



Review

Vanadium complexes: Recent progress in oxidation catalysis



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ARTICLE INFO

Article history:

Received 24 October 2014

Received in revised form 13 January 2015

Accepted 31 January 2015

Available online 10 February 2015

Keywords:

Oxidovanadium complexes

Oxidation of alkanes

Oxidation of alcohols

Epoxidation

Sulfoxidation

Homogeneous and supported catalysis

ABSTRACT

Oxidovanadium complexes and, to a less extent, some non-oxido ones, are widely used as catalysts or catalyst precursors for various oxidative catalytic reactions by H_2O_2 , $t\text{BuOOH}$ or O_2 under mild conditions. Oxidation reactions (oxidation of alkanes and alcohols, epoxidation of alkenes and allylic alcohols, oxidative bromination, sulfoxidation and oxidative Strecker reactions) of organic compounds are the most relevant ones and are reviewed considering the recent advances in the last five years (2010–2014). The main types of both homogeneous and supported vanadium catalysts and the most efficient catalytic systems in the different reactions are presented and compared. The proposed mechanisms of various catalytic oxidation processes are also outlined.

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1. Introduction

Oxidovanadium complexes in high-oxidation states have a high relevance in oxidation catalysis [1–3]. They have been widely used as homogeneous or heterogeneous (supported) catalysts in oxidation processes of industrial interest in the presence of a suitable oxidant e.g., alkyl hydroperoxides, H_2O_2 or O_2 , under mild conditions [3–6]. The relevance of vanadate-dependent enzymes in various biological catalytic processes [7–10] has further stimulated research on vanadium based catalysis, which has been applied in various organic transformations [1–12]. The use of high valent vanadium complexes in oxidation catalysis is encouraged by (a) the easily interconvertible vanadium oxidation states (where +4 and +5 are the most stable ones under aerobic conditions), (b) the various possible coordination numbers, (c) the high affinity of the metal toward oxygen and (d) the Lewis acid character of the vanadium centers. The synthesis of oxidovanadium complexes in high-oxidation states is thus of potential interest in this field, and azine fragment ($\text{C}=\text{N}-\text{N}=\text{C}$) ligands are particularly promising since they can form stable oxidovanadium complexes of different metal oxidation states [13–15].

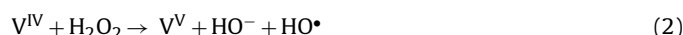
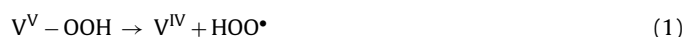
This review discusses recent advances in the last five years (2010–2014) of the use of mainly oxidovanadium complexes (a few non-oxido ones have also been disclosed) in oxidation catalytic reactions, viz., oxidation of alkanes and alcohols, epoxidation of alkenes and allylic alcohols, oxidative bromination or sulfoxidation of organic compounds, as catalysts or catalyst precursors or promoters. The review covers mainly homogeneous catalytic systems, but supported catalysts are also included, allowing their comparison in terms of selectivities, yields, TONs, etc.

2. Oxidation of alkanes and alkylaromatics

Vanadium complexes are useful and efficient catalysts or catalyst precursors for the functionalization of alkanes. A number of studies have already been reported where effective vanadium based catalytic systems are used toward the carboxylation [16,17] and oxidation [18–24] of alkanes (Scheme 1, for cyclohexane). The addition of a small amount of an acid as promoter, such as, 2-pyrazinecarboxylic acid (PCA) [18–23], nitric [25], sulfuric [26] or oxalic [26] acid, can dramatically improve the activity. The catalytic efficiency of the vanadate salt ($n\text{-Bu}_4\text{N}$)[VO_3], in the presence of PCA as a promoter, toward the oxidation of organic compounds (alkanes, arenes, alcohols) with hydrogen peroxide under mild conditions (20–60 °C, in acetonitrile solution) was discovered by Shul'pin and co-workers in 1993 [27]. Thereafter, several studies proved that PCA in combination with vanadium compounds can provide rather efficient and versatile catalytic systems for the mild oxidation of both liquid and gaseous alkanes [18–21,23].

On the basis of selectivity, kinetic and theoretical studies, the oxidation of alkanes is believed to proceed via hydroxyl radicals (HO^\bullet) which act as hydrogen atom abstractors from the alkanes (RH) to form the alkyl radicals (R^\bullet) and are generated upon metal catalyzed decomposition of H_2O_2 [21–28]. A general reaction scheme to form HO^\bullet via a hydroperoxide-V complex is shown by reactions (1) and (2), and a possible catalytic mechanism is given by Scheme 2 [21,22].

Oxidation of H_2O_2 by an oxido- V^{V} complex (reaction (1) and steps i–iii of Scheme 2) forms the HOO^\bullet radical and a V^{IV} species to which a second molecule of H_2O_2 coordinates to form a vanadium(IV) hydrogen peroxido complex (step iv of Scheme 2). Reduction of the H_2O_2 ligand (reaction (2) and steps v–vi of Scheme 2) leads to O–O bond cleavage yielding HO^\bullet . A dioxidovanadium(V) complex follows a similar mechanism, where the second proton transfer (step v of Scheme 2) occurs from the coordinated hydrogen peroxido ligand to the other oxido ligand [21]. Some steps consist of proton transfer reactions from H_2O_2 to oxido or hydroxido ligands and possible transition states are shown in Scheme 3 [18–22]. The involvement of PCA [18–23], H_2O [22] or an oxido-vanadium group [22] in the transition state (Scheme 3(b), (c) or (d), respectively) forming a 6-membered metallacycle markedly lowers the energy of the transition state relative to that for the direct proton-transfer (Scheme 3(a)), thus effectively promoting the reaction.



2.1. Oxidation of liquid alkanes

2.1.1. PCA as promoter

The efficiency of PCA as a promoter is often much more pronounced than those of other acids (HCl, HNO_3 , H_2SO_4 , oxalic acid, trifluoroacetic acid, etc.) in the vanadium catalyzed oxidation of alkanes. The main role of PCA (co-catalyst/promoter) is beyond that of simple acid and has been assumed to accelerate the proton transfer from a coordinated hydrogen peroxide molecule to an oxido, hydroxido or peroxido ligand via the so-called “robot’s arm mechanism” (Scheme 4) [20b,20c,21a,21c,22a].

The use of PCA (for a typical case, [cyclohexane]₀ ca. 0.5 M and [PCA]₀ ca. 0.005 M) as a promoter has been extended to diverse vanadium catalysts and a comparison of various oxido-V-cat/PCA/aq. H_2O_2 / CH_3CN systems is shown in Table 1. Complexes 1–6 possess azine fragment ($\text{C}=\text{N}-\text{N}=\text{C}$) ligands, which are capable of stabilizing vanadium complexes in various coordination forms and oxidation states [13–15], and may enhance the catalytic activity of the vanadium centers. 1 and 2 are dinuclear

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