

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

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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.

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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 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 H_2O_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 H_2O_2 or *tert*-butyl

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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 H_2O_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

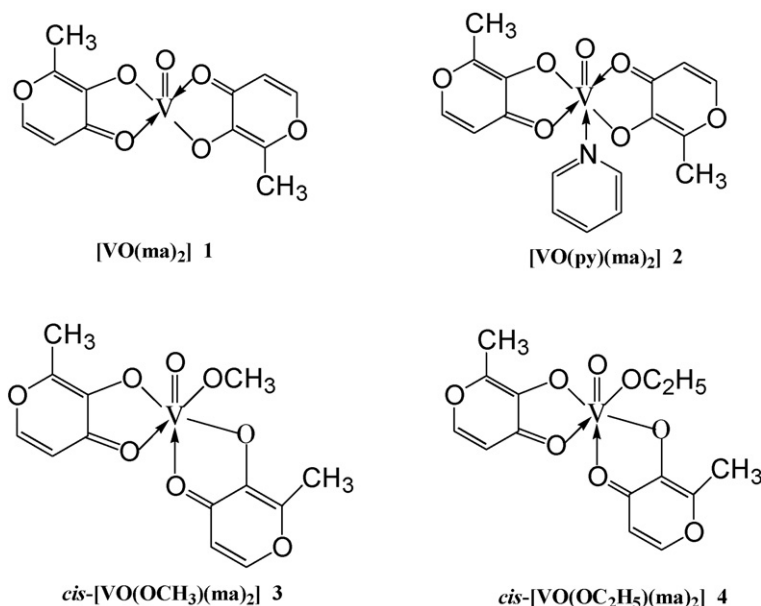
All the reactions were performed under an atmosphere of N_2 using standard vacuum and inert-gas flow Schlenk techniques. Solvents were purified by standard procedures and freshly distilled immediately prior to use. The compound $[\text{VO}(\text{ma})_2]$ (**1**) was prepared by the overnight reaction 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 NaN_3 with PhCOCl [26]) to the silanol groups [27] to give carbamated silica gel which is further treated with 1,2-dichloroethane in the presence of 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 (3×100 mL) and dried at 35 °C for 6 h, under 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 (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 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.

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