to lower the activity of these materials.

In the present study, Nafion[®]-supported vanadium-oxo species have been prepared and characterized; they were used as catalyst precursors for the aerobic cleavage of C–C bonds in 2-hydroxycyclohexanone (**1**) and 2-methylcyclohexanone (**2**) to afford carboxylic acids derivatives (adipic (**3**) and 6-oxoheptanoic (**4**)). We hoped that combinations of cationic vanadium species in the proximity of SO₃[−] groups would give analogues of catalytically active systems based on various vanadium-containing HPA-*n*. The performances of “Nafion[®]/vanadium (V/IV)/O₂/substrate/solvent” systems can be compared to those of homogeneous systems with “PMoV” species.

2. Experimental

2.1. Materials and apparatus

The organic chemicals (Aldrich), VOSO₄·5H₂O (Pro-labo), H₃PO₄ (85%, Carlo Erba) and commercial sol-

vents, methanol, and acetonitrile (Carlo Erba and Riedel-de Haën, respectively) were used without further purification. Nafion[®] NR50 (7–9-mesh or 10–35-mesh beads, surface area ca. 0.02 m² g^{−1}) were obtained from Aldrich and Lancaster, respectively.

GC analyses were carried out on a Girdel chromatograph (FID) fitted with a SPBTM 1701 capillary column with helium as the carrier gas. Analyses were performed by temperatures ranging from 70 to 200 °C (5 °C min^{−1}, P_{He}: 0.16 MPa). GC-MS analyses were performed on a Trace GC 2000 series (ThermoFinnigan) coupled to a Trace MS mass spectrometer (EI or CI/NH₃). The IR spectra were obtained, in the transmission mode, on a FTIR Bruker Vector-22 apparatus. ¹H NMR and ¹³C spectra were recorded on a Bruker NMR spectrometer model AC 200 (200.13 MHz for ¹H, 50.32 MHz for ¹³C) using TMS as internal reference. Multiplicity is designated as s, singlet; m, multiplet. ESR spectra at the X-band were measured at 298 K with a Varian E4 spectrometer operating at 9.15 GHz and 100 kHz magnetic field modulation. The beads were analysed in quartz tubes. Typical spectra were performed with scan time 4 mn, sweep width 2000 G, time constant 0.1 s.

The vanadium, sulfur and copper compositions of the exchanged polymers were obtained by atomic absorption spectroscopy at the CNRS Analysis Centre in Vernaison (France).

2.2. Preparation of Nafion[®]-exchanged catalysts

Supported metal complexes were prepared by a ligand exchange reaction using a vanadyl sulfate solution and commercial Nafion[®] NR50 (7–9-mesh or 10–35-mesh beads) in the H form (Chemical analyses: %S=2.78, %Cu=0.002). Acidimetric titrations performed on these Nafion[®]-H according to the Aldrich Technical Bulletin Number AL-163 showed that their ion exchange capacities are 0.8 meq. H⁺ g^{−1} in both cases.

The required amount (see Table 1) of vanadyl sulfate (VOSO₄·5H₂O) was introduced into 30 ml of distilled water or acetonitrile. Nafion[®] (1.00 g) was added, and the resulting mixture was stirred for 10 h at room temperature. During this period the resin was blue. The exchanged catalysts prepared in water were separated by filtration, repeatedly washed with distilled water until the pH of the washings was ca. 5.5, then dried under vacuum. The materials prepared in acetonitrile were filtered off and washed with this solvent (3 × 30 ml) and finally dried under vacuum.

2.3. Catalytic testing

Unless otherwise stated, all catalysis tests were carried out using Schlenk techniques (20 ml max.). Dioxygen uptake was monitored with gas burettes connected to the reactor. The substrate (2-hydroxycyclohexanone dimer (**1**) (0.43 g), 2-methylcyclohexanone (**2**) (0.45 ml), 2-hydroxyacetophenone (**5**) (0.52 g), 2-hydroxy-2-methylpropionophenone

Table 1
Determination of the amount (% H⁺ exchanged) of sulfonic acid groups exchanged under various conditions^a

| Entry | Solvent | Bead size (mesh) ^b | Chemical analyses | | % H ⁺ exchanged | | |
|-------|------------------|-------------------------------|-------------------|------|---|-----------------------------------|---------------------------------|
| | | | %S | %V | Expected from IEC ^c and [[VO] ²⁺] ₀ | From pH measurements ^d | From chemical analysis (% S, V) |
| 1 | H ₂ O | 7–9 | 2.95 | 0.41 | 35 | 28.5 | 20 |
| 2 | H ₂ O | 10–35 | – | – | 31 | 28.5 | – |
| 3 | H ₂ O | 7–9 | 2.83 | 0.56 | 50 | 26 | 29 |
| 4 | H ₂ O | 7–9 | 2.86 | 0.97 | >100 | 43 | 53 |
| 5 | H ₂ O | 10–35 | – | – | >100 | 43 | 53 |
| 6 | MeCN | 7–9 | 3.12 | 0.48 | 35 | – | 24 |

^a Preparations in deionized water (entries 1–5) or acetonitrile (entry 6) according to the procedure described in Section 2.

^b 7–9 mesh, 2000–2800 μm; 10–35 mesh, 425–1700 μm.

^c Ion-exchange capacity (IEC) of the 7–9 mesh and 10–35 mesh materials is 0.8 meq. H⁺ g⁻¹.

^d %H⁺ exchanged (from pH measurements) = [(10^{-pH_f} - 10^{-pH_i}) / (ion exchange capacity × amount of Nafion)] × 100, where pH_i and pH_f are the initial and final pH of the solution, respectively. The stoichiometry of exchange in acetonitrile was not checked quantitatively by pH measurements.

(**6**) (0.62 g) i.e. 3.8 mmol) was dissolved in the solvent (methanol or acetonitrile, 3.5 ml) before adding the heterogeneous catalyst precursor ([VO]²⁺/Nafion[®], see Tables 2 and 4; Nafion[®], see Table 3) or H₃PO₄ (see Fig. 3) and the reaction was performed with stirring at 65 °C. After 24 h, the catalytic system was diluted in 30 ml of diethyl ether and a small aliquot was treated with ethereal diazomethane in excess. The products (**7–12**) were identified by GC-MS using the NIST 98 library (**7–8**) or according to literature (**10** and **12**) and quantified with methyl heptanoate or naphthalene as internal standards. Recycling of the catalyst was accomplished by simple filtration, washing with the reaction solvent and drying under vacuum before reuse. Some tests were performed under dioxygen-free dinitrogen atmosphere using standard vacuum line techniques. The corresponding solvents were deoxygenated by three freeze-pump-thaw cycles and stored in sealed Schlenk tubes under dinitrogen.

2.4. Characterizations

Methyl 6,6-dimethoxyhexanoate (**9**): GC-MS (70 eV), *m/e* 158 (M⁺-32, 22), 127 (158-31, 10), 97 (46,7), 84 (100), 71(83).

3,3-Dimethoxycyclohexene (**11**): GC-MS (70 eV), *m/e* 142 (M⁺, 15), 127 (M⁺-15, 2), 114 (16), 111 (45), 99 (18), 95 (18).

The solid, 2,5-dimethoxy-2,5-diphenyl-1,4-dioxane (**13**), isolated from the reaction involving 2-hydroxyacetophenone (**5**) and Nafion[®]-H, was identified by elemental analysis. C₁₈H₂₀O₄: calculated: C, 71.98; H, 6.71; found: C, 72.95; H, 6.94%. IR (KBr, cm⁻¹): 3063, 3035, 2965, 2940, 2835, 1494, 1451, 1248, 1207, 1177, 1073, 1041, 1007, 913, 765, 708. ¹³C NMR (J MOD, CDCl₃): 49.8 (OMe), 67.0

(OCH₂), 126.7, 128.8, 138.2. ¹H NMR (CDCl₃): 3.07 (s, 6H, OCH₃), 3.86 (s, 4H, OCH₂), 7.43–7.61 (m, 10H, CH).

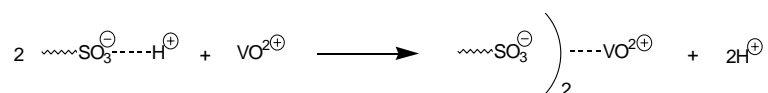
The salt, NH₄Cl_{0.96}(SO₄)_{0.02}·0.03H₂O, recovered from the catalysis tests carried out after heating the cation-exchanged Nafion[®] with MeCN and HCl for 24 h was identified by elemental analysis. Calculated: N, 25.6; H, 7.4; Cl, 62.5; S, 1.18; found: N, 25.4; H, 7.2; Cl, 63.03; S, 1.10%. IR (KBr, cm⁻¹): 3211, 3028, 1998, 1750, 1405 (see Section 3.4).

3. Results

3.1. Characterization of vanadyl-exchanged Nafion[®]

Vanadyl-exchanged Nafion[®] were prepared in aqueous solutions or in acetonitrile using VO₂·5H₂O at room temperature, under aerobic conditions. Various vanadium concentrations were tested (Table 1). Vanadyl sulfate is very soluble in water but not in acetonitrile. In the latter case, exchange nevertheless occurred but took more time than in water. A priori percentages of exchanged protons are based on the ion exchange capacity (IEC) and on the assumption that one vanadyl cation is associated with two sulfonic acid groups, thus releasing two protons (see Table 1: %H⁺ exchanged from IEC and [[VO]²⁺]₀) (Scheme 1).

Preparations in aqueous solution were monitored by pH measurements on the liquid phase. The initial concentration of vanadyl salt (4 × 10⁻³ to 6.4 × 10⁻² mol l⁻¹) and the pH ranges (3.4–1.8) are consistent with the involvement of [VO]²⁺ cations as the major vanadium (IV) species [39,40]. Potentiometric data compare favorably with the ion exchange capacity (IEC) and [[VO]²⁺]₀ (Table 1, entries 1–2) and chemical analysis (Table 1, entries 1, 3 and 4). The proton exchange loading determined by pH measurements



Scheme 1.

Table 2
Oxidation of 2-hydroxycyclohexanone with different “Nafion[®]/[VO]²⁺/O₂/MeOH” systems

| Run | Bead size (mesh) | Solvent (preparation) | %H ⁺ exchanged from chemical analysis | Substrate/V or (H ⁺) ^a (molar ratio) | Substrate conversion (%) ^b | Dimethyl adipate yield (%) ^{b,c} |
|-----|------------------|-----------------------|--|---|---------------------------------------|---|
| 1 | 7–9 | MeCN | 24 (see entry 6) | 35 (5) | 96 (98) | 29 (58) |
| 2 | 7–9 | MeCN | 24 | 65 (10) | 94 (93) | 36 (40) |
| 3 | 10–35 | MeCN | 24 (see entry 6) | 70 (10) | 94 (99) | 78 (88) |
| 4 | 10–35 | MeCN | 92 | 19 (114) | 87 (n.d.) ^d | 59 (n.d.) ^d |
| 5 | 7–9 | H ₂ O | 20 (see entry 1) | 58 (8) | 87 (97) | 18 (34) |
| 6 | 7–9 | H ₂ O | 53 (see entry 4) | 35 (20) | 89 (94) | 52 (62) |
| 7 | 10–35 | H ₂ O | 53 (see entry 4) | 52 (30) | 100 (99) | 74 (68) |
| 8 | 7–9 | H ₂ O | 5 | 305 (10) | 92 (94) | 31 (38) |

Reaction conditions: substrate (3.8 mmol), MeOH (3.5 ml), dioxygen (0.1 MPa), 24 h, 65 °C.

^a Substrate/proton ratios are given in parentheses.

^b Results obtained in the second run are shown in parentheses.

^c Dimethyl adipate (after diazomethane treatment) = dimethyl adipate + methyl adipate + adipic acid (in the crude reaction mixture).

^d Not determined.

may be slightly underestimated due to the existence of [(VO)₂(OH)₂]²⁺ or monomeric species like [VO(OH)]⁺ [40]. Our results show clearly that exchange in water is limited to roughly half the capacity of the perfluorosulfonic acid polymer even when more than the stoichiometric amounts of vanadyl salt are used (Table 1, entries 4 and 5). Vanadium analyses performed on the materials prepared at the lower loadings in acetonitrile (Table 1, entry 6) and in water (Table 1, entry 1) in the presence of the same amount of vanadyl salts are very similar.

3.1.1. Characterization of the native materials by EPR

EPR analysis of the exchanged materials was carried out at 298 K to characterize the paramagnetic cation embedded in the polymer matrix. EPR of the isolated or very diluted vanadyl cations displays the characteristic eight-line spectrum produced by the coupling of the unpaired electron of V(IV) with the 7/2 vanadium nuclear spin [41]. The changes in the paramagnetic cation in confined environments can markedly affect these patterns, and vanadyl salts were used recently to probe the swelling of Nafion[®] in various solvents [42].


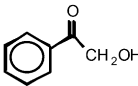
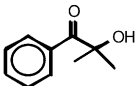
Spectra recorded on vanadyl-exchanged Nafion[®] prepared with low (20% H⁺ exchanged, Fig. 1a) and high metal contents (53%, Fig. 1b) in water show that the first is better resolved with narrow lines. Heavily loaded materials are characterized by broad lines due to the delocalization of electrons (Fig. 1b). This observation is consistent with short distances between the vanadium centres.

Water is a more efficient swelling agent than acetonitrile; this is the reason why the spectra of the samples exchanged in these two solvents to 20 (Fig. 1a) and 24% (Fig. 1c) are different. Clearly, water allows the existence of a slow motional regime of vanadyl cations within the swollen beads. The spectrum of the material prepared in acetonitrile is typical of solid compounds with high anisotropy.

3.2. Assessment of vanadyl-exchanged Nafion[®] for the oxidation of α -hydroxyketones in methanol

Previous work [6,14,43] showed that simple vanadyl salts are efficient homogeneous catalyst precursors for the C–C bond cleavage of α -alkyl- or α -hydroxy-substituted ketones (α -ketols) in the presence of dioxygen. One of the model

Table 3
Nafion[®]-H-assisted reactions of model substrates

| Run | Substrate | Conversion (%) | Products (yields (%)) | O ₂ consumed/substrate consumed |
|-----|---|----------------|---|--|
| 9 |  | 83 | MeO ₂ C(CH ₂) ₄ CO ₂ Me (37) ^a OHC(CH ₂) ₄ CO ₂ Me (14) ^a | 1.0 |
| 10 |  | 97 | PhCO ₂ Me (28.5) ^a PhC(OMe) ₂ CH ₂ OMe (11) PhC(OMe) ₂ CH ₂ OH (1) | 0.8 |
| 11 |  | 0 | – | – |

Reaction conditions: substrate (3.8 mmol), NR50 7–9 mesh (0.56 g, i.e. 0.45 meq. of H⁺), MeOH (3.5 ml), dioxygen (0.1 MPa), 24 h, 65 °C.

^a Yields after diazomethane treatment of the reaction crude mixture (in situ esterification yield about 25%).

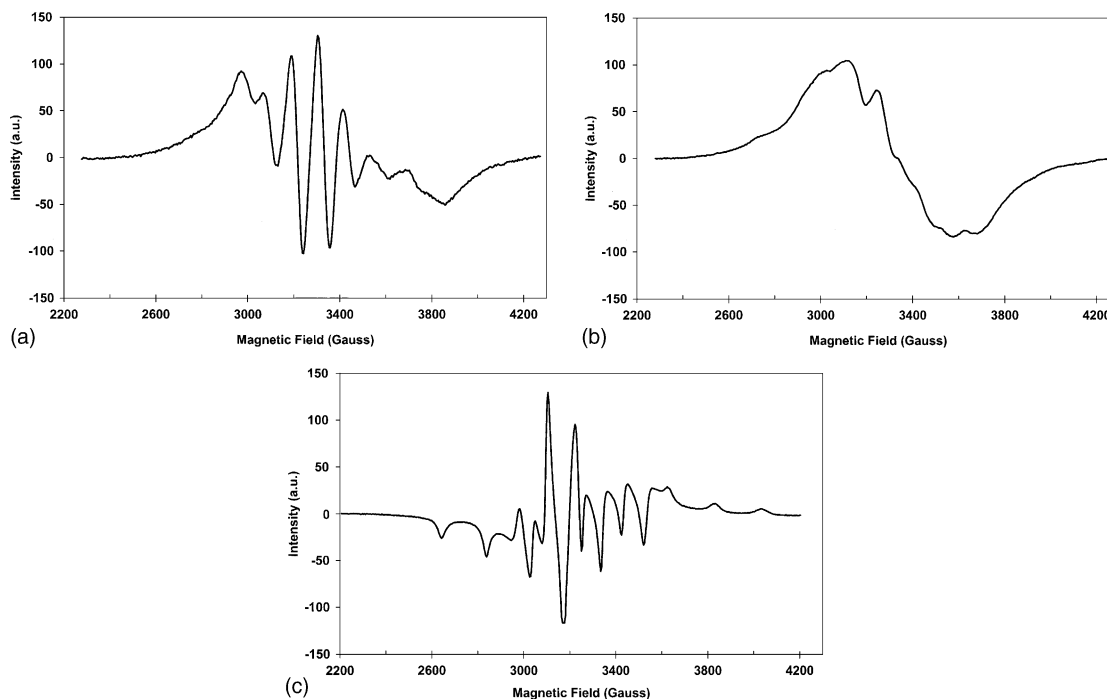


Fig. 1. X-band EPR spectra at 298 K of three native materials: vanadyl-exchanged Nafion[®](7–9 mesh). (a) %H⁺ exchanged in H₂O: 20 (see entry 1, Table 1), (b) %H⁺ exchanged in H₂O: 53 (see entry 4, Table 1) and (c) %H⁺ exchanged in MeCN: 24 (see entry 6, Table 1).

substrates, 2-hydroxycyclohexanone (**1**) can be converted quantitatively to adipic derivatives (acid + methyl esters (**3**)) within 20 h in methanol at 65 °C (Scheme 2).

Experiments were carried out to investigate the influence of the bead granulometry, the loading of the support (%H⁺ exchanged), the solvent used for the preparation as well as the reaction conditions (Table 2). Under acidic conditions with methanol as solvent (Scheme 2), adipic acid was 30–85% esterified to dimethyl adipate. The results (Table 2) correspond to the overall yield of C–C bond cleavage products expressed as dimethyl adipate. The latter was obtained after diazomethane treatment of the reaction mixture (see Section 2).

For comparison with homogeneous systems [43], all the heterogeneous catalysis tests were carried out in methanol (*vide supra*). The conversion of 2-hydroxycyclohexanone under these conditions is better than 85% and the molar ratio of dioxygen to substrate consumed is 1.2–1.4. Only the selectivity was seriously affected by the parameters studied; for pure homogeneous systems [43], it was as high as 91% at 99% conversion.

Moreover, the results (Table 2) are highly dependent upon the nature of the solvent used for the preparation of the cat-

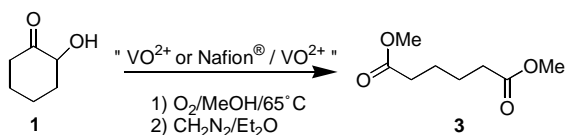
alysts. When vanadyl cation/proton exchange was carried out in water instead of acetonitrile [using beads with similar sizes (7–9 mesh) and exchange levels], the material thus prepared was a less efficient catalyst precursor (runs 1, 2 and 5).

The size of the beads is important: the use of smaller Nafion[®] particles (10–35 instead of 7–9 mesh; see Tables 1 and 2) with the same vanadyl content leads to a significant increase in the yield of C–C bond cleavage products (runs 2 and 3).

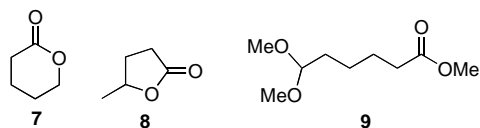
The number of protons exchanged does not need to be very high. Indeed, the catalysis tests performed with the 24 and 92% H⁺/vanadyl-exchanged Nafion[®] (runs 3 and 4), led to a lower conversion and a poorer selectivity in the latter case. This differs from the results under homogeneous conditions where the more vanadium there is, the higher are the conversion and the selectivity [43].

Thus, similar observations are obtained with the materials prepared in water (runs 6 and 7). However, higher but still moderate vanadium contents of the polymer (from 20 to 53% H⁺ exchanged) improved their catalytic activity (runs 5 and 6).

For equivalent loadings and reaction conditions, the vanadium-exchanged ionomer prepared in acetonitrile (run 3) is the most selective catalyst. Most of the tested solids were reused at least once after filtering off, rinsing with hot methanol and drying under vacuum. The first recycling of the 10–35 mesh catalysts prepared in acetonitrile (Table 2, run 3) led to better results than the others. The heterogeneous process under the best conditions leads to slightly poorer results than for homogeneous counterparts



Scheme 2.



Scheme 3.

involving $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$. The lower selectivity for “Nafion[®]/[VO]²⁺/O₂/2-hydroxycyclohexanone/MeOH” is due to the formation of oxidation products like δ - and γ -valerolactone (**7**, **8**), methyl 6,6-dimethoxyhexanoate (**9**) (Scheme 3); other compounds are obtained through acid-catalysed processes (vide infra).

Dimethyl adipate and the same by-products were formed to the same extent upon the three reuses of the catalyst recovered under the best conditions (Table 2, run 3 and Fig. 2a). The ratio of dioxygen uptake to substrate consumed was 1.2 mol/mol on average. However, the profiles (not reported here) are different; in particular the third and fourth catalysis runs were characterized by 1 h induction periods. The beads go from blue to green during the first test; they are green after the second and third, and brown after the fourth catalysis test. This observation is consistent with the variation of the oxidation state of vanadium and its involvement in redox cycles.

These materials are not stable toward leaching under oxidizing conditions of 2-hydroxycyclohexanone in the liquid phase. The vanadium weight content of the exchanged Nafion[®] prepared in acetonitrile decreased from 0.48 to 0.22% after four runs (i.e. a 54% loss) under the best conditions (run 3, with 10–35 mesh granules). This result is confirmed by measurements performed on a less efficient system using 7–9 mesh beads (Table 2, run 2). In this case, the vanadium weight content decreased from 0.48% to 0.45% and 0.40% after the first and second runs, respectively, i.e. 16.7% of the total amount of metal. A different behaviour toward leaching is observed with less exchanged Nafion[®] (5%) prepared in H₂O (see Table 2, run 8 and Fig. 2b). In this case, the decrease was not monotonous. The vanadium weight content, initially 0.12%, fell to 0.043, 0.032 and 0.013% after the first, second and fourth runs, respectively. In the presence of the substrate or not, analysis of the materials recovered after the first test showed 64% loss of vanadium, after which the lowering of metal was less dramatic.

These results indicate clearly that the solvents used (water or acetonitrile) and the granulometry are key parameters.

3.3. Nafion[®]-H-assisted blank reactions of α -hydroxyketones in methanol

Protonated Nafion[®] beads are not inert supports toward α -ketols. Blank experiments using Nafion[®]-H were carried out with different substrates in MeOH (Table 3).

Acid-sensitive substrates like 2-hydroxycyclohexanone (**1**) and 2-hydroxyacetophenone (**5**) react with dioxygen in the presence of Nafion[®]. Surprisingly, these experiments led to unrecorded C–C bond cleavage products. For instance, 2-hydroxycyclohexanone gave adipic acid derivatives (Table 3, run 9) and 2-hydroxyacetophenone was converted to methylbenzoate (Table 3, run 10) besides the expected ketals. On the other hand, 2-hydroxy-2-methylpropiophenone (**6**) was completely recovered under the same conditions (Table 3, run 11). These results are reproducible and cannot be ascribed to the contamination of the reaction vessels by traces of transition metal salts. Furthermore, we have checked that the small amount of copper in commercial Nafion[®] is not involved in these oxidation reactions. Similarly, a blank experiment showed that 2-hydroxycyclohexanone is totally recovered upon heating in methanol solution in dioxygen (Fig. 3). In the absence of dioxygen, Nafion[®]-H does catalyse the formation of products arising from proton-mediated reactions. The following compounds: 1,1,2-trimethoxycyclohexane (**10**) [44] and 3,3-dimethoxycyclohexene (**11**) together with traces of a dimeric product, 2,5-dimethoxy-2,3:5,6-bis(tetramethylene)-1,4-dioxane (**12**) [45] were identified in the crude reaction mixture by GC–MS analyses. They are oxidized to adipic acid derivatives after 24 h treatment in dioxygen at 65 °C (Scheme 4).

Interestingly, other Brønsted acids were able to induce the C–C bond cleavage of 2-hydroxycyclohexanone in dioxygen (Fig. 3). One of the most selective systems involves orthophosphoric acid. However, none of them was as efficient and selective as the vanadium-exchanged Nafion[®] studied above or the HPA-*n* (*n* = 2, 3, etc.) [11]. In the absence of vanadium, the main products are probably polymeric derivatives which are hardly detectable by

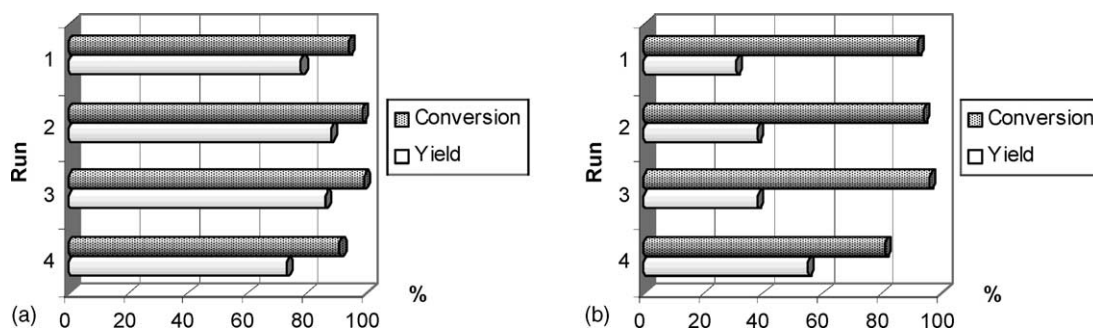
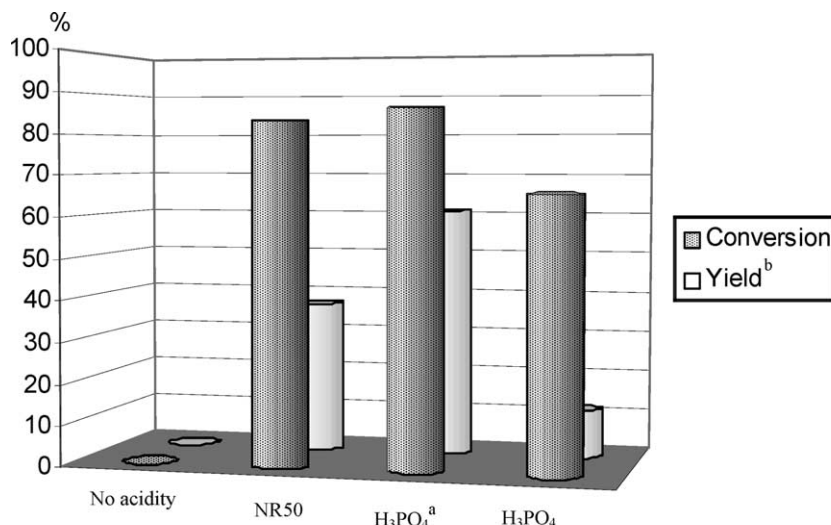


Fig. 2. Recycling of “Nafion[®]/[VO]²⁺/O₂/MeOH” in the C–C bond cleavage of 2-hydroxycyclohexanone by dioxygen. (a) 24% H⁺ exchanged in MeCN (see Table 2, run 3). (b) 5% H⁺ exchanged in H₂O (see Table 2, run 8).

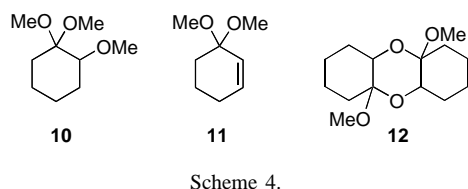


Reaction conditions : Substrate (3.8 mmol), Brönsted acid (0.45 meq of H⁺), MeOH (3.5 ml), dioxygen (0.1 MPa), 24 h, 65°C.

^a Brönsted acid (0.13 meq of H⁺).

^b Yield of dimethyl adipate after diazomethane treatment of the reaction crude mixture. The *in situ* esterification yield was about 65%.

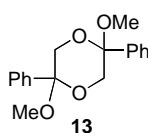
Fig. 3. Acid-assisted conversion of 2-hydroxycyclohexanone to dimethyl adipate in dioxygen (see conditions Table 2, run 1).



GC analysis. A white powder precipitated at room temperature in the experiments on 2-hydroxyacetophenone. A compound, 2,5-dimethoxy-2,5-diphenyl-1,4-dioxane (**13**), was characterized by chemical analysis, FT-IR, ¹H and ¹³C NMR in agreement with data published by Moriarty et al. [45]. The lack of carbonyl and hydroxyl substituents is consistent with the formula shown below (Scheme 5).

3.4. Assessment of solid Nafion[®]/[VO]²⁺ catalysts for oxidation of α -alkyl-substituted ketones: 2-methylcyclohexanone as model substrate in acetonitrile

It is worth nothing that vanadyl precursors exhibit some activity in methanol even in the absence of an acid. In some cases, the presence of an acid has been shown to accelerate vanadium-catalysed oxygenations and to increase the yields [12]. Hence, supporting vanadyl salts on solid acids was expected to be an easier and “greener” way



to develop these reactions, given that no oxidation occurs with Nafion[®]-H alone. The homogeneous C–C bond cleavage of α -alkyl-substituted ketones by dioxygen in the presence of [VO]²⁺ salt precursors is less efficient and selective than the reaction for 2-hydroxycyclohexanone. Indeed 2-methylcyclohexanone (**2**) was 100% converted in methanol yielding 57% of 6-oxoheptanoic derivatives (**4**) at 65 °C (substrate/VOSO₄ · 5H₂O = 33). The conversion of **2** and the yield were lower, 75 and 35%, respectively, in acetonitrile [43]. Low mass balances were found under both homogeneous and heterogeneous conditions, probably as a result of side oligomerization/polymerization reactions (Scheme 6).

First heterogeneous catalysis runs with vanadyl-exchanged Nafion[®] displayed very low efficiency in methanol. On the other hand, the reactions performed in acetonitrile are as successful as in solution (Table 4).

Unlike 2-hydroxycyclohexanone (**1**), 2-methylcyclohexanone (**2**) is not completely consumed during the catalysis tests. As shown previously, conversion and C–C bond cleavage can be improved by decreasing the bead size (Table 4, runs 13 and 14) and/or by working in the presence of more vanadium beads (runs 12 and 13) when 24% H⁺ exchanged materials are considered. In the latter case, the use of greater amounts of these materials is preferred to

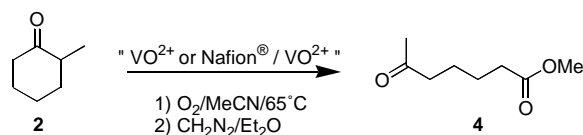


Table 4
Oxidation of 2-methylcyclohexanone with “Nafion[®]/[VO]²⁺/O₂/MeCN” systems

| Run | Granulometry (mesh) | %H ⁺ exchanged from chemical analysis | Solvent (preparation) | Substrate/V or (H ⁺) ^a (molar ratio) | Substrate conversion(%) ^b | 6-oxoheptanoic acid yield (%) ^{b,c} |
|-----|---------------------|--|-----------------------|---|--------------------------------------|--|
| 12 | 7–9 | 24 (see entry 6) | MeCN | 35 (5) | 70 (76) | 21 (18) |
| 13 | 7–9 | 24 | MeCN | 70 (10) | 55 (65.5) | 11 (23) |
| 14 | 10–35 | 24 (see entry 6) | MeCN | 70 (10) | 77 (74) | 33 (38) |
| 15 | 10–35 | 92 | MeCN | 19 (114) | 55 (69) | 43 (28) |
| 16 | 7–9 | 20 (see entry 1) | H ₂ O | 48 (6) | 71 (56) | 36 (2.5) |

Reaction conditions: substrate (3.83 mmol), MeCN (3.5 ml), dioxygen (0.1 MPa), 24 h, 65 °C.

^a Substrate/proton ratios are reported in parentheses.

^b Results obtained in the second run are shown in parentheses.

^c 6-oxoheptanoic acid was quantified after diazomethane treatment.

increasing the loading of the supports (from 24 to 92% of H⁺ exchanged, runs 14 and 15). Lower yields in the first reuse were obtained when vanadyl salts are exchanged in water (runs 12 and 16). This decrease is probably due to extensive leaching of the vanadium species in acetonitrile during the first test. Of all the materials tested, vanadyl-exchanged Nafion[®] beads prepared in acetonitrile were the most efficient catalysts for the C–C bond cleavage of 2-methylcyclohexanone. For the best set of conditions (Table 4, run 14 and Fig. 4), the conversion did not vary over four catalytic runs, whereas the selectivity was slightly improved.

No significant leaching of vanadium species was detected after the first and second runs on the 24% H⁺ exchanged polymers prepared in acetonitrile (run 13). The vanadium weight content remained constant (0.48–0.54%).

Results obtained with H₆[PMo₉V₃O₄₀].aq as catalyst precursors under the same conditions led to 100% conversion of 2-methylcyclohexanone but the 6-oxoheptanoic acid selectivity (60%) [43] was less than those after the second and third reuse of 24% H⁺ exchanged Nafion[®] (Fig. 4). There are many examples of heterogeneous catalytic processes and even homogeneous systems where a first contact between the metal and one of the reactants improves the subsequent performance of the system [46]. Here it was expected that 24% H⁺ exchanged Nafion[®] (prepared either in water or acetonitrile) and dioxygen in acetonitrile would give better results

for the C–C bond cleavage of 2-methylcyclohexanone. Indeed, the oxidation of [VO]²⁺ into [VO₂]⁺ by dioxygen is a rather slow reaction [47] and we thought that this preliminary step would lead to an accumulation of the pervanadyl cation before the addition of the substrate 24 h later. In fact, these modified systems (“aged Nafion[®]”) did not afford improvements. Indeed acetonitrile is hydrolysed under these acidic conditions. The conversion of CH₃CN first to acetamide (CH₃C(O)NH₂) and then CH₃CO₂NH₄ is not easy [48] but it can be catalysed by Brønsted acids [49] and/or cations like Zn²⁺ [50,51] and Cu²⁺ [52] or may be by [VO]²⁺ in our case. Since ammonium acetate is soluble in acetonitrile, a precipitating agent was needed. Addition of a soluble chloride salt, i.e. hydrochloric acid, in the second step allowed the precipitation of mainly ammonium chloride NH₄Cl_{0.96}(SO₄)_{0.02}·0.03H₂O a few hours after the introduction of the substrate in all the corresponding catalysis tests. The coordination sphere of [VO]²⁺ in the as-prepared catalysts would consist mainly of acetonitrile. We propose that acetamidate ions may be coordinated to [VO]²⁺ after heating the exchanged Nafion[®] for 24 h in MeCN. Then, these would be released from the vanadyl (or pervanadyl, [VO₂]⁺) coordination sphere in the reaction mixture through a competitive ligand exchange mechanism involving the enol of 2-methylcyclohexanone.

4. Discussion

To the best of our knowledge, the present work reports the first use of vanadyl-exchanged Nafion[®] as oxidation catalysts. Many other polymers have been loaded with [VO]²⁺ salts and were tested in different reactions with peroxides or alkyl peroxides [53–55]. Direct use of dioxygen without any co-reductant is proposed here in order to perform C–C bond cleavage with the same catalyst precursor. Previous studies under homogeneous conditions distinguish between α-ketols and other α-substituted ketones, the activation of the latter being more difficult unless they are converted to the corresponding enol by acid-catalysis. Two model substrates were considered here: 2-hydroxycyclohexanone (1) and 2-methylcyclohexanone (2).

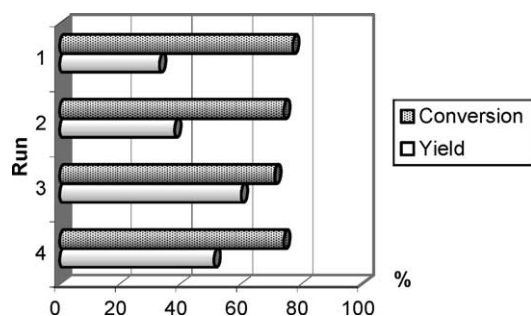


Fig. 4. Recycling of “Nafion[®]/[VO]²⁺/O₂/MeCN” in the C–C bond cleavage of 2-methylcyclohexanone by dioxygen (see conditions Table 4, run 14).

4.1. Choice of solvents used for preparation and catalysis tests

As thoroughly described in the literature, the structure of Nafion[®] is strongly dependent on the solvent [56,57]. Studies of the protonated polymer by small-angle X-ray scattering methods [58] suggest that the sulfonic acid groups are organized in polar clusters embedded in an apolar phase consisting of the perfluorinated chains. In the presence of water, these polar pools can be compared to reverse micelles (diameter $\approx 3\text{--}5$ nm) connected by ca. 1 nm channels. Less polar solvents favour the shrinkage of the clusters, as shown previously by the EPR analyses of $[\text{VO}]^{2+}$ in low-exchanged Nafion membranes [42]. In the present work, we have shown that $[\text{VO}]^{2+}$ cations in aqueous pools are more prone to coupling than in acetonitrile (see Fig. 1a and c). Ions pairs $[-(\text{SO}_3^-)_2 \dots [\text{VO}]^{2+}]$ are stronger in this solvent and their motion is hindered due to narrower pools.

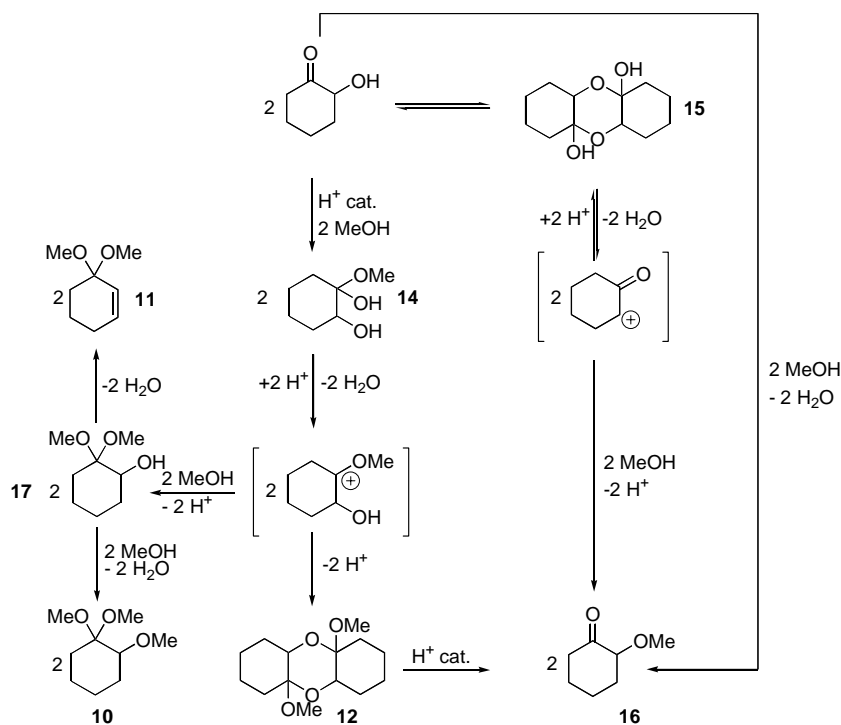
According to this study, whatever the substrate, the most important parameter of our supported catalytic systems is the solvent used for the ion exchange. Vanadyl sulfate, the only precursor tested, is very soluble in water and methanol but it is insoluble in acetonitrile. However, better ion exchange yields were obtained in this solvent due to its lesser ability to swell the polymers than water. This leads to a slow exchange which is not reversible as it may be in the polar solvent. The vanadium entity associated with sulfonic acid groups is probably $[\text{VO}(\text{MeCN})_5]^{2+}$ [59,60], at least for the oxidation of 2-methylcyclohexanone which is also carried out in acetonitrile.

Homogeneous catalysis tests with both substrates are more efficiently performed in methanol because of the higher solubility of vanadyl sulfate in this medium. However, methanol is potentially more easily oxidized than acetonitrile, that is why the latter solvent has been tested under our heterogeneous conditions. Furthermore, less polar solvents were expected to reduce the extent of metal salt leaching during the catalysis tests.

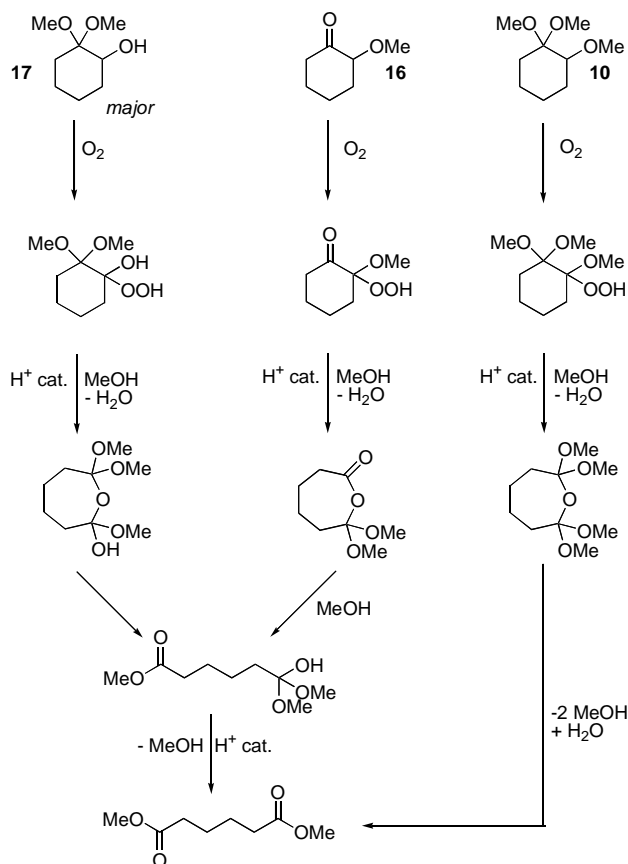
In fact, two systems can be described on the basis of the reactivity of the substrate toward methanol. Primary and secondary α -ketols, which are easily converted to α -hydroxy or α -methoxy ketals and α -methoxyketone under the acidic conditions used, were more efficiently oxidized by our system in methanol. On the other hand, acetonitrile was shown to be a better solvent for 2-methylcyclohexanone (**2**), although undesirable products due to a Ritter reaction cannot be neglected [61].

4.2. Mechanism of the acid-dependent C–C bond cleavage of α -hydroxyketones in methanol

It has been shown that the C–C bond cleavage of α -ketols can proceed in the absence of vanadium salts. The expected products can be formed also by the oxygenation of the primary and secondary compounds in the presence of the perfluorinated ionomer or of other various Brønsted acids in methanol. 2-Methylcyclohexanone (**2**) and tertiary α -ketols like 2-hydroxy-2-methylpropiophenone (**6**) do not react under these conditions. The contamination of the polymer by traces of transition metal ions like copper (II) can be discarded because the resulting process would have been



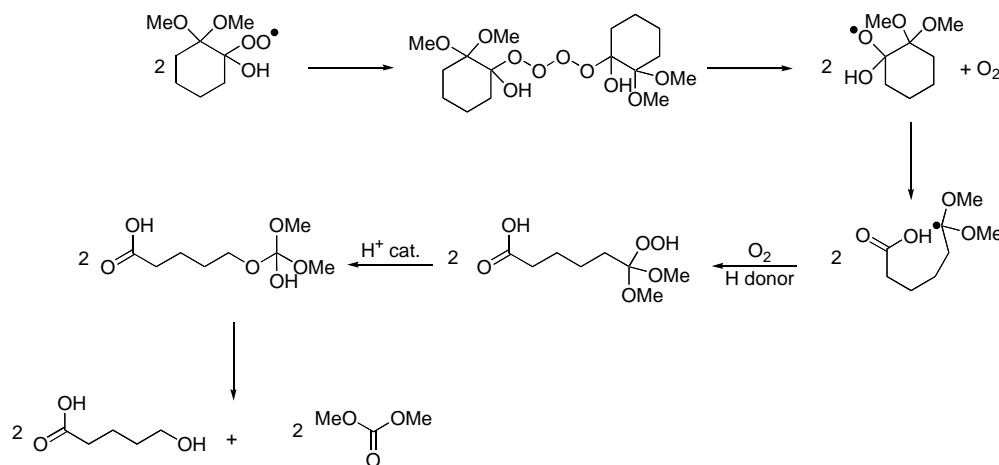
Scheme 7.



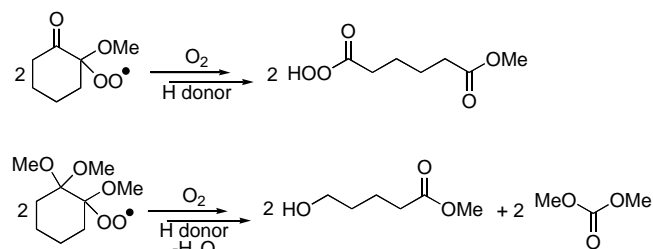
Scheme 8.

characterized by a much lower TON than that observed in our blank experiments.

The combination of acidity and methanol seems to have a determining role in this non-metal-based process, affording various ethers in equilibrium. Compounds like **10–12** have been identified unambiguously under anaerobic conditions. The mechanism proposed in Scheme 7 shows that two hemiketals **14** and **15** can be formed from 2-hydroxycyclohexanone in methanol.



Scheme 9.



Scheme 10.

The 2-methoxycyclohexanone (**16**) can arise from **12** or **15** depending, amongst other things, on the temperature [62,63]. Under our conditions, 2,2-dimethoxycyclohexanol (**17**) would be the major product. As already known, tertiary α -CH groups involved in the ether linkage are prone to H abstraction. This should facilitate the autoxidation of methyl ethers like 2-methoxycyclohexanone (**16**) and **10** as well as secondary alcohols like **17** (Scheme 8) [64,65].

Various hydroperoxides could be formed under our conditions but none of them has been isolated, due to their acid-catalysed decomposition affording seven-membered cyclic anhydrides derivatives. These compounds were shown to decompose into dimethyl adipate [66–69]. Coupling of the peroxy radicals arising from the autoxidation of **10**, **16** and **17** is also possible by a Russel mechanism (Schemes 9 and 10) [70,71]. It should afford the corresponding tertiary alkoxy centres which are prone to β -scission giving rise to the expected C–C bond homolytic cleavage of the six-membered rings. Further evolution would lead mainly to glutaric instead of adipic derivatives, which are observed as minor products under our conditions.

The better selectivities obtained in the presence of the vanadyl-exchanged materials are consistent with a metal-catalysed conversion of 2-hydroxycyclohexanone (or more probably its products with methanol under acidic conditions) to adipic acid derivatives (Table 2).

4.3. Limitations related to the choice of Nafion[®] beads and their exchange rate

Catalytic homogeneous system involving vanadyl salt precursor transposed onto Nafion[®] polymers are still efficient whatever the substrate tested. The present work points out the importance of bead size. Both materials tested, i.e. 7–9- and 10–35-mesh NR50, are commercial compounds with similar elemental analyses and exchange capacities. The best catalytic results obtained with the smaller Nafion[®] particles (10–35-mesh) could be simply attributed to an increase in the external surface of the solids. For a given amount of catalyst (i.e. number of sulfonic acid groups), the latter is multiplied by at least two when 10–35 mesh beads are used instead of 7–9 meshes.

The acidic support employed is not inert toward α -hydroxyketones. Indeed, elemental analyses of the exchanged materials indicate only partial substitution of the protons in all the solids tested. High vanadium content clearly has a pernicious influence because of the slower diffusion of 2-hydroxycyclohexanone and 2-methylcyclohexanone through the polymer matrix. Similar remarks were made recently by Seen et al. for hydrogenation catalysts deposited on Nafion[®] [23,26]. Whatever the size of the particles, diffusion limitation of the substrates was important. Indeed, the beads usually become bicoloured when the dioxygen consumption rate is maximum. The external layer is green as a consequence of the coexistence of V(V) and V(IV) species due to the relatively fast consumption of the high oxidation state species by the substrate. On the other hand, higher concentrations of vanadium (V) compounds are located in the core of the beads, in agreement with the lower availability of the substrate.

At first glance, such an observation would favor a true heterogeneous catalysed process. In fact, our catalysts should be classified in categories I and II for 2-methylcyclohexanone and 2-hydroxycyclohexanone, respectively, according to recent proposals [72]. Direct coordination of α -ketols or the enols of α -alkyl-substituted ketones is a prerequisite for their aerobic oxidation under homogeneous conditions which is why leaching of vanadium will not be totally stopped. The stronger affinity of the α -hydroxyketones for the metal centre and the use of a polar solvent (MeOH) for their oxidation are severe handicaps. However, the less exchanged materials are still active, due to acid catalysis and probably autoxidation of the corresponding ethers. On the other hand, promising results were obtained with 2-methylcyclohexanone, and further efforts will be focused on similar ketones which can be oxidized in less polar solvents.

5. Conclusions

Perfluorinated ionomers like Nafion[®] are, at the first glance, very convenient supports for oxidation catalysts because of the relatively strong resistance of their polymer

backbone to chemically active species. In this work, we have shown that the C–C bond cleavage of ketones by dioxygen can be catalysed by vanadyl salts under liquid/solid heterogeneous conditions through the iono-covalent linkage of the metal to the sulfonate groups.

For the first time, various exchanged polymers with different vanadyl/H⁺ ratios have been prepared either in water or in an organic solvent, acetonitrile. The resulting materials characterized by EPR and elemental analysis showed a limitation of the % H⁺ exchanged to roughly 50%. It is worth nothing that high loadings do not give better catalysts, probably as the effect of the resulting diffusion limitations of the substrate. Quantitative analysis of the leaching behaviour of the different catalysts indicates that materials prepared in water are more prone to vanadium loss whatever the substrate tested.

More generally, the oxidation of α -hydroxyketones, like 2-hydroxycyclohexanone, is leading to more leaching of vanadium species. These substrates easily form complexes with the metal, hence competing with the sulfonate groups of the polymer matrix. In this case, the loss of metal is more or less compensated by the autoxidation of ether derivatives of the substrate that are produced by acid catalysis in methanol. However, blank experiments showed clearly that the acid-catalysed pathway is less selective than its pure redox counterpart.

Other substrates, like 2-methylcyclohexanone do not lead to any significant leaching in acetonitrile when vanadium-exchanged Nafion[®] prepared in the same solvent is used. Under these conditions, the solid catalyst was reused three times without any loss of activity.

Efforts are now directed to the oxidation of other α -alkyl-substituted ketones and cyclohexanone with the aim of developing applications using membrane reactor technology [32]. In a countercurrent membrane reactor, the substrate and dioxygen can be circulated at each side of the membrane and cyclohexanone can be oxidized with peroxide species without solvents. The system would carry all the advantages of membrane reactors: continuous operation and easy separation. Moreover new supports, vanadyl and pervanadyl precursors are now being used in order to improve the catalytic performances of the original system and reduce the leaching of vanadium.

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