

Selective single-pot oxidation of cyclohexane by molecular oxygen in presence of bis(maltolato)oxovanadium complexes covalently bonded to carbamated modified silica gel

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Abstract

The bis(maltolato)oxovanadium complexes $[\text{VO}(\text{ma})_2]$, *cis*- $[\text{VO}(\text{OCH}_3)(\text{ma})_2]$ and $[\text{VO}(\text{py})(\text{ma})_2]$ have been covalently bonded to carbamated modified silica gel and these systems are shown to serve as effective heterogeneous catalysts for cyclohexane oxidation by molecular oxygen without any additive. The $[\text{VO}(\text{ma})_2]$ catalyst gives the best results which are further promoted in the presence of 2-pyrazinecarboxylic acid which acts as a co-catalyst, while picolinic acid proved to be almost inactive. The reaction occurs under mild conditions (175 °C, 10 atm O_2) forming two major products, cyclohexanol and cyclohexanone in a smaller amount, with a good selectivity. The TGA analysis of the catalyst shows that it is stable up to 273 °C and inductive couple plasma (ICP) indicates a limited metal loss after 20 h use of the catalyst up to 175 °C. The morphology of the catalyst was analyzed by SEM. Evidence is presented in favour of the involvement of a free-radical mechanism.

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1. Introduction

The selective partial oxidation of alkanes [1–16] to oxygen containing compounds (alcohols, aldehydes, ketones, acids, etc.) is a current challenge to modern chemistry towards the development of highly important and useful reactions for the chemical industry. Normally, more than one oxygenated products [17,18] are produced from a given starting material and they are susceptible to complete oxidation to CO_2 [19] which should be avoided. The oxidation of cyclohexane is an important reaction in the framework of commercial production of nylon. Past studies have revealed that the main products formed during its oxidation are cyclohexanol, cyclohexanone, adipic acid and several minor products (cyclohexene, cyclohexene-2-one, valeraldehyde and valeric acid) [20,21]. The cyclohexanol and cyclohexanone (formed

in almost equivalent amounts) in the reaction mass are further processed for the production of adipic acid and caprolactam, which are ultimately used in the manufacture of nylon-6,6 and nylon-6, respectively [22]. Many efforts have been made to develop new catalysts to oxidize cyclohexane under mild conditions with high selectivity for the target products (cyclohexanol, cyclohexanone or adipic acid) using different oxidizing agents (hydrogen peroxide, *t*-butyl hydroperoxide and molecular oxygen) [23,24]. Normal catalytic systems used for industrial cyclohexane oxidation employ cobalt salts (cobalt naphthenate or cobalt acetate), molecular oxygen and temperatures above 150 °C [25]. A low conversion (~4%) is obtained to avoid the formation of side products and to obtain a high selectivity (~85%) towards a mixture of cyclohexanone and cyclohexanol [26]. To overcome the usual problem of separating the catalyst from the products in homogeneous catalysis, many heterogeneous catalysts have been developed for this reaction. Generally, these catalysts are either oxides or metal cations incorporated in inorganic

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mixtures, such as silica, alumina, zirconia, active carbon, zeolites [27–29] or aluminophosphates [30]. The activity of these systems is dependent on the solvent, which determines the polarity of the medium and structure of the substrate that needs to be adsorbed on the catalytic surface [31]. For example, the solvent effect [32] has been investigated by oxidizing cyclohexane over CoAPO-5 molecular sieves using different carboxylic acids (formic acid, ethanoic acid, propionic acid, butyric acid, pentanoic acid and n-hexanoic acid), and the conversion was found to be maximum in the case of propionic acid. Sometimes, promoters or co-reactants, like acetaldehyde and azo-bisisobutyronitrile (AIBN), are also added to reduce the induction period and to increase the cyclohexane conversion with high selectivity for target products [33]. Other normal oxidation catalysts recently investigated are transition metal-substituted poly-oxo metals, which generally show high activity in the oxidation of alkanes [2,34].

In this article, we report that (i) oxovanadium complexes with maltolato ligands, i.e. the bis(maltolato)oxovanadium (IV) complex $[\text{VO}(\text{ma})_2]$, the bis(maltolato)(methoxy)oxovanadium(V) complex *cis*- $[\text{VO}(\text{OCH}_3)(\text{ma})_2]$ and the bis(maltolato)oxo(pyridine)vanadium(IV) complex $[\text{VO}(\text{py})(\text{ma})_2]$ can be covalently bonded to carbamated modified silica gel, and (ii) these systems act as efficient and selective heterogeneous catalysts for the oxidation by molecular oxygen of neat cyclohexane, without requiring the addition of any solvent, mainly to cyclohexanol and cyclohexanone in a smaller amount, under relatively low temperature and O_2 pressure (e.g. overall conversion of 12%, TON ca. 5×10^3 , at 175°C , $p(\text{O}_2) = 10 \text{ atm}$, 20 h reaction time).

2. Experimental

2.1. Materials and complexes

All the synthetic work was performed under dinitrogen atmosphere using standard Schlenk techniques. The solvents were dried and degassed by standard methods. Vanadium(IV)oxydisulfate, sodium azide, bromotrichloromethane (Merck), potassium hydroxide, 3-hydroxy-2-methyl-4-pyrone (maltol, Hma), benzoyl chloride, picolinic acid (Aldrich), 2-pyrazinecarboxylic acid and 2,6-pyridinedicarboxylic acid (Janssen) were used as received. 2,2'-Azobis(2-methylpropionitrile) (Aldrich) was used after recrystallization from methanol and cyclohexane (99%, Aldrich) was purified by distillation prior to use. The vanadium complexes $[\text{VO}(\text{ma})_2]$, *cis*- $[\text{VO}(\text{OCH}_3)(\text{ma})_2]$ and $[\text{VO}(\text{py})(\text{ma})_2]$ were prepared according to literature procedures [35].

2.2. Preparation of the modified silica gel support

Phenyl isocyanate is prepared [36] by the reaction of sodium azide, NaN_3 , (16.8 g, 0.26 mol) with an equivalent number of moles of benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$ (35.0 g, 0.26 mol) in benzene (20 cm^3) at 0°C . The NaN_3 is added

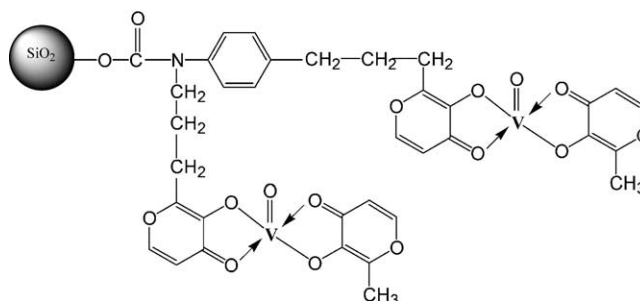
to a flask with dry benzene and the system is stirred for 4 h in an ice bath. The benzoyl chloride is then added dropwise with stirring, and the reaction is carried out for 8 h, whereafter the reaction mixture is vacuum filtered and the filtrate liquid phase is collected.

The modified silica gel is prepared by the reaction of above filtrate liquid-phase phenyl isocyanate (35 ml) with the silanol groups ($-\text{OH}$) on the surface [37] of silica gel (2.0 g). The mixture is stirred at 40°C for 6 h and the presence of carbamate bonds on the silica gel was confirmed by FTIR: 3027 aromatic $\nu(\text{CH})$, 1690 $\nu(\text{C}=\text{O})$ and 1595 $\delta(\text{NH}) \text{ cm}^{-1}$.

In the next step, the carbamated modified silica gel (5.0 g) is reacted with dichloroethane (50 cm^3) in the presence of ZnCl_2 as catalyst (2.0 mg, 0.0185 mol) at 60°C for 2 h.

2.3. Formation of final supported catalyst

Each of the above vanadium complexes, $[\text{VO}(\text{ma})_2]$, *cis*- $[\text{VO}(\text{OCH}_3)(\text{ma})_2]$ or $[\text{VO}(\text{py})(\text{ma})_2]$ (16 mg) was separately dissolved in acetone (10 ml), the solution added to the carbamate-modified silica (1.0 g each) and the mixture heated at 50°C for 4-h reaction. The expected structure of the final supported $[\text{VO}(\text{ma})_2]$ catalyst is given below (the other complexes should be similarly attached to the carbamate-modified silica gel).



Carbamated modified silica gel supported $[\text{VO}(\text{ma})_2]$ complex catalyst

The solid (vanadium complex loaded on the modified silica gel) was washed several times with acetone and finally dried at 35°C for 6 h under N_2 . After washing, we found that 14 mg of $[\text{VO}(\text{ma})_2]$ or 13 mg of *cis*- $[\text{VO}(\text{OCH}_3)(\text{ma})_2]$ or $[\text{VO}(\text{py})(\text{ma})_2]$ were separately loaded per gram of carbamated modified silica gel support (in the case of $[\text{VO}(\text{ma})_2]$, this was confirmed by ICP). The colours of the carbamated supported catalysts are as follows: green for $[\text{VO}(\text{ma})_2]$, light brown for *cis*- $[\text{VO}(\text{OCH}_3)(\text{ma})_2]$ and brown for $[\text{VO}(\text{py})(\text{ma})_2]$.

FTIR spectra of the final supported catalysts: 3493 $\nu(\text{NH})$, 3450 $\nu(\text{OH})$, 3030 $\nu(\text{CH}, \text{aromatic})$, 2966 $\nu(\text{CH}, \text{aliphatic})$, 1700 $\nu(\text{C}=\text{O}) \text{ cm}^{-1}$. The considerable reduction of the peak at 760 cm^{-1} corresponding to $\nu(\text{C}-\text{Cl})$ confirms the bond formation between the complex and the modified support.

2.4. Characterization of the supported catalyst

The vanadium metal content of the fresh catalyst 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 assess whether 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 on a Jasco FTIR-430 spectrometer in transmission mode using KBr pellets. Scan electron microspectroscopy (SEM) of the supported catalyst, before and after the catalytic reaction, was performed by using a Hitachi-2400 instrument at the Material Engineering Department, IST.

2.5. Setup and reaction procedure

A high-pressure cylindrical stainless steel batch reactor (13 cm^3) is used for conducting the reactions. The reactor has a provision for gas inlet and pressure gauge. An external heating oil bath provides heating and the temperature is controlled using an on/off controller with a suitable thermocouple. Oxygenation reactions are carried out in the batch reactor with 5.0 ml (46.4 mmol) of neat cyclohexane and 20 mg of supported vanadium catalyst. After the oxidation reaction, the catalysts whose colours (see above) had turned into light brown were separated from the solutions by filtration using filter paper and washed three times with acetone.

The products were analyzed by gas chromatography ($30\ \mu\text{l}$ of cyclopentanone added as internal standard) using a Fisons chromatograph model 8000 equipped with an 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 analyzed 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 turnover number (TON) was estimated as the molar ratio of product/supported V-complex on modified silica gel and the yield was calculated as the molar ratio (%) of product/substrate. Blank experiments with silica gel or carbamated modified silica gel but without the vanadium catalyst were also performed, giving maximum conversions to cyclohexanol and cyclohexanone of 1.9 and 1.1%, respectively.

2.6. Recycling studies

After the first reaction run, the catalyst was filtered off, washed with acetone for three times and dried in an air-oven followed by activation at 473 K for 6 h. The activated catalyst was used for the subsequent recycling studies.

3. Results and discussion

We have tested the three heterogeneous carbamated-modified silica gel-supported complexes $[\text{VO}(\text{ma})_2]$,

$\text{cis-}[\text{VO}(\text{OCH}_3)(\text{ma})_2]$ and $[\text{VO}(\text{py})(\text{ma})_2]$ in the oxidation reaction of neat cyclohexane by molecular oxygen to give cyclohexanol and cyclohexanone, and found (results are given in Table 1) that they serve as effective heterogeneous catalysts (typical TONs in the $4 \times 10^3\text{--}6 \times 10^3$ range) for such a reaction without the need of using any additive. The $[\text{VO}(\text{ma})_2]$ catalyst provides the best results (12% conversion of the alkane, essay 4 with $p(\text{O}_2) = 10\text{ atm}$, $175\text{ }^\circ\text{C}$) in comparison with those of the other catalysts (compare with essays 17 and 18 that lead to 9.7 and 6.9% alkane conversions, respectively), and therefore, we focused our catalytic studies on the former catalyst. Blank experiments demonstrate that our catalysts are necessary for the cyclohexane oxidation to proceed significantly, since no product (or only in a very low yield) was detected when the reaction was attempted without the vanadium catalyst for as long as 20 h at $200\text{ }^\circ\text{C}$. The strong smell at the end of the reaction, when carried out in the presence of the catalyst, indicated the product formation which was further confirmed by GC and GC-MS analyses that allow to quantify the amounts of cyclohexanol and cyclohexanone, the main products. As a result of the chemical reaction, the colour of the supported catalyst changes from light green, i.e. that of $[\text{VO}(\text{ma})_2]$, to dark brown. The alkane conversions and the effects of temperature, time, $p(\text{O}_2)$ pressure, amount of catalyst, other catalysts and co-catalysts are summarized in Table 1.

The effect of temperature on the oxidation reaction of cyclohexane was examined by varying it up to $225\text{ }^\circ\text{C}$ (Table 1, essays 1–6 and Fig. 1 for $p(\text{O}_2) = 10\text{ atm}$ and 20 h reaction time). For each of the products, the conversion increases slowly until ca. $150\text{ }^\circ\text{C}$ (overall 6.8%) beyond which a sharp increase occurs until $175\text{ }^\circ\text{C}$ (overall 11.9%). At $225\text{ }^\circ\text{C}$, an overall conversion of 14.4% is achieved but the reaction temperature was not allowed to go beyond this value due to the formation of a slight amount of an unidentified black material. The dependence of the selectivity with the temperature is shown in Fig. 2 which indicates only a small

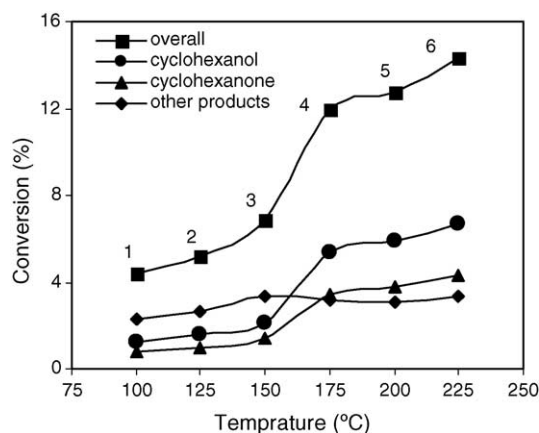


Fig. 1. Effect of temperature on the conversion of cyclohexane upon oxidation by O_2 , in the presence of the carbamated modified silica gel supported bis(maltolato) oxovanadium(IV) catalyst ($p(\text{O}_2) = 10\text{ atm}$, reaction time = 20 h). Point numbering corresponds to essays of Table 1.

Table 1

Effect of different parameters on the oxidation of cyclohexane by molecular oxygen in the presence of carbamated modified silica gel supported bis(maltolato)oxovanadium complex [VO(ma)₂] and related ones^a

Essay	Temperature (°C)	<i>p</i> (O ₂) (atm) ^b	Time (h)	Catalyst (mg)	Other V-catalyst	Co-catalyst	Conversion (%) ^c				TON ^d Units of 10 ³)	
							Overall	Cy-ol	Cy-one	Other products	Cy-ol	Cy-one
1	100	10	20	20	–	–	4.4	1.3	0.8	2.3	0.7	0.4
2	125	10	20	20	–	–	5.2	1.6	1.0	2.7	0.8	0.5
3	150	10	20	20	–	–	6.8	2.1	1.4	3.3	1.1	0.8
4	175	10	20	20	–	–	11.9	5.4	3.4	3.2	2.8	1.8
5	200	10	20	20	–	–	12.8	5.9	3.8	3.1	3.1	2.0
6	225	10	20	20	–	–	14.4	6.7	4.3	3.3	3.5	2.3
7	175	5	20	20	–	–	3.2	1.1	0.8	1.1	0.7	0.4
8	175	15	20	20	–	–	13.0	5.9	3.8	3.2	3.1	2.0
9	175	20	20	20	–	–	13.9	6.4	4.1	3.4	3.1	2.2
10	175	30	20	20	–	–	14.8	6.9	4.4	3.5	3.6	2.3
11	175	10	10	20	–	–	2.4	1.0	0.6	0.8	0.5	3.3
12	175	10	30	20	–	–	13.7	6.4	4.5	2.5	3.4	2.4
13	175	10	50	20	–	–	15.1	7.1	5.0	3.0	3.7	2.6
14	175	10	20	10	–	–	4.4	1.9	1.2	1.4	1.0	0.6
15	175	10	20	30	–	–	13.1	6.1	3.9	3.1	3.2	2.0
16	175	10	20	50	–	–	14.2	6.7	4.3	3.2	3.5	2.2
17	175	10	20	–	^e	–	9.7	4.4	2.6	2.7	2.6	1.5
18	175	10	20	–	^f	–	6.9	3.2	2.1	1.5	2.3	1.5
19	175	10	20	20	–	^g	15.8	6.7	4.5	4.6	3.5	2.4
20	175	10	20	20	–	^h	14.4	6.4	4.3	3.7	3.4	2.3
21	175	10	20	20	–	ⁱ	12.2	5.6	3.5	3.1	2.9	1.8

^a Reaction conditions (unless stated otherwise): [VO(ma)₂] supported catalyst = 20 mg, O₂ pressure = 10 atm, cyclohexane = 5.0 ml, 175 °C, 20 h, in an autoclave (13 cm³ capacity).

^b Measured at 25 °C.

^c Molar yield (%) based on moles of product per mole of cyclohexane.

^d Turnover number (moles of product per mole of metal complex supported on carbamated modified silica gel).

^e *cis*-[VO(OCH₃)(ma)₂] supported catalyst.

^f [VO(py)(ma)₂] supported catalyst.

^g 2-Pyrazinecarboxylic acid.

^h 2,6-Pyridinedicarboxylic acid.

ⁱ Picolinic acid.

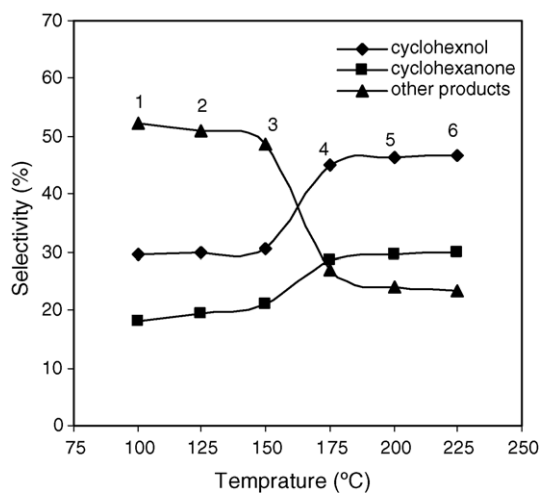


Fig. 2. Effect of temperature on the selectivity of the oxidation of cyclohexane by molecular O₂, in the presence of the bis(maltolato)oxovanadium(IV) complex supported on carbamated modified silica gel (*p*(O₂) = 10 atm, reaction time = 20 h). Point numbering corresponds to essays of Table 1.

effect in the 100–150 °C range, with relatively low cyclohexanol and cyclohexanone selectivities. However, at 175 °C or a higher temperature, these products are clearly the major ones.

The reaction time was varied from 10 to 50 h at 175 °C (*p*(O₂) = 10 atm) and shown (Table 1, essays 4, 11–13 and Fig. 3) that the alkane conversion towards the desired cyclohexanol and cyclohexanone products does not increase substantially after 20 h. Nevertheless, extending the reaction time above 20 h results in an improvement of the selectivity (Fig. 4) towards such products.

The effect of oxygen pressure was also investigated. The alkane conversion markedly increases with *p*(O₂) until 10 atm (Fig. 5; at 175 °C, 20 h) but only slightly beyond this pressure (overall conversion of 11.9% and 14.8% for 10 and 30 atm, essays 4 and 10, respectively). The increase of the conversion with the O₂ pressure is consistent with the promotion of the solubility of this gas with the pressure. Above 10 atm, the selectivity towards cyclohexanol and cyclohexanone also remains practically constant (Fig. 6), whereas the relative amount of the other products decreases up to 15 atm. Hence, the use of O₂ pressures above 15 atm is not advantageous. We have also found that the conversion increases with the amount

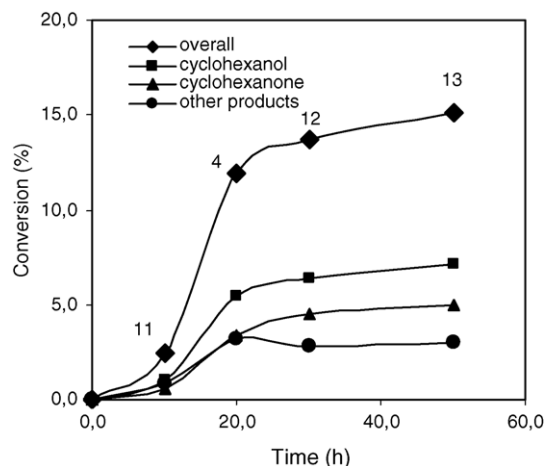


Fig. 3. Effect of time on the conversion of cyclohexane upon oxidation by O_2 , in the presence of the carbamated modified silica gel supported bis(maltolato)oxovanadium(IV) catalyst (temperature = $175^\circ C$, $p(O_2) = 10$ atm). Point numbering corresponds to essays of Table 1.

of supported catalyst (4.4–14.2% for 10–50 mg, respectively, essays 14, 4, 15 and 16, Table 1) up to a limit. Beyond 50 mg of catalyst, no appreciable further increase in the conversion is observed. After being used, the catalyst can be recycled and reactivated by heating, showing a comparable activity to that of the initial run. This is consistent with the ICP analysis that shows only a small metal loss upon use. In fact, the fresh supported catalyst $[VO(ma)_2]$ with measured 0.20 wt.% of vanadium after 20-h reaction shows a metal content of 0.16 wt.%. TGA analysis of the freshly supported $[VO(ma)_2]$ catalyst shows that it is stable up to $273^\circ C$ (Fig. 7), when decomposition occurs (the loss of weight at ca. $100^\circ C$ corresponds to the loss of moisture from the support).

The SEM picture of the freshly prepared supported $[VO(ma)_2]$ catalyst is shown in Fig. 8 (4000 times magnification); the dark particles on the cavity of the supported matrix being assigned to the presence of the $[VO(ma)_2]$

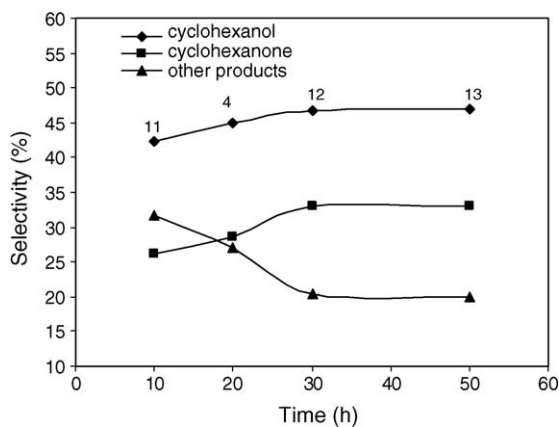


Fig. 4. Effect of time on the selectivity of the oxidation of cyclohexane by O_2 , in presence of the carbamated modified silica gel supported bis(maltolato)oxovanadium(IV) catalyst (temperature = $175^\circ C$, $p(O_2) = 10$ atm). Point numbering corresponds to essays of Table 1.

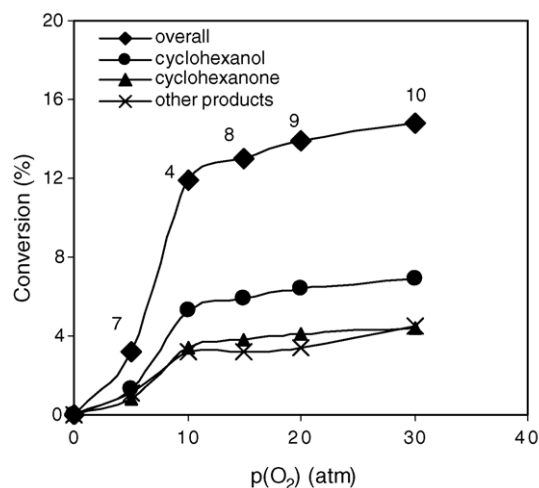


Fig. 5. Effect of O_2 pressure on the conversion of cyclohexane upon oxidation by molecular oxygen, in the presence of the carbamated modified silica gel supported bis(maltolato)oxovanadium(IV) catalyst (temperature = $175^\circ C$, reaction time = 20 h). Point numbering corresponds to essays of Table 1.

complex and the white particles to the untreated carbamate. The used catalyst still shows dark particles stuck on the surface of the support matrix, although in a smaller amount, as well as a bunch of round shaped forms seeming to correspond to the charring material from the oxidation reaction of cyclohexane. The presence of vanadium was further confirmed by chemical analysis by the SEM instrument.

Some heteroaromatic acids have also been tested as possible co-catalysts and 2-pyrazinecarboxylic acid was found to promote quite considerably the reaction overall yield (increase from 11.9 to 15.8%, essays 4 and 19, Table 1). A high accelerating effect of this acid on the peroxidative oxidation of alkanes (and other substrate) by various homogeneous vanadium species has previously

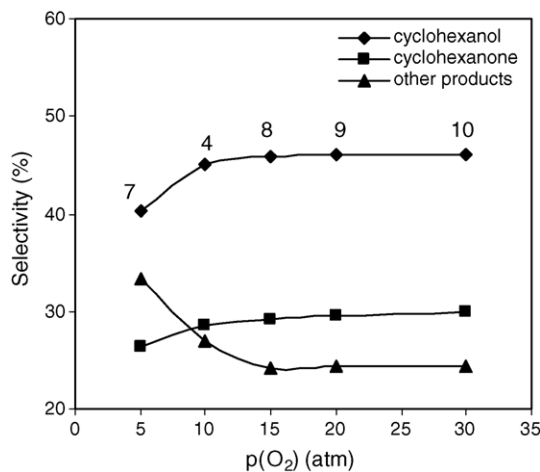


Fig. 6. Effect of O_2 pressure on the selectivity of the oxidation of cyclohexane by O_2 , in the presence of the bis(maltolato)oxovanadium(IV) complex supported on carbamated modified silica gel (temperature = $175^\circ C$, reaction time = 20 h). Point numbering corresponds to essays of Table 1.

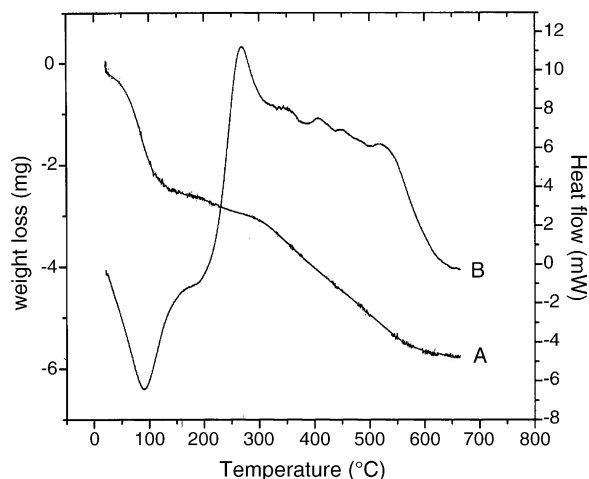


Fig. 7. Thermogravimetric analysis (TGA) of the freshly modified silica gel supported bis(maltolato) oxovanadium(IV) complex catalyst: percentage weight loss (A) and heat flow (B).

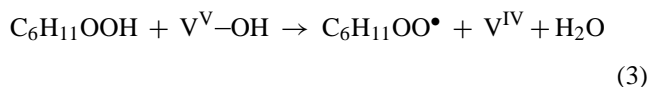
been recognized by Shul'pin and Süß-Fink [38,39]. 2,6-Pyridinedicarboxylic acid and picolinic acid have a less pronounced effect, in particular the latter which is almost inactive and is also less effective than 2-pyrazinecarboxylic acid [38,39] in the above V-catalyzed alkane oxidation by H_2O_2 .

The mechanisms of the oxidation reactions can be divided into three main general groups [40,41]: (i) oxidation via a free-radical chain process, (ii) oxidation through coordination of the substrate, and (iii) catalytic oxygen transfer. They depend upon the reaction conditions (gas or liquid phase, temperature and pressure) and the nature of the metal and the oxidizing agent used. In our case, a free-radical mechanism appears to be followed, since when the reaction is carried out in the presence of the liquid radical trap CBrCl_3 , no cyclohexanol is formed and the amount of cyclohexanone

drops considerably to a lower value (2% under the conditions of essay 4). The use of common solid radical traps was prevented by their insolubility in cyclohexane.

Moreover, the addition of a free-radical initiator, such as 2,2'-azobis(2-methylpropionitrile) reduces the induction period of the reaction, e.g. after 6 h under the conditions of essay 4, the conversions to cyclohexanol and cyclohexanone increase from 0.7 and 0.3% to 1.3 and 0.8%, respectively, in the presence of a catalytic amount ($1:1.5 \times 10^3$ molar ratio relatively to the alkane) of that reagent.

Cyclohexyl ($\text{C}_6\text{H}_{11}\bullet$) and cyclohexylperoxy ($\text{C}_6\text{H}_{11}\text{OO}\bullet$) radicals can be initially formed by reaction with O_2 (the former conceivably very slowly, induction period). Homolytic C–H bond cleavage of the alkane can occur by H-atom abstraction by the alkylperoxy radical to generate a further alkyl radical ($\text{C}_6\text{H}_{11}\bullet$) and the hydroperoxide $\text{C}_6\text{H}_{11}\text{OOH}$ (reaction 1) whose homolytic decomposition to cyclohexyloxy ($\text{C}_6\text{H}_{11}\text{O}\bullet$) and further cyclohexylperoxy ($\text{C}_6\text{H}_{11}\text{OO}\bullet$) (reactions 2 and 3) can be catalyzed by the vanadium catalyst. Cyclohexanol can then be formed by H-atom abstraction from cyclohexane by the cyclohexyloxy radical (reaction 4). This type of radical mechanism is known [40,42] to occur for metal catalysts with two metal oxidation states of comparable stability, like $\text{Mn}^{\text{II/III}}$, $\text{Fe}^{\text{II/III}}$, $\text{Co}^{\text{II/III}}$ or $\text{Cu}^{\text{I/II}}$, and this condition is fulfilled also in our case involving $\text{V}^{\text{IV/V}}$ systems. Cyclohexanone can be obtained by decomposition of the cyclohexylperoxy radical (reaction 5) which also forms further cyclohexanol, thus in accord with the higher yield of the alcohol relatively to the ketone.



The formation of the hydroperoxide $\text{C}_6\text{H}_{11}\text{OOH}$ is confirmed by the increase of the detected amount of cyclohexanol with concomitant decrease of that of cyclohexanone, if the final reaction solution before the GC analysis, is treated with an excess of PPh_3 as indicated by Shul'pin [3,43]. The hydroperoxide still present is deoxygenated by PPh_3 to the alcohol $\text{C}_6\text{H}_5\text{OH}$ (with formation of the phosphine oxide Ph_3PO) a reaction that replaces the $\text{C}_6\text{H}_{11}\text{OOH}$ decomposition to both cyclohexanol and cyclohexanone in the chromatograph [3,43]. However, the amount of $\text{C}_6\text{H}_{11}\text{OOH}$ in the end of the reaction under our usual experimental oxidation (175°C) is relatively small since the variations in the yields of the alcohol and ketone upon the above treatment with PPh_3 are typically not higher than 15%.

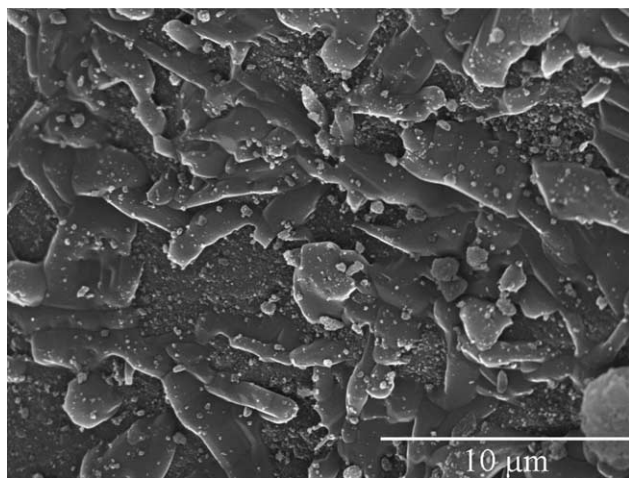


Fig. 8. SEM photograph (4000 \times magnification) of freshly modified silica gel supported $[\text{VO}(\text{ma})_2]$ catalyst.

4. Conclusion

On the basis of the above discussion, we conclude that [VO(ma)₂] within those tested, is the best oxidation-supported catalyst for cyclohexane oxidation, leading to the formation of two major products with a good selectivity, i.e. cyclohexanol and cyclohexanone in a smaller amount. The TGA analysis shows the catalyst is stable up to 273 °C with complex breaking at 293 °C and ICP indicates that the metal does not leach out markedly for at least 20 h of oxidation reaction. 2-Pyrazinecarboxylic acid acts as a co-catalyst leading to a yield increase of the products. The study of the effects of temperature, time, pressure and the amount of catalyst on the conversions indicates that the most adequate operating conditions are 175 °C, $p(\text{O}_2) = 10$ atm and 20 h reaction time, when an overall yield and TON of 12% and ca. 5×10^3 are obtained. Experiments with radical traps and initiators provide some supporting testimony in favour of a free-radical mechanism.

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