

# Supported bis(maltolato)oxovanadium complexes as catalysts for cyclopentane and cyclooctane oxidations with dioxygen

Gopal S. Mishra, João J.R. Fraústo da Silva, Armando J.L. Pombeiro\*

*Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal*

Received 23 August 2006; received in revised form 26 September 2006; accepted 28 September 2006

Available online 7 October 2006

## Abstract

Carbamated silica gel supported bis(maltolato)oxovanadium(IV or V) complexes,  $[\text{VO}(\text{ma})_2]$  (**1**),  $[\text{VO}(\text{py})(\text{ma})_2]$  (**2**) (py = pyridine),  $\text{cis-}[\text{VO}(\text{OCH}_3)(\text{ma})_2]$  (**3**) and  $\text{cis-}[\text{VO}(\text{OC}_2\text{H}_5)(\text{ma})_2]$  (**4**), were used as catalysts for the oxidation of cyclopentane and cyclooctane by molecular oxygen in a batch reactor, under moderate reaction conditions (typically  $p(\text{O}_2)$  ca. 10–14 atm, at 150–160 °C). The corresponding ketones, i.e. cyclopentanone and cyclooctanone are the main products (up to 10 and 25% yields, respectively) of the cycloalkane oxidations, but cyclopentanol and cyclooctanol are also formed in smaller amounts. The supported complex **1** shows the best activity and selectivity. The reaction is further promoted by the use of some heteroaromatic acids as co-catalysts, namely 2-pyrazine-carboxylic acid. Experiments with radical traps suggest the involvement of a free-radical mechanism.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Oxovanadium complexes; Modified silica gel; Dioxygen; Cycloalkanes; Catalyst recycling; Mechanism

## 1. Introduction

Transition metal complexes anchored to inorganic supports have been found to act as efficient catalysts for various reactions of alkanes [1–8]. In particular, supported vanadium compounds have already been applied in oxidation [9,10] and isomerization reactions [11] of alkanes but, although promising, the use of this metal still constitutes an underdeveloped field of research. In this area, we have already used some bis(maltolato)oxovanadium complexes immobilized on carbamate modified silica gel as catalysts for the oxidation, by molecular oxygen, of linear alkanes i.e. *n*-pentane and *n*-hexane [12] and of one cycloalkane, i.e. cyclohexane [13]. We now extend these studies to other cycloalkanes, i.e. cyclopentane and cyclooctane which are much less studied (in particular the former) than cyclohexane, the cycloalkane usually investigated in alkane functionalization reactions.

The oxidation of cyclopentane with molecular oxygen commonly exhibits a low selectivity because several side reactions often occur (namely thermal cracking, isomerization, dehydration, dehydrocyclization, alkylation, metathesis, oligomeriza-

tion or polymerization) [14]. Milas and Walsh [15] have carried out air oxidation (at 410 °C) of cyclopentane using, as catalyst, vanadium pentoxide deposited on pumice. The main reaction product was maleic anhydride (26% conversion). Air oxidation of cyclopentane [16] by a  $\text{PdCl}_2$  heteropolyacid at 300 °C gave several products such as butanol, pentanol, cyclopentanol, pentane diol and allyl cyclopentane, apart from other unidentified species. Copper-salen complexes, encapsulated in a zeolite, have been used for oxidation of cyclopentane (6.5% overall conversion) to cyclopentanone and cyclopentanol [17]. Alcohol and ketone products were also formed by the photocatalytic ( $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  catalyst) oxidation of cyclopentane [18]. In the presence of iron porphyrins and using  $\text{H}_2\text{O}_2$  as the oxidant, cyclopentane (in acetonitrile solution) is oxidized to cyclopentanol, cyclopentanone and cyclopentyl hydroperoxide, formed by a radical mechanism [19].

Air oxidation of cyclooctane (and other cycloalkanes) to the corresponding cycloketone and cycloalcohol has been catalyzed by both soluble and supported metalloporphyrins and metallophthalocyanines, e.g. anchored on functionalized aminoalkyl-silica gel, -polystyrene or -montmorillonite K10, or encapsulated in zeolite NaX supercages [20,21]. Cr-MCM-41 materials showed high activity and selectivity for the oxidation of cyclooctane to cyclooctanone, using dilute aqueous  $\text{H}_2\text{O}_2$  or *tert*-butyl

\* Corresponding author. Fax: +351 21 8464455.

E-mail address: [pombeiro@ist.utl.pt](mailto:pombeiro@ist.utl.pt) (A.J.L. Pombeiro).

hydroperoxide as an oxidant, under mild reaction conditions [22]. Gold(III and I) complexes [23a], vanadium containing phosphomolybdates complexes [23b] and Keggin-type polyoxotungstates [24] catalyse the oxidation of cyclooctane (to the corresponding hydroperoxide, ketone and alcohol) by  $\text{H}_2\text{O}_2$  in acetonitrile, at 60–80 °C.

We now report that some carbamated silica gel supported oxovanadium complexes with maltolato ligands, i.e. bis(maltolato)oxovanadium(IV)  $[\text{VO}(\text{ma})_2]$  (**1**), bis(maltolato)oxo(pyridine) vanadium(IV)  $[\text{VO}(\text{py})(\text{ma})_2]$  (**2**), *cis*-bis(maltolato)-methoxyoxovanadium(V) *cis*- $[\text{VO}(\text{OCH}_3)(\text{ma})_2]$  (**3**) and *cis*-ethoxybis(maltolato)oxovanadium(V) *cis*- $[\text{VO}(\text{OC}_2\text{H}_5)(\text{ma})_2]$  (**4**), catalyse the oxidation reactions of neat cyclopentane and cyclooctane by molecular oxygen, without requiring the addition of any solvent, under relatively mild reaction conditions. This follows our earlier studies on the application of such catalysts to the oxidation of linear alkanes (*n*-pentane and *n*-hexane) [12] and cyclohexane [13].

## 2. Experimental

### 2.1. Synthesis of vanadium complexes and preparation of the modified silica gel

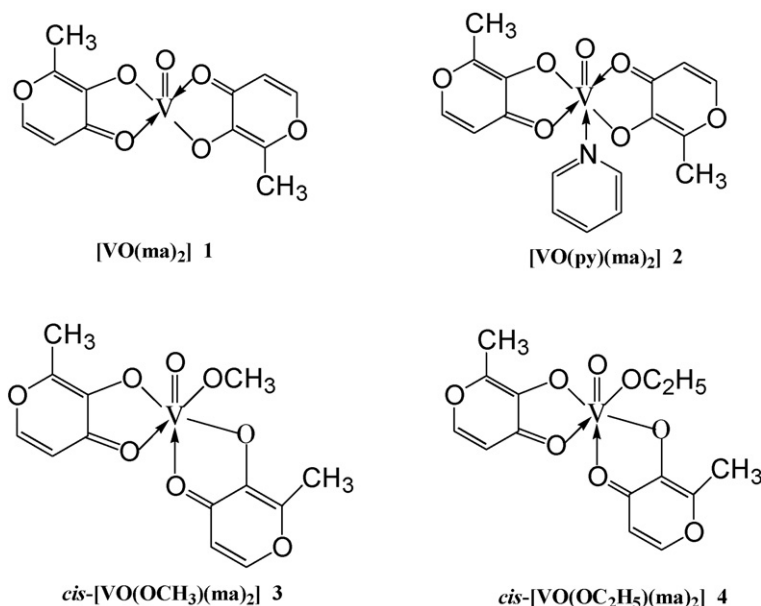
All the reactions were performed under an atmosphere of  $\text{N}_2$  using standard vacuum and inert-gas flow Schlenk techniques. Solvents were purified by standard procedures and freshly distilled immediately prior to use. The compound  $[\text{VO}(\text{ma})_2]$  (**1**) was prepared by the overnight reaction of  $\text{VO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  with maltol (1:2 molar ratio) in hot water (pH 8.5 adjusted by KOH), according to a published procedure [25]. The other complexes (Scheme 1), i.e.  $[\text{VO}(\text{py})(\text{ma})_2]$  (**2**), *cis*- $[\text{VO}(\text{OCH}_3)(\text{ma})_2]$  (**3**) and *cis*- $[\text{VO}(\text{OC}_2\text{H}_5)(\text{ma})_2]$  (**4**), were obtained by the reaction of complex **1** with pyridine, methanol or ethanol, respectively, following reported methods [25].

The organochloride functionalized silica gel  $\text{Si-OC(=O)N(CH}_2\text{CH}_2\text{Cl)}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Cl-4}$  was also prepared according to a known procedure [26] that involves the coupling of phenyl isocyanate (prepared by the reaction of  $\text{NaN}_3$  with  $\text{PhCOCl}$  [26]) to the silanol groups [27] to give carbamated silica gel which is further treated with 1,2-dichloroethane in the presence of  $\text{ZnCl}_2$  as catalyst [the overall reaction is indicated in Scheme 2(a)].

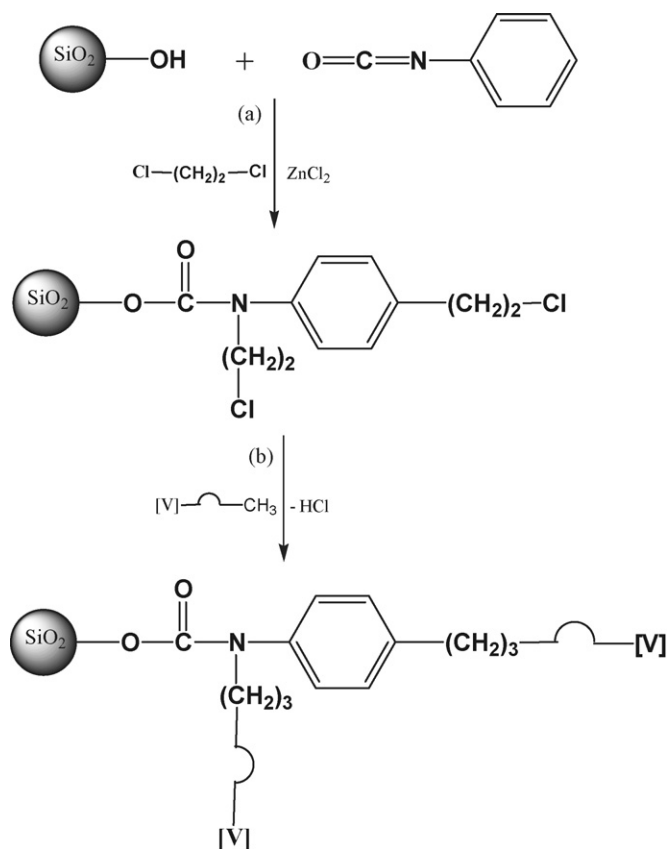
### 2.2. Preparation of the supported catalysts

The preparation of the supported catalysts followed the procedure used earlier [12]. Each of the above vanadium complexes, **1–4** (16.0 mg), was separately dissolved in acetone (10 mL), the solution added to the modified silica (1.00 g) and the mixture heated at 50 °C for 6 h. The solid (vanadium complex loaded on the modified silica gel) was filtered off, washed with acetone ( $3 \times 100$  mL) and dried at 35 °C for 6 h, under  $\text{N}_2$ . After washing, we found that 14.0 mg of **1**, 12.8 mg of **2**, 13.0 mg of **3** and 13.8 mg of **4** were separately loaded per gram of the modified silica gel support (in the case of **1** this was confirmed by ICP). The colours of the carbamated supported catalysts are green for **1**, brown for **2** and light reddish for **3** and **4**.

FTIR spectra ( $\text{cm}^{-1}$ , KBr disk) of the final supported catalysts: 3450  $\nu(\text{OH})$ , 3030  $\nu(\text{CH, aromatic})$ , 2966  $\nu(\text{CH, aliphatic})$ , 1700  $\nu(\text{C=O})$ , 1560  $\nu(\text{C=C})$  and 970  $\nu(\text{V=O})$ . The significant reduction of the  $\nu(\text{C-Cl})$  peak at  $760 \text{ cm}^{-1}$  is indicative of the bond formation between the modified support and the complex via coupling (with HCl liberation) of the organochloride group in the former with the methyl group of the maltol ligand and/or, in the cases of complexes **3** and **4**, with the alkyl group of the alkoxide ligand [Scheme 2(b)]. In fact, the carbonyl and oxide oxygen atoms of the chelated maltol are protected by coordination and thus not expected to be particularly reactive towards the organochloride moiety. Besides, the acidity of the methyl group



Scheme 1.



Scheme 2.

of maltol and of the alkyl group of the alkoxide (for complexes **3** and **4**) is promoted by coordination to the metal of maltol and of the alkoxide, respectively, thus favouring the coupling suggested above, although we have not yet succeeded in fully establishing the detailed structure of the final supported species.

### 2.3. Catalyst characterization instrumentation

The vanadium metal content of the catalysts was determined by Inductive Couple Plasma (ICP) using a Perkin Elmer Plasma-400 (the sample was digested in hot  $\text{H}_2\text{SO}_4 + \text{HF} + \text{HNO}_3$  solution) in the Analytical Laboratory, Instituto Superior Técnico (IST). In order to test if the loaded complex on the silica gel is stable at the reaction temperature, a thermogravimetric analysis (TGA) of the catalyst was performed at a Setaram TG/DTA/DSC-92 instrument at the Chemical Engineering Department (DEQ), IST. FTIR spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded (see above) on a Jasco FTIR-430 spectrometer using KBr pellets.

### 2.4. Oxidation experiments and catalyst regeneration

An autoclave rocking type batch reactor having a 22 mL capacity was used for conducting the oxidation reactions. The reactor has a provision for gas inlet and pressure gauge. The inside reactor temperature was controlled by using an on/off controller with a suitable thermocouple. The reactor was initially charged with 3.0 mL of cyclopentane (32.1 mmol) or of

cyclooctane (22.3 mmol) and 20 mg of supported vanadium catalyst. It was then closed, the air removed by vacuum pump and molecular oxygen was introduced at the required pressure, and the reaction mixture was stirred for 8 and 5 h, respectively, at the desired temperature. The colours of the catalysts, after the oxidation reactions, had turned to brown. In the end of the reactions, these catalysts were separated from the solutions by filter paper and washed three times with acetone. They could be regenerated for further use by heating in a static atmosphere of air, in an oven at  $100\text{ }^\circ\text{C}$  for 1 h.

In the experiments with *unsupported* vanadium catalysts, the reactions were carried out in a similar way to that of the supported catalysts, but by using the former (0.28 mg) instead of the latter (20 mg) catalysts.

### 2.5. Product analysis

After the oxidation reaction, the products were analyzed by gas chromatography by the internal standard method (adding  $30\text{ }\mu\text{L}$  of cyclohexanone to 1.0 mL of the final reaction solution separated by filtration from the supported catalyst) using a Fisons chromatograph model 8000 equipped with a FID detector and a capillary column (DB-WAX; column length: 30 m, internal diameter: 0.32 mm). Helium was used as the carrier gas. They were further analysed by GC–MS measurements carried out in a mass spectrometer Trio 2000 Fisons Instruments with a coupled gas chromatograph Carlo Erba Instruments, Auto/HRGC/MS. The yield was calculated as the molar ratio (%) of product/substrate. Blank experiments were also conducted in the absence of catalyst, at the above reaction conditions, and no product was then detected.

At the end of the oxidation reaction, we have followed Shul'pin's [28,29] procedure for the detection of the hydroperoxide ROOH ( $\text{R} = \text{cyclopentyl, cyclooctyl}$ ), by treating the final reaction solution with an excess of  $\text{PPh}_3$  before the GC analysis. The ROOH still present is deoxygenated by  $\text{PPh}_3$  to the alcohol ROH (with formation of the phosphine oxide  $\text{Ph}_3\text{PO}$ ) and therefore the hydroperoxide decomposition to both alcohol and ketone in the chromatograph is suppressed [28,29].

## 3. Results and discussion

We have applied the four carbamated modified-silica gel immobilized catalyst complexes  $[\text{VO}(\text{ma})_2]$  (**1**),  $[\text{VO}(\text{py})(\text{ma})_2]$  (**2**), *cis*- $[\text{VO}(\text{OCH}_3)(\text{ma})_2]$  (**3**) and  $[\text{VO}(\text{py})(\text{ma})_2]$  (**4**), to the oxidation of cyclopentane and cyclooctane by molecular oxygen in a rocking batch type reactor. The oxyfunctionalization experiments of these alkanes have been performed within the  $p(\text{O}_2)$  and temperature ranges of 6.8–20.4 atm and  $100\text{--}225\text{ }^\circ\text{C}$ , respectively, and the results are summarized in Tables 1–4 and Figs. 1–12. The strong smell at the end of the experiments is indicative of the formation of functionalized products which have been analysed by GC and GC–MS that show they are mainly the corresponding cycloketones and cycloalcohols, the latter in smaller amounts (Scheme 3). Blank experiments demonstrate that the V-catalysts play a key role for the cycloalkanes oxidations since no products (or only in very low

Table 1  
Cyclopentane oxidation by O<sub>2</sub> catalyzed by carbamated silica supported bis(maltolato)oxovanadium complexes: effects of various factors<sup>a</sup>

| Run | Catalyst | Temperature (°C) | <i>p</i> (O <sub>2</sub> ) (atm) <sup>b</sup> | Time (h) | Catalyst (mg) | Percentage conversion <sup>c</sup> |                |               |                |
|-----|----------|------------------|---|----------|---------------|------------------------------------|----------------|---------------|----------------|
|     |          |                  |   |          |               | Overall                            | Cyclopentanone | Cyclopentanol | Other products |
| 1   | 1        | 100              | 13.6  | 8        | 20            | 1.9                                | 0.6            | 0.3           | 1.0            |
| 2   | 1        | 120              | 13.6  | 8        | 20            | 3.6                                | 1.3            | 0.5           | 1.8            |
| 3   | 1        | 140              | 13.6  | 8        | 20            | 8.1                                | 3.2            | 1.7           | 3.2            |
| 4   | 1        | 160              | 13.6  | 8        | 20            | 13.2                               | 6.3            | 3.5           | 3.4            |
| 5   | 1        | 180              | 13.6  | 8        | 20            | 16.1                               | 7.0            | 2.8           | 6.3            |
| 6   | 1        | 200              | 13.6  | 8        | 20            | 17.5                               | 7.1            | 3.1           | 7.3            |
| 7   | 1        | 160              | 6.8   | 8        | 20            | 1.3                                | 0.8            | 0.3           | 0.2            |
| 8   | 1        | 160              | 10.2  | 8        | 20            | 8.2                                | 4.2            | 2.4           | 1.6            |
| 9   | 1        | 160              | 17.0  | 8        | 20            | 16.7                               | 8.1            | 4.5           | 4.1            |
| 10  | 1        | 160              | 20.4  | 8        | 20            | 20.1                               | 10.1           | 5.3           | 4.6            |
| 11  | 1        | 160              | 13.6  | 4        | 20            | 1.3                                | 0.8            | 0.4           | 0.1            |
| 12  | 1        | 160              | 13.6  | 6        | 20            | 7.8                                | 4.1            | 2.4           | 1.3            |
| 13  | 1        | 160              | 13.6  | 10       | 20            | 15.6                               | 7.6            | 4.2           | 3.8            |
| 14  | 1        | 160              | 13.6  | 12       | 20            | 17.8                               | 7.8            | 4.5           | 5.5            |
| 15  | 1        | 160              | 13.6  | 24       | 20            | 23.3                               | 3.6            | 2.3           | 17.4           |
| 16  | 1        | 160              | 13.6  | 8        | 10            | 6.7                                | 3.3            | 1.6           | 1.8            |
| 17  | 1        | 160              | 13.6  | 8        | 30            | 16.4                               | 8.4            | 4.4           | 3.6            |
| 18  | 1        | 160              | 13.6  | 8        | 50            | 18.0                               | 9.0            | 4.7           | 4.3            |
| 19  | 2        | 160              | 13.6  | 8        | 20            | 7.4                                | 3.0            | 2.1           | 2.3            |
| 20  | 3        | 160              | 13.6  | 8        | 20            | 10.3                               | 4.6            | 2.8           | 2.9            |
| 21  | 4        | 160              | 13.6  | 8        | 20            | 9.7                                | 4.4            | 2.9           | 2.4            |

<sup>a</sup> For the other reaction conditions see Section 2.

<sup>b</sup> Measured at 25 °C (1 atm = 1.01 bar = 101 kPa).

<sup>c</sup> Molar percentage yield based on moles of product per mole of cyclopentane.

yield) were detected when the reaction was attempted in their absence.

The most effective catalyst is the supported complex **1** which, typically for its amount of 20 mg, *p*(O<sub>2</sub>) = 13.6 atm, at

160–150 °C, leads to cyclopentane or cyclooctane overall conversions of ca. 13% or 30% (run 4, Table 1, or run 3, Table 2, respectively), corresponding to remarkable overall turnover numbers (TONs) (estimated as the number of moles of products

Table 2  
Cyclooctane oxidation by O<sub>2</sub> catalyzed by carbamated silica supported bis(maltolato)oxovanadium complexes: effects of various factors<sup>a</sup>

| Run | Catalyst | Temperature (°C) | <i>p</i> (O <sub>2</sub> ) (atm) <sup>b</sup> | Time (h) | Catalyst (mg) | Percentage conversion <sup>c</sup> |               |              |                |
|-----|----------|------------------|---|----------|---------------|------------------------------------|---------------|--------------|----------------|
|     |          |                  |   |          |               | Overall                            | Cyclooctanone | Cyclooctanol | Other products |
| 1   | 1        | 100              | 13.6  | 5        | 20            | 3.0                                | 1.8           | 0.4          | 0.8            |
| 2   | 1        | 125              | 13.6  | 5        | 20            | 4.4                                | 2.8           | 0.6          | 1.0            |
| 3   | 1        | 150              | 13.6  | 5        | 20            | 30.3                               | 18.6          | 5.3          | 6.4            |
| 4   | 1        | 175              | 13.6  | 5        | 20            | 36.3                               | 22.2          | 6.1          | 8.0            |
| 5   | 1        | 200              | 13.6  | 5        | 20            | 40.6                               | 24.5          | 5.9          | 10.2           |
| 6   | 1        | 225              | 13.6  | 5        | 20            | 41.7                               | 25.0          | 4.8          | 11.9           |
| 7   | 1        | 150              | 6.8   | 5        | 20            | 4.2                                | 1.6           | 0.6          | 2.0            |
| 8   | 1        | 150              | 10.2  | 5        | 20            | 17.4                               | 9.3           | 2.1          | 6.0            |
| 9   | 1        | 150              | 17.0  | 5        | 20            | 37.5                               | 16.9          | 5.6          | 15.0           |
| 10  | 1        | 150              | 20.4  | 5        | 20            | 41.8                               | 14.6          | 6.7          | 20.5           |
| 11  | 1        | 150              | 13.6  | 2        | 20            | 1.3                                | 0.7           | 0.2          | 0.4            |
| 12  | 1        | 150              | 13.6  | 3        | 20            | 3.8                                | 2.2           | 0.5          | 1.1            |
| 13  | 1        | 150              | 13.6  | 4        | 20            | 19.9                               | 11.5          | 3.2          | 5.2            |
| 14  | 1        | 150              | 13.6  | 6        | 20            | 33.1                               | 20.8          | 5.8          | 6.5            |
| 15  | 1        | 150              | 13.6  | 7        | 20            | 38.5                               | 21.2          | 5.4          | 11.9           |
| 16  | 1        | 150              | 13.6  | 8        | 20            | 39.8                               | 18.9          | 5.4          | 15.5           |
| 17  | 1        | 150              | 13.6  | 5        | 10            | 17.2                               | 9.1           | 2.1          | 6.0            |
| 18  | 1        | 150              | 13.6  | 5        | 30            | 35.9                               | 22.0          | 6.0          | 7.9            |
| 19  | 1        | 150              | 13.6  | 5        | 50            | 39.8                               | 22.4          | 6.8          | 10.6           |
| 20  | 2        | 150              | 13.6  | 5        | 20            | 13.1                               | 7.1           | 3.4          | 2.6            |
| 21  | 3        | 150              | 13.6  | 5        | 20            | 23.5                               | 14.6          | 5.2          | 3.7            |
| 22  | 4        | 150              | 13.6  | 5        | 20            | 19.3                               | 12.1          | 3.9          | 3.3            |

<sup>a</sup> For the other reaction conditions see Section 2.

<sup>b</sup> Measured at 25 °C (1 atm = 1.01 bar = 101 kPa).

<sup>c</sup> Molar percentage yield based on moles of product per mole of cyclooctane.

Table 3

Co-catalysts effects on cyclopentane and cyclooctane oxidation by O<sub>2</sub> catalyzed by carbamated silica gel supported [VO(ma)<sub>2</sub>] (1)

| Carboxylic acid (as co-catalyst)   | Percentage conversion     |         |                |               |                          |         |               |              |
|------------------------------------|---------------------------|---------|----------------|---------------|--------------------------|---------|---------------|--------------|
|                                    | Cyclopentane <sup>a</sup> |         |                |               | Cyclooctane <sup>b</sup> |         |               |              |
|                                    | Run                       | Overall | Cyclopentanone | Cyclopentanol | Run                      | Overall | Cyclooctanone | Cyclooctanol |
| Picolinic acid                     | 1                         | 13.8    | 6.5            | 3.5           | 6                        | 33.0    | 20.8          | 4.8          |
| 2,6-Pyrazine-dicarboxylic acid     | 2                         | 16.8    | 8.1            | 4.0           | 7                        | 35.2    | 21.0          | 5.7          |
| 2,3-Pyrazine-dicarboxylic acid     | 3                         | 17.0    | 8.8            | 4.2           | 8                        | 37.1    | 21.2          | 5.8          |
| 3-Amino-2-pyrazine-carboxylic acid | 4                         | 16.4    | 8.0            | 3.9           | 9                        | 35.6    | 22.0          | 5.9          |
| 2-Pyrazine-carboxylic acid         | 5                         | 18.4    | 9.3            | 4.5           | 10                       | 39.9    | 24.2          | 6.8          |

<sup>a</sup> Same conditions as those indicated for the run 4 in Table 1.<sup>b</sup> Same conditions as those indicated for the run 3 in Table 2.

Table 4

Cycloalkanes oxidation by O<sub>2</sub> catalyzed by *unsupported* bis(maltolato)oxovanadium complexes<sup>a</sup>

| Run | Catalyst | Alkane       | Percentage conversion <sup>b</sup> |           |          |
|-----|----------|--------------|------------------------------------|-----------|----------|
|     |          |              | Overall                            | Cyclo-one | Cyclo-ol |
| 1   | <b>1</b> | Cyclopentane | 1.3                                | 0.6       | 0.4      |
| 2   | <b>2</b> | Cyclopentane | 0.4                                | 0.2       | 0.0      |
| 3   | <b>3</b> | Cyclopentane | 0.9                                | 0.3       | 0.2      |
| 4   | <b>4</b> | Cyclopentane | 0.7                                | 0.3       | 0.2      |
| 5   | <b>1</b> | Cyclooctane  | 2.7                                | 1.3       | 0.6      |
| 6   | <b>2</b> | Cyclooctane  | 0.6                                | 0.2       | 0.1      |
| 7   | <b>3</b> | Cyclooctane  | 2.0                                | 0.9       | 0.4      |
| 8   | <b>4</b> | Cyclooctane  | 1.1                                | 0.5       | 0.2      |

<sup>a</sup> Reaction conditions: temperature = 160 °C (C<sub>5</sub>H<sub>10</sub>) or 150 °C (C<sub>8</sub>H<sub>16</sub>), p(O<sub>2</sub>) = 13.6 atm (measured at 25 °C, 1 atm = 1.01 bar = 101 kPa), time = 8 h (C<sub>5</sub>H<sub>10</sub>) or 5 h (C<sub>8</sub>H<sub>16</sub>), catalyst amount = 0.28 mg, alkane amount = 3 mL.<sup>b</sup> Molar percentage yield based on moles of product per mole of cycloalkane.

per mole of supported V-complex loaded on the modified silica gel) of ca.  $3.6 \times 10^3$  or  $6.0 \times 10^3$  for the total formation of the respective cycloketone plus cycloalcohol. Those yields can increase when using e.g. a greater amount of catalyst or a higher temperature. For identical experimental conditions, the

other tested supported catalysts 2–4, are less effective (compare runs 19–21 with run 4, Table 1, for cyclopentane oxidation, and runs 20–22 with run 3, Table 2, for cyclooctane oxidation). The *unsupported* vanadium complexes (1–4) are much less active (overall conversions below 3% and overall TONs

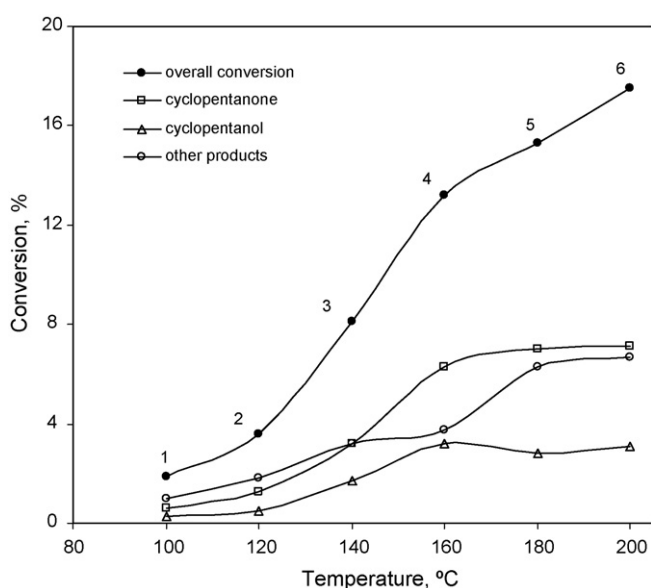


Fig. 1. Temperature effect on the % conversion of cyclopentane, upon oxidation by O<sub>2</sub>, in the presence of the [VO(ma)<sub>2</sub>] (1) supported catalyst (p(O<sub>2</sub>) = 13.6 atm, reaction time = 8 h). Point numbering corresponds to runs of Table 1.

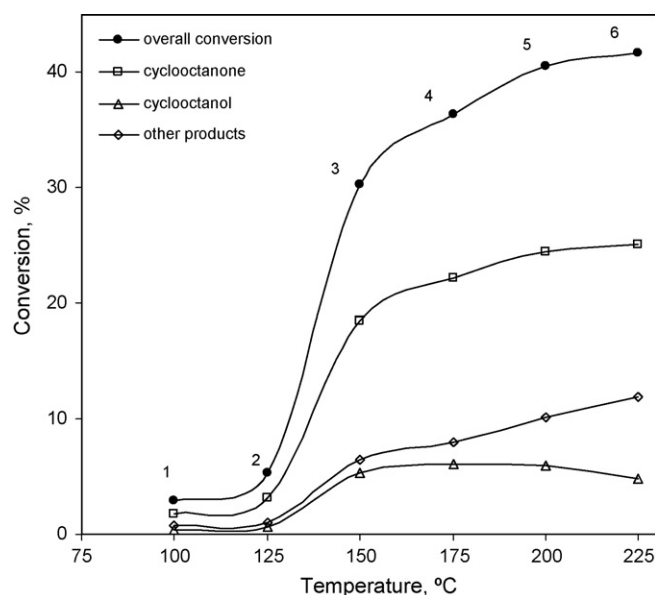


Fig. 2. Temperature effect on the % conversion of cyclooctane, upon oxidation by O<sub>2</sub>, in the presence of the [VO(ma)<sub>2</sub>] (1) supported catalyst (p(O<sub>2</sub>) = 13.6 atm, reaction time = 5 h). Point numbering corresponds to runs of Table 2.

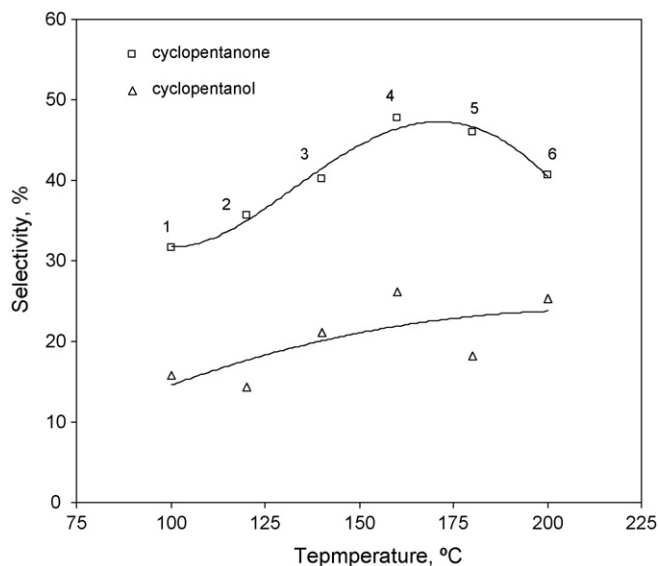


Fig. 3. Temperature effect on the selectivity of the oxidation products of cyclopentane by  $O_2$ , in the presence of the  $[VO(ma)_2]$  (**1**) supported catalyst ( $p(O_2) = 13.6$  atm, reaction time = 8 h). Point numbering corresponds to runs of Table 1.

below  $4.8 \times 10^2$ ) for the cycloalkanes oxidations (Table 4) than the supported ones, under same reaction conditions; complex **1** remains as the most active one. The effects of various factors (temperature, oxygen pressure, reaction time, amount of catalyst and presence of a co-catalyst) on the catalyst activity and selectivity were studied in detail for the case of the supported complex **1** which provides the most active catalytic system.

The effect of temperature (100–200 °C) on the oxidation of cyclopentane (Table 1, runs 1–6, and Fig. 1) and of cyclooctane (Table 2, runs 1–6, and Fig. 2) was examined at  $p(O_2) = 10$  atm

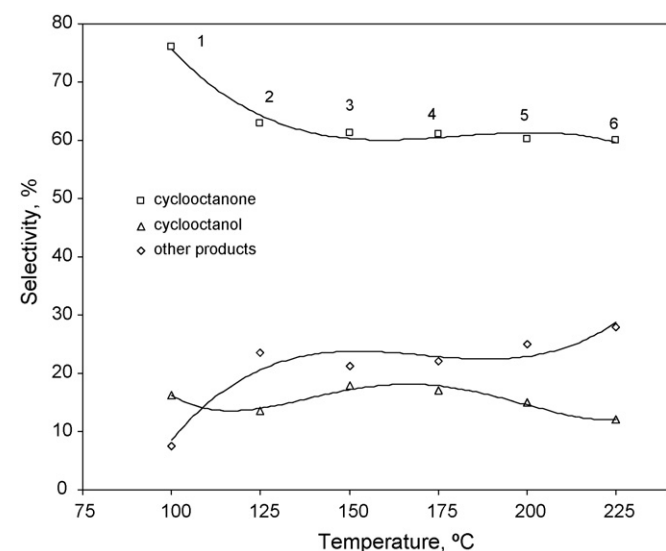


Fig. 4. Temperature effect on the selectivity of the oxidation products of cyclooctane by  $O_2$ , in the presence of the  $[VO(ma)_2]$  (**1**) supported catalyst ( $p(O_2) = 13.6$  atm, reaction time = 5 h). Point numbering corresponds to runs of Table 2.

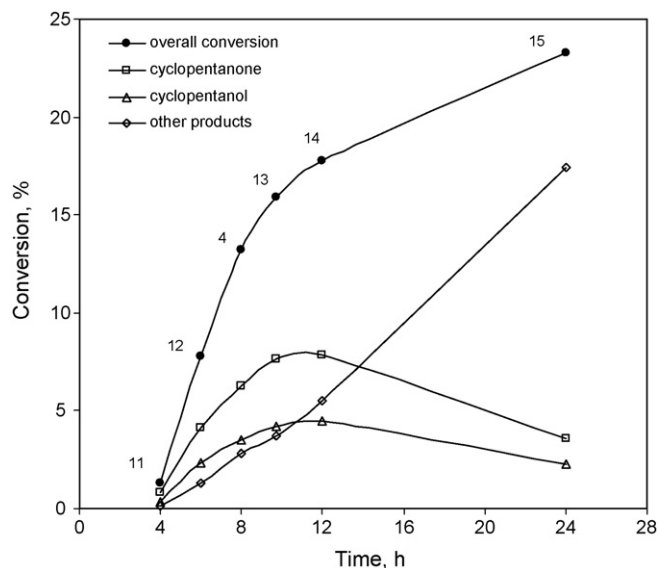


Fig. 5. Time effect on the % conversion of cyclopentane, upon oxidation by  $O_2$ , in the presence of the  $[VO(ma)_2]$  (**1**) supported catalyst (temperature = 160 °C,  $p(O_2) = 13.6$  atm). Point numbering corresponds to runs of Table 1.

(for 8 and 5 h reaction time, respectively). The overall conversion and that for the main product (ketone) increase slowly until ca. 120–125 °C, beyond which a sharp increase occurs until 160 °C (the conversions into cyclopentanone and cyclooctanone are then ca. 6% and 20%, respectively). At 200 °C, an overall conversion of 18% or 42%, respectively, is achieved but the reaction temperature was not allowed to go beyond that value due to the formation of an unidentified black material. The dependence of the selectivity on the temperature is shown in Fig. 3 (for cyclopentane) and Fig. 4 (for cyclooctane). The former indicates that the highest selectivity towards cyclopentanone (48%) is reached at ca. 160 °C, whereas the latter figure shows that the

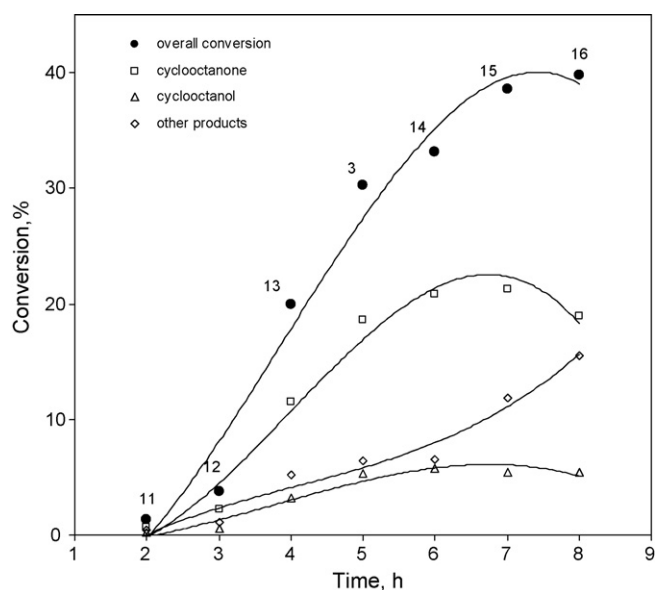


Fig. 6. Time effect on the % conversion of cyclooctane, upon oxidation by  $O_2$ , in the presence of the  $[VO(ma)_2]$  (**1**) supported catalyst (temperature = 150 °C,  $p(O_2) = 13.6$  atm). Point numbering corresponds to runs of Table 2.

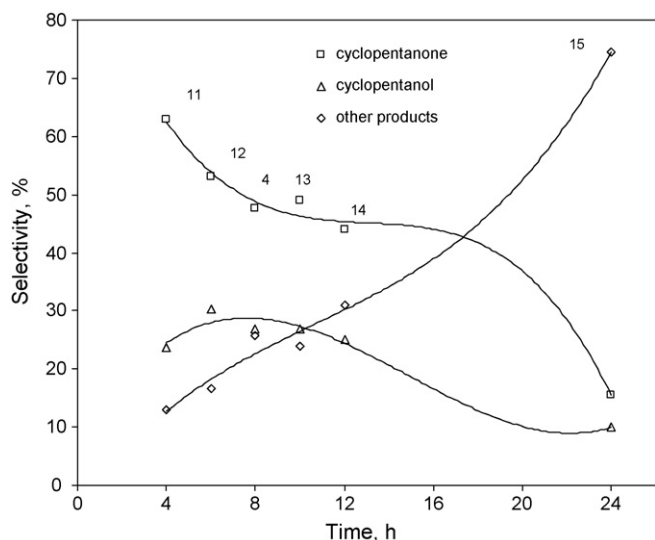


Fig. 7. Time effect on the selectivity of the oxidation products of cyclopentane by O<sub>2</sub>, in the presence of the [VO(ma)<sub>2</sub>] (1) supported (temperature = 160 °C,  $p(\text{O}_2) = 13.6$  atm). Point numbering corresponds to runs of Table 1.

selectivity towards cyclooctanone (ca. 70–60%) is little dependent on the temperature.

Reaction *time* was varied from 4 to 24 h at 160 °C for cyclopentane (Table 1, runs 4, 11–15 and Figs. 5 and 7) and at 150 °C for cyclooctane (Table 2, runs 3, 11–16 and Figs. 6 and 8) under a constant O<sub>2</sub> pressure (13.6 atm). The maximum yields of cyclopentanone (ca. 8%) and cyclooctanone (ca. 20%) are reached after ca. 10 or 6 h, respectively. Higher reaction times are also unfavorable in terms of selectivity due to the increased formation of other products.

The effect of O<sub>2</sub> pressure (from 6.8 to 20.4 atm) was studied for cyclopentane (Figs. 9 and 11, runs 4, 7–10, Table 1)

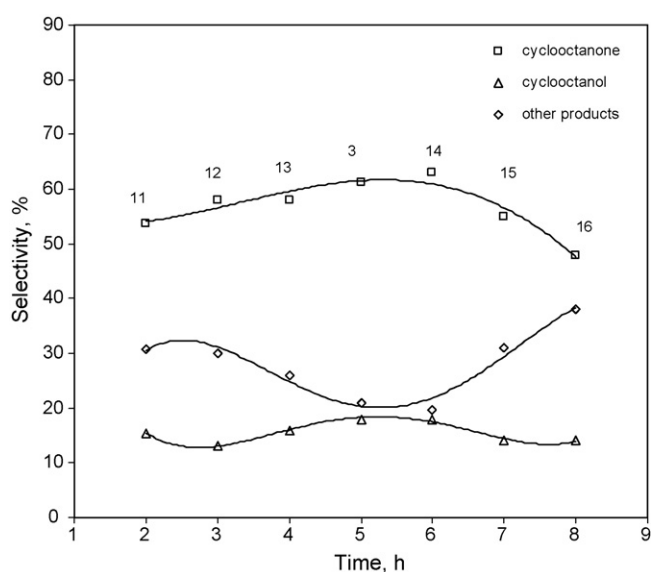


Fig. 8. Time effect on the selectivity of the oxidation products of cyclooctane by O<sub>2</sub>, in the presence of the [VO(ma)<sub>2</sub>] (1) supported catalyst (temperature = 150 °C,  $p(\text{O}_2) = 13.6$  atm). Point numbering corresponds to runs of Table 2.

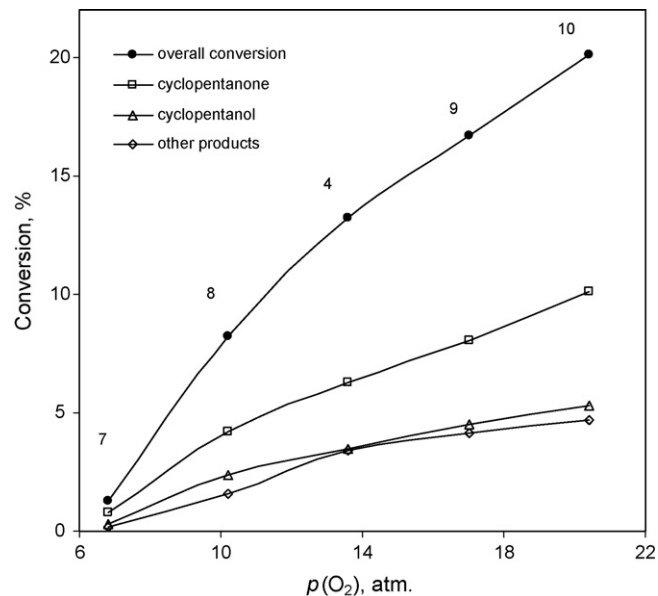


Fig. 9. Effect of O<sub>2</sub> pressure on the % conversion of cyclopentane, upon oxidation by O<sub>2</sub>, in the presence of the [VO(ma)<sub>2</sub>] (1) supported catalyst (temperature = 160 °C, time = 8 h). Point numbering corresponds to runs of Table 1.

and cyclooctane (Figs. 10 and 12, runs 3, 7–10, Table 2). The overall conversions of both cycloalkanes into the corresponding products increase with the O<sub>2</sub> pressure within the studied range, what is consistent with the promotion of the solubility of this gas with the pressure. The conversions of cyclopentane into cyclopentanone and cyclopentanol increase also with  $p(\text{O}_2)$ , but the selectivities very differently: that of cyclopentanone decreases with the increases of pressure until ca. 14 atm, while that of cyclopentanol is little affected. Hence, in terms of selectivity towards the main product of cyclopentane oxidation, i.e.

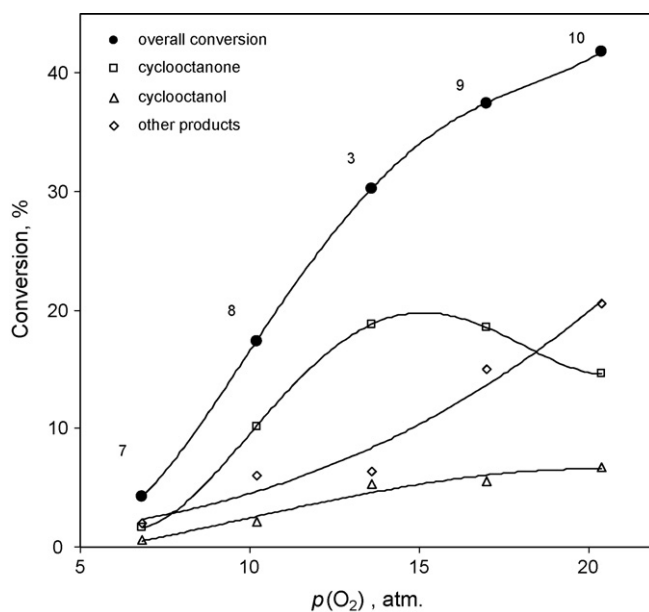


Fig. 10. Effect of O<sub>2</sub> pressure on the % conversion of cyclooctane, upon oxidation by O<sub>2</sub>, in the presence of the [VO(ma)<sub>2</sub>] (1) supported catalyst (temperature = 150 °C, time = 5 h). Point numbering corresponds to runs of Table 2.

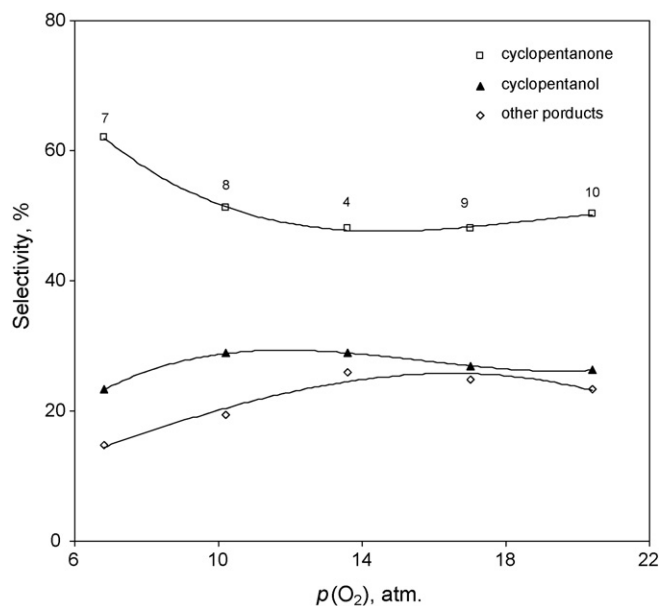


Fig. 11. Effect of O<sub>2</sub> pressure on the selectivity of the oxidation products of cyclopentane by O<sub>2</sub>, in the presence of the [VO(ma)<sub>2</sub>] (**1**) supported catalyst (temperature = 160 °C, time = 8 h). Point numbering corresponds to runs of Table 1.

cyclopentanone, p(O<sub>2</sub>) should not be higher than ca. 10 atm. For the case of cyclooctanone production, p(O<sub>2</sub>) in the 13–15 atm range leads to the highest conversion and selectivity.

The conversions of the cycloalkanes are promoted by increasing the amount of the supported vanadium catalyst (compare runs 4, 16–18, Table 1, for increasing catalyst amount from 10 to 50 mg, in the case of cyclopentane oxidation, and runs 4, 17–19, Table 2, in the case of cyclooctane oxidation). Hence, the over-

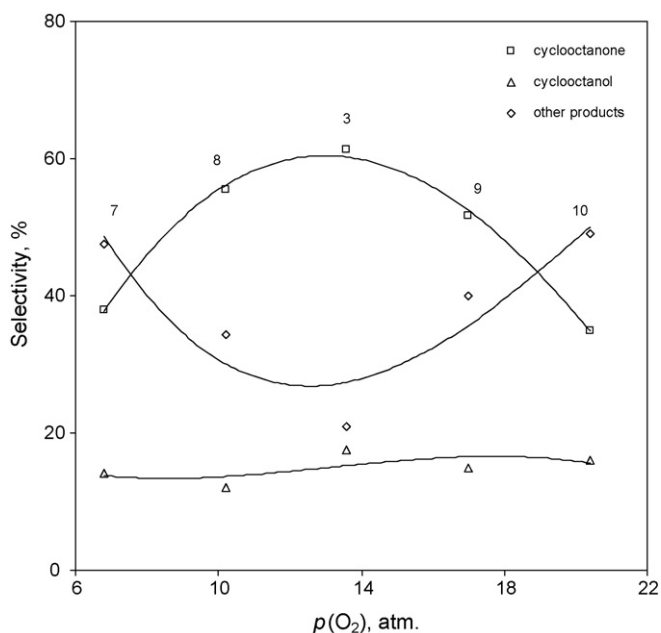
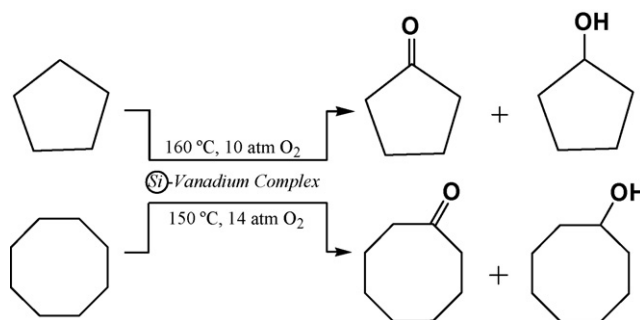


Fig. 12. Effect of O<sub>2</sub> pressure on the selectivity of the oxidation products of cyclooctane by O<sub>2</sub>, in the presence of the [VO(ma)<sub>2</sub>] (**1**) supported catalyst (temperature = 150 °C, reaction time = 5 h). Point numbering corresponds to runs of Table 2.



Scheme 3.

all cycloalkane conversions of ca. 18% (cyclopentane) and ca. 40% (cyclooctane), obtained when using 50 mg of supported catalyst (runs 18, Table 1, and 19, Table 2), corresponding to yields of cyclopentanone (9%) and of cyclooctanone (23%), are much higher than those obtained for 10 mg of catalyst (overall cyclopentane conversion of ca. 7%, 3% yield of cyclopentanol, run 16, Table 1; overall cyclooctane conversion of ca. 17%, 9% yield of cyclooctanone, run 17, Table 2).

Some heteroaromatic carboxylic acids, such as picolinic acid, 2,6-pyrazinedicarboxylic acid, 2,3-pyrazinedicarboxylic acid, 3-amino-2-pyrazinecarboxylic acid and 2-pyrazinecarboxylic acid, have been checked as possible *co-catalysts* (Table 3), and we found that 2-pyrazinecarboxylic acid was the most effective one. It promotes the oxidation of the both cyclopentane (increase of the overall conversion, cyclopentanone and cyclopentanol yields from 13.2, 6.3 and 3.5%, run 4, Table 1, to 18.4, 9.3 and 4.5%, respectively, run 5, Table 3) and cyclooctane (increase of the overall conversion, cyclooctanone and cyclooctanol yields from 30.3, 18.6 and 5.3%, run 3, Table 3, to 39.9, 24.2 and 6.8%, respectively, run 10, Table 3).

A marked promoting effect of that acid on the peroxidative oxidation of alkanes (and other substrates) by various homogeneous V-catalysts has been recognized by Shul'pin and Süß-Fink [30,31], whereas picolinic acid, practically inactive in our case, is also less effective than 2-pyrazine-carboxylic acid [30,31] in the former systems. The role of 2-pyrazinecarboxylic acid in the vanadate/H<sub>2</sub>O<sub>2</sub> systems appears to be associated to its assistance in hydrogen transfer from H<sub>2</sub>O<sub>2</sub> to a vanadyl group, via hydrogen-migration from ligated H<sub>2</sub>O<sub>2</sub> to the coordinated oxygen of the carboxylate of a 2-pyrazinecarboxylate ligand, as recently suggested by DFT calculations [32].

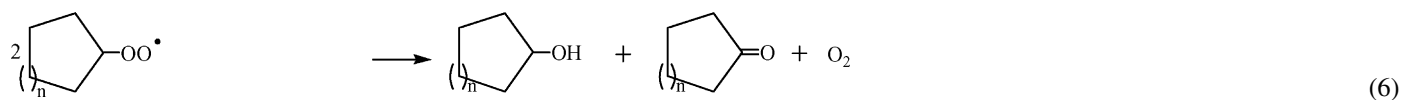
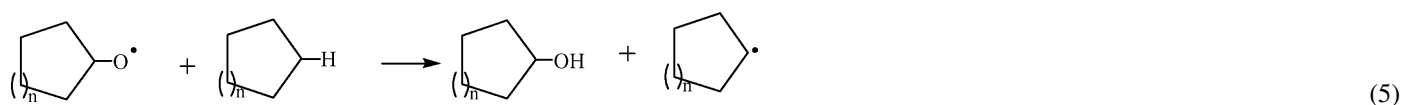
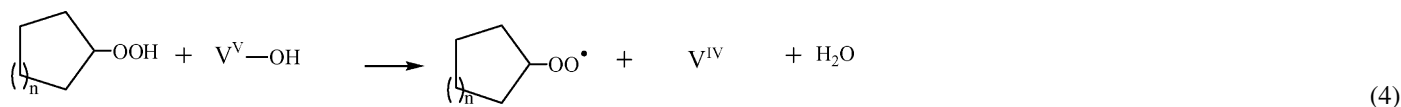
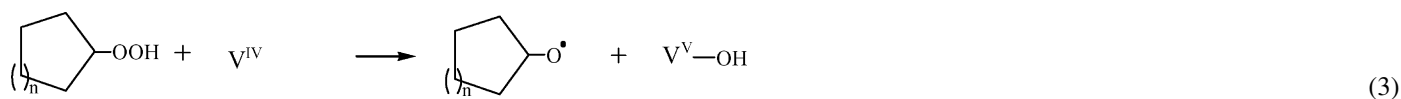
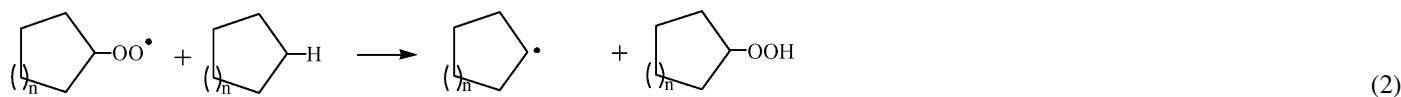
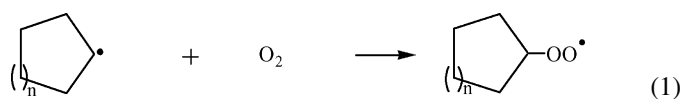
After being used, the catalyst can be reactivated by heating and recycled, still displaying activity. Thus, after cyclopentane oxidation (run 4, Table 1) and cyclooctane oxidation (run 3, Table 2), the catalyst was filtered off, washed three times with acetone and dried in an oven at 100 °C for 1 h. It was then used again, under the same reaction conditions, leading to further (although lower) overall conversions of cyclopentane and cyclooctane of 9.5 and 18.6%, respectively. The preservation of most of the catalytic activity is consistent with the ICP analysis that shows only a partial metal loss upon use. In fact, the freshly supported catalyst **1** shows 0.20 wt.% of vanadium whereas after runs 4 (Table 1, for cyclopentane) and 3 (Table 2, for cyclooctane), followed by separation, washing and drying of



the catalyst, a metal content of 0.15 and 0.14 wt.%, respectively, is still present. These observations also indicate that the catalyst is not leached out in the experiments, what is consistent with anchoring to the silica support by a covalent bond rather than by physical adsorption. In addition, TGA analysis of the freshly carbamated silica gel supported vanadium catalysts shows that the supported complex **1** is stable up to ca. 240 °C.

### 3.1. Reaction mechanism

The catalytic activity of the system is almost suppressed when performing the reactions in the presence of the liquid carbon-radical trap bromotrichloromethane or oxygen-radical trap diphenylamine (common solid radical traps were not used in view of their insolubility in the cycloalkanes). These results suggest the involvement of a free radical mechanism which can follow the reaction pathway ((1)–(6)) ( $n = 1$  or 4) [33,34].

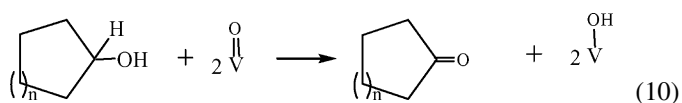
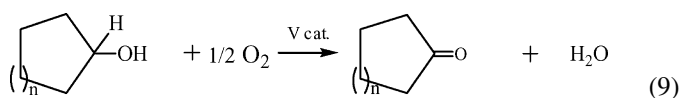
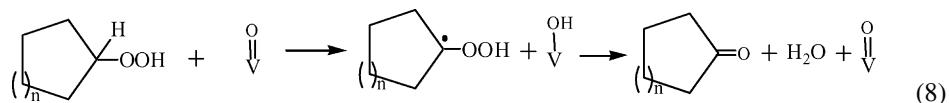
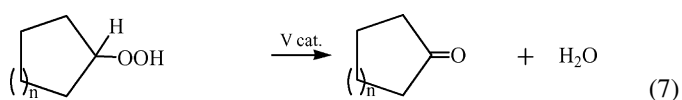


The alkyl radical ( $\text{R}^\bullet$ ), initially formed by reaction of the alkane ( $\text{RH}$ ) with  $\text{O}_2$  upon homolytic C–H bond rupture (slow induction period), can be oxidized by  $\text{O}_2$  to the alkylperoxy radical  $\text{ROO}^\bullet$  (reaction (1)). This can react further with the

$\text{Co}^{\text{II/III}}$  or  $\text{Cu}^{\text{I/II}}$ . The involvement of the hydroperoxide  $\text{ROOH}$  in our systems is supported by the observed promotion of the detected amount of the alcohol (cyclopentanol or cyclooctanol) with a concomitant decrease of that of the ketone (cyclopentanone or cyclooctanone, respectively) upon treatment of the final reaction solution with  $\text{PPh}_3$  prior to GC analysis, according to Shul'pin's method [28,29]. However, the amount of  $\text{ROOH}$  in the end of the reaction, under our usual experimental conditions (160 and 150 °C for cyclopentane and cyclooctane, respectively) is low since the variations in the yields of the alcohol and ketone upon that treatment with  $\text{PPh}_3$  are lower than 15%.

In our work, we obtained higher amounts of ketones than alcohols what indicates that ketones can also be formed by other reactions besides (6), e.g. from decomposition of  $\text{ROOH}$  (reaction (7) or (8)) or further oxidation of the alcohol  $\text{ROH}$  (reaction (9) or (10)), catalyzed by vanadium species. Reactions of the types (8) and (10) have been proposed, e.g. for cyclohexane or cyclododecane oxidation with  $\text{O}_2$ , catalyzed by a photoexcited polyoxododecatungstate immobilized on amorphous or MCM-41 silicas [36], which commonly also lead to a predominance of

the ketone over the alcohol.



alkane to give the alkyl hydroperoxide  $\text{ROOH}$  (reaction (2)) whose homolytic decomposition to alkoxy ( $\text{RO}^\bullet$ ) and alkyl peroxy ( $\text{ROO}^\bullet$ ) radicals (reactions (3) and (4)) can be catalyzed by a vanadium catalyst. The alcohol ( $\text{ROH}$ ) can be obtained by H-abstraction from the alkane by  $\text{RO}^\bullet$  (reaction (5)) or by decomposition of the alkylperoxy radical (reaction (6)) which forms also the ketone.

Such a type of mechanism has been proposed [13,34,35] when the metal in the catalyst has two available oxidation states of comparable stability, such as  $\text{V}^{\text{IV/V}}$  (our case),  $\text{Mn}^{\text{II/III}}$ ,  $\text{Fe}^{\text{II/III}}$ ,

An alternative  $\text{ROOH}$  decomposition pathway proceeding via adsorbed intermediates without the involvement of free radicals has been very recently proposed [37], on the basis of kinetic

studies, for the cyclohexane oxidation with O<sub>2</sub> on MnAPO-5 catalysts (APO-5 = aluminophosphate molecular sieves), but it accounts for an alcohol/ketone product ratio of 2 which is quite different from that observed in our case.

#### 4. Conclusions

The study shows that the bis(maltolato)oxovanadium(IV or V) complexes we have used, supported on carbamate modified silica gel, act as catalysts for the oxidation, with molecular oxygen, of neat cycloalkanes (i.e. cyclopentane and cyclooctane) without requiring the addition of any solvent, under moderate reaction conditions. The supported complexes are much more active than the unsupported ones, under identical experimental conditions, and the heterogenized [VO(ma)<sub>2</sub>] (**1**) compound is the most effective of all. The major products are the corresponding cycloketones (i.e. cyclopentanone and cyclooctanone formed with yields up to 10 and 25%, respectively), while the cycloalcohols are obtained in lower amounts. A selectivity up to 75% (Fig. 4) or 60% (Fig. 11) can be reached for cyclooctanone or cyclopentanone, respectively, under corresponding optimized conditions which, however, are not those that lead to the highest catalytic activities.

The detailed study of the effects of a variety of factors indicates that the most adequate operating conditions are 160 °C (for cyclopentane), 150 °C (for cyclooctane), ca. 10 and 6 h reaction time, respectively. The *p*(O<sub>2</sub>) of ca. 14 atm provides the highest conversion and selectivity towards cyclooctanone, while higher pressures promote the conversions of cyclopentane into its products (however, the highest selectivity towards cyclopentanone is achieved for the lower pressure of 7 atm). Carboxylic acids can act as co-catalysts and 2-pyrazinecarboxylic acid is the most effective one within those tested. The TGA analysis shows the [VO(ma)<sub>2</sub>] (**1**) supported catalyst is stable at the reaction temperatures and ICP indicates that the metal does not leach out extensively during a normal run, what allows its reutilization.

These silica supported oxovanadium catalysts provide remarkable TONs (estimated in the abovementioned way) for the oxidations of the cycloalkanes, as observed earlier for the oxidations of linear alkanes (*n*-pentane and *n*-hexane) [12] and of cyclohexane [13], that are quite higher than those we have previously quoted for the peroxidative oxidation or carboxylation of alkanes catalyzed by various homogeneous vanadium [38–40], rhenium [41,42] or copper [43] catalysts with N,O- or O-ligands. However, the latter catalysts can lead to comparable or higher yields than the heterogeneous oxovanadium catalysts of the current study.

As a final comment, one can mention that bis(maltolato)-oxovanadium compounds have attracted much attention in view of their significance in medicinal chemistry [44], being effective for treatment against *diabetes mellitus* [45–47] and inhibiting several enzymes such as phosphatases, ATPases, nucleases and kinases [48,49]. Their application in catalysis, namely as illustrated by this study, also deserves further exploration.

#### Acknowledgements

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal and its POCI 2010 program (FEDER funded). One of the authors (GSM) is grateful to FCT for a post-doctoral fellowship (SFRH/BPD/14957/2004). We also thank Prof. C. Henriques for kindly performing the TGA measurements and Mr. I. Marques for running the GC–MS.

#### References

- [1] E.G. Derouane, F. Parmon, F. Lemos, F. Ramôa, Ribeiro (Eds.), Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities, NATO Science series, vol. 191, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2005.
- [2] G. Centi, F. Trifiro, F. Cavani, Selective Oxidation by Heterogeneous Catalysis, Kluwer Academic/Plenum Publishers, New York, 2005.
- [3] C. Copéret, M. Chabanas, R.P.S. Arroman, J.M. Basset, *Angew. Chem. Int. Ed.* 42 (2003) 156.
- [4] J.H. Clark, D.J. Macquarrie, *Chem. Soc. Rev.* 25 (1996) 303.
- [5] B.K. Hodnett, Heterogeneous Catalytic Oxidation: Fundamental and Technological Aspects of the Selective and Total Oxidation of Organic Compounds, John Wiley & Sons, New York, 2000.
- [6] C.G. Bond, Metal-Catalysed Reactions of Hydrocarbons, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2005.
- [7] J.A. Labinger, J.E. Bercaw, *Nature* 417 (2002) 507.
- [8] G. Bhalla, O. Mironov, C. Jones, W.J. Tenn III, S. Nakamura, R.A. Periana, in: Gerald Dyker (Ed.), Transition Metal-Catalyzed Oxidation of Alkanes in Handbook of C–H Transformations, vol. 2, Wiley–VCH, Weinheim, 2005, p. 529.
- [9] G.S. Mishra, A. Kumar, *Catal. Lett.* 81 (2002) 113.
- [10] T. Garcia, B. Solsona, D.M. Murphy, K.L. Antcliff, S.H. Taylor, *J. Catal.* 229 (2005) 1.
- [11] J.M. López Nieto, P. Concepción, A. Dejoz, H. Knözinger, F. Melo, M.I. Vázquez, *J. Catal.* 189 (2000) 147.
- [12] G.S. Mishra, A.J.L. Pombeiro, *Appl. Catal. A: Gen.* 304 (2006) 185.
- [13] G.S. Mishra, A.J.L. Pombeiro, *J. Mol. Catal. A: Chem.* 239 (2005) 96.
- [14] G.A. Olah, A. Molnar, *Hydrocarbon Chemistry Textbook*, 2nd ed., John Wiley & Sons, New York, 2003.
- [15] N.A. Milas, W.L. Walsh, *J. Am. Chem. Soc.* 61 (1939) 633.
- [16] L.K. Volkova, V.P. Tretyakov, E.S. Rudakov, *Kinet. Catal.* 36 (1995) 373.
- [17] C. Jin, W. Fan, Y. Jia, B. Fan, J. Ma, R. Li, *J. Mol. Catal. A: Chem.* 249 (2006) 23.
- [18] K. Teramura, T. Tamka, T. Hosokawa, T. Ochuchi, M. Kani, T. Funabiki, *Catal. Today* 96 (2004) 205.
- [19] E.I. Karasevich, Y.K. Karasevich, *Kinet. Catal.* 43 (2002) 19.
- [20] (a) J. Połtowicz, E. Tabor, K. Pamin, J. Haber, *Inorg. Chem. Commun.* 8 (2005) 1125;  
(b) J. Haber, K. Pamin, J. Połtowicz, *J. Mol. Catal. A: Chem.* 224 (2004) 153;  
(c) J. Połtowicz, J. Haber, *J. Mol. Catal. A: Chem.* 220 (2004) 43;  
(d) J. Haber, L. Matachowski, K. Pamin, J. Połtowicz, *J. Mol. Catal. A: Chem.* 162 (2000) 105;  
(e) J. Połtowicz, K. Pamin, L. Matachowski, E.M. Serwicka, R. Mokaya, Y. Xia, Z. Olejniczak, *Catal. Today* 114 (2006) 287.
- [21] J. Połtowicz, K. Pamin, E. Tabor, J. Haber, A. Adamski, Z. Sojka, *Appl. Catal. A: Gen.* 299 (2006) 235.
- [22] S. Samanta, N.K. Mal, A. Bhaumik, *J. Mol. Catal. A: Chem.* 236 (2005) 7.
- [23] (a) G.B. Shul'pin, A.E. Shilov, G. Süß-Fink, *Tetrahedron Lett.* 42 (2001) 7253;  
(b) G. Süß-Fink, L. Gonzalez, G.B. Shul'pin, *Appl. Catal. A: Gen.* 217 (2001) 111.
- [24] M.M.Q. Simões, I.C.M.S. Santos, M.S.S. Balula, J.A.F. Gamelas, A.M.V. Cavaleiro, M. Graça, P.M.S. Neves, J.A.S. Cavaleiro, *Catal. Today* 91 (2004) 211.

- [25] P. Caravan, L. Gelmini, N. Glover, F.G. Herring, H. Li, J.H. McNeill, S.J. Retting, I.A. Setyawati, E. Shuter, Y. Sun, A.S. Tracey, V.G. Yuen, C. Orvig, *J. Am. Chem. Soc.* 117 (1995) 12759.
- [26] G.S. Mishra, A. Kumar, *J. Mol. Catal. A: Chem.* 192 (2003) 275.
- [27] R.S. Drago, S.C. Petrosius, C.W. Chronister, *Inorg. Chem.* 33 (1994) 367.
- [28] G.B. Shul'pin, *J. Mol. Catal. A: Chem.* 189 (2002) 39.
- [29] M. Vennat, P. Herson, J.M. Bregeault, G.B. Shul'pin, *Eur. J. Inorg. Chem.* (2003) 908.
- [30] G.B. Shul'pin, Y.N. Kozlov, G.V. Nizova, G. Süß-Fink, S. Stanislas, A. Kitaygorodskiy, S. Kulikova, *Perkin Trans. 2* (2001) 1351.
- [31] G. Süß-Fink, S. Stanislas, G.B. Shul'pin, G.V. Nizova, H. Stoekli-Evans, A. Neels, C. Bobillier, S. Claude, *Dalton Trans.* (1999) 3169.
- [32] R.Z. Khaliullin, A.T. Bell, M. Head-Gordon, *J. Phys. Chem. B* 109 (2005) 17984.
- [33] R. Gopinath, B.K. Patel, *Org. Lett.* 2 (2000) 577.
- [34] M. Hartman, S. Ernst (Eds.), *Angew. Chem. Int.* 39 (2000) 888.
- [35] A. Kumar, G.S. Mishra, A. Kumar, *Trans. Met. Chem.* 28 (2003) 913.
- [36] A. Maldotti, A. Molinari, G. Varani, M. Lenarda, L. Storaro, F. Bigi, R. Maggi, A. Mazzacani, G. Sartori, *J. Catal.* 209 (2002) 210.
- [37] B. Modén, Bi-Z. Zhan, J. Dakka, J.G. Santiesteban, E. Iglesia, *J. Catal.* 239 (2006) 390.
- [38] P.M. Reis, J.A.L. Silva, A.F. Palavara, J.J.R. Fraústo da Silva, T. Kitamura, Y. Fujiwara, A.J.L. Pombeiro, *Angew. Chem. Int. Ed.* 42 (2003) 821.
- [39] P.M. Reis, J.A.L. Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, *Chem. Commun.* (2000) 1845.
- [40] P.M. Reis, J.A.L. Silva, A.F. Palavara, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, *J. Catal.* 235 (2005) 333.
- [41] A.M. Kirillov, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, *Eur. J. Inorg. Chem.* (2005) 2071.
- [42] A.M. Kirillov, M. Haukka, M.V. Kirillova, A.J.L. Pombeiro, *Adv. Synth. Catal.* 347 (2005) 1435.
- [43] A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, *Angew. Chem. Int. Ed.* 44 (2005) 4345.
- [44] D.I. Shah, M. Singh, *Vascular Pharmacol.* 44 (2006) 177.
- [45] M.Z. Mehdi, A.K. Srivastava, *Arch. Biochem. Biophys.* 440 (2005) 158.
- [46] G.R. Willsky, A.B. Goldfine, P.J. Kostyniak, J.H. McNeill, L.Q. Yang, H.R. Khan, D.C. Crans, *J. Inorg. Biochem.* 85 (2001) 33.
- [47] K.H. Thompson, J. Chiles, V.G. Yuen, J. Tse, J.H. McNeill, C. Orvig, *J. Inorg. Biochem.* 98 (2004) 683.
- [48] L. Coderre, A.K. Srivastava, *Can. J. Physiol. Pharmacol.* 82 (2004) 833.
- [49] D.C. Crans, M.M. Tahir, A.D. Keramidas, *Mol. Cell. Biochem.* 153 (1995) 17.