C. R. Chimie 20 (2017) 888–895

Contents lists available at ScienceDirect

Comptes Rendus Chimie

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Full paper/Mémoire

Efficient and selective oxidation of aldehydes with dioxygen catalysed by vanadium-containing heteropolyanions

Oxydation catalytique des aldéhydes par les hétéropolyacides à base de vanadium en présence de dioxygène

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ARTICLE INFO

Article history:
Received 14 March 2017
Accepted 22 May 2017
Available online 19 June 2017

Keywords:
Heteropolyacids
Aldehyde oxidation
Dioxygen
Carboxylic acids

ABSTRACT

The heteropolyacids “$H_{3+n}[PMo_{12-n}V_nO_{40}]\cdot aq$” (denoted as HPA-$n$; $n = 2, 3, 8$) catalyse the oxidation of aldehydes to carboxylic acids in the presence of dioxygen with very good yields. The effect on the catalytic activity of various parameters such as the precursors, solvent, temperature or catalyst/substrate ratio was examined. The process is particularly selective for linear and aromatic aldehydes. The oxidation of adipaldehyde with dioxygen in mild conditions, in the presence of HPA-2 as a catalyst, leads to the formation of adipic acid together with a significant amount of other byproducts. Thus, several modifications of the catalytic systems have been carried out to improve their selectivity. The effect of co-catalysts was investigated and, among the species tested, complex $Ni(acac)_2$ was found to be the most efficient yielding 60% of adipic acid.

Mots clés:
Hétéropolyacides
Oxydation des aldéhydes
Dioxygène
Acide carboxylique

RESUMÉ

Les hétéropolyacides, du type “$H_{3+n}[PMo_{12-n}V_nO_{40}]\cdot aq$” (noté HPA-$n$; $n = 2, 3, 8$), catalysent l'oxydation des aldéhydes en acides carboxyliques, en présence du dioxygène, avec de très bons rendements et des sélectivités élevées. Différents paramètres, comme les précurseurs, le solvant, la température ou le rapport catalyseur: substrat ont été examinés. Ce processus catalytique est particulièrement sélectif dans le cas des aldéhydes linéaires et aromatiques. L'adipaldéhyde est oxydé en acide adipique, mais aussi en d'autres sous-produits, en présence d'une quantité catalytique d'HPA-2 et de dioxygène, dans des conditions peu exigeantes. Plusieurs modifications des systèmes catalytiques ont été définies afin de limiter les oxydations subséquentes. Ainsi, l'effet des co-catalyseurs sur l'activité

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http://dx.doi.org/10.1016/j.crci.2017.05.007

catalytique a été étudié dans ce dernier cas. Parmi les co-catalyseurs testés, nous avons montré que le complexe Ni(acac)$_2$ était le plus efficace, donnant ainsi de l'acide adipique avec un rendement de 60%.

1. Introduction

Heteropolyacids presenting the Keggin structure, “$H_{3+n}[PMo_{12-n}V_nO_{40}]\cdot aq$” (denoted as HPA-*n*, with $n = 2, 3, 4$ or 5), have been attracting considerable interest over recent years for acid- or redox-catalysed reactions [1–9]. These HPA-*n* species are easy to prepare from cheap reagents as $MoO_3/V_2O_5/H_3PO_4/H_2O_2$ [10–12] and display high thermal stability. They are soluble in aqueous media and in organic solvents such as MeCN or AcOH among others.

Regarding their chemical behaviour, HPA-*n* present a noticeable Brönsted acidity and are efficient oxidants, exhibiting fast reversible multielectron redox transformations under rather mild conditions. These properties make HPA-*n* appropriate bifunctional catalysts in both homogeneous and heterogeneous phases. In particular, heteropolyacids are highly suitable catalysts for the oxidative cleavage of cycloalkanones, and protocols for the preparation of keto acids or diacids involving oxidation of α-substituted cycloalkanones (including cyclohexanone) in the presence of dioxygen along with HPA-*n* ($n = 2, 3, 4$ or 5) or copper(II) salts have been described [6,8,10–21]. Treatment of cyclohexanone with HPA-2/O_2/AcOH/H_2O in different solvents leads to the formation of adipic acid as a main product, together with minor amounts of glutaric and succinic acids [10,15]. In addition to oxidative ring opening, gas chromatography-mass spectrometry (GC-MS) coupling experiments indicate the formation of intermediates such as adipaldehyde acid (6-oxohexanoic acid) [15].

Although some oxovanadium complexes are suitable catalysts for such oxidations [13], heteropolyacids display better performances because of the redox properties of the VO_2^+ species and also to their Brönsted acidity, which is essential for the enolisation process. Here, we develop the transformation of aldehydes into the corresponding carboxylic acids under nearly identical experimental conditions with the idea of exerting some control on the aforementioned side reaction, and we also explore novel properties of HPA-*n* in the oxidation of aldehydes, as these species are important intermediates in synthetic chemistry and widespread pollutants in the human environment [22–24], reason why the development of fast and efficient protocols for their removal is a subject of increasing interest.

Various oxidants such as *t*-BuOOH, H_2O_2 [25–27] and molecular oxygen [28–31] have been used in the catalytic oxidation of aldehydes to the corresponding carboxylic acids. In particular, the oxidation with molecular oxygen is highly attractive because of its low cost/effectiveness ratio and environmentally friendly nature.

Oxidation of aldehydes to carboxylic acids catalysed by polyoxometalates has scarcely been investigated as a synthetically useful transformation. Hill et al. [32] have studied this process using formaldehyde as a substrate. Formaldehyde constitutes one of the main targets for aerobic oxidation under ambient conditions, as it is suspected of being a carcinogenic agent fairly ubiquitous in indoor air. Its easy, O_2-driven oxidation to the far less toxic formic acid is a process of remarkable interest. Also, some aldehydes can be used for the epoxidation of alkenes and for the Baeyer–Villiger oxidation of ketones to esters. This has been carried out for instance using $(NH_4)_5H_4PV_6W_6O_{40}$ as a catalyst, with isobutyraldehyde as acylperoxo/peracid precursor [33].

Simple linear aliphatic aldehydes can be selectively oxidised with molecular oxygen but, in contrast, 2- and 4-methoxybenzaldehydes constitute a family of substrates that is difficult to oxidise in homogeneous catalytic systems. As an example, a study performed by Shi and Ji [34] on the oxidation of these types of substrates leads to low yield (<7%) of the corresponding carboxylic acids and demonstrate that strong electron-donating groups induce the formation of the corresponding phenols instead through the migration of the aromatic group.

Other groups have also recently reported the oxidation of aromatic aldehydes to the corresponding carboxylic acids by aqueous H_2O_2 catalysed by VO(acac)$_2$ [35] or $H_5PV_2Mo_{10}O_{40}$ [36]. Nevertheless, from an industrial point of view the use of oxovanadium together with H_2O_2 is highly dangerous as the reaction is exothermic and, in some cases, it becomes explosive. Thus, new polyoxometalates of the ε-Keggin structure, with formula $[Mo_{12}O_{39}(\mu_2\text{-}OH)_{10}H_2\{X^{II}(H_2O)_3\}_4]$ (X = Ni, Co, Mn and Cu), have been synthesised and used as heterogeneous catalysts for the aerobic oxidation of aldehydes into the corresponding carboxylic acids. For linear aliphatic and benzylic aldehydes the reactions are selective but some substrates display low selectivity because of the formation of formate esters through Dakin-type reactions or also to allylic oxidations that can lead to decarboxylation and formation of ketones or allylic alcohols depending on the specific substrate [37].

In this article, we report the ability of heteropolyacids to catalyse the transformation of aldehydes into carboxylic acids in the presence of molecular oxygen, and we also investigate the role of novel low-cost triggers. The effects of solvent, temperature, reaction times and the presence of other precursors are considered.

2. Experimental section

2.1. Chemicals

The heteropolyacids HPA-n ($n = 2, 3, 8$) were prepared according to previously described oxoperoxo procedures [10–12] and were soluble in all solvents.