



Preparation, characterization and use of V₂O₅-TiO₂ mixed xerogels as catalysts for sustainable oxidation with hydrogen peroxide of 2,3,6-trimethylphenol

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ABSTRACT

V₂O₅-TiO₂ mixed xerogels were prepared with different loads of TiO₂ and V₂O₅ (5%, 10%, 15% V₂O₅ w/w) by the sol-gel method using titanium isopropoxide and vanadyl acetylacetonate as precursors. The solids obtained were characterized by XRD, FT-IR and SEM. Their textural properties were determined by adsorption-desorption isotherms of N₂ at 77 K. Also the acidity of the catalysts was measured by means of potentiometric titration with a solution of *n*-butylamine in acetonitrile.

The catalysts were tested in the liquid phase oxidation of 2,3,6-trimethylphenol (2,3,6-TMF) to 2,3,5-trimethyl-*p*-benzoquinone (2,3,5-TMBQ) at 20 °C, using ethanol as solvent and aqueous hydrogen peroxide as clean oxidizing agent. The conversion increases with time to reach at 3 h a plateau of 93% and 88% for the samples without V and with 5% of V respectively. An increase of the V concentration to 10% leads to a conversion value of only 22% at 4 h of reaction. However, the selectivity to 2,3,5-TMBQ increases with the V content in the catalyst. The stability and leaching of catalysts and the influence of the xerogel calcination temperature were also studied. By reusing the same catalyst sample with 5% of V, a difference of 5% in the selectivity values between use and reuse was observed. A decrease from 88% to 8% of 2,3,6-TMP conversion for 4 h of reaction, when the calcination temperature of xerogel increased from 200 °C to 400 °C, was observed. When *t*-butanol was added as radical scavenger, the oxidation was strongly suppressed. This makes it possible to propose a radical mechanism for 2,3,6-trimethylphenol oxidation.

Substrates with different substitutes in phenol were also tested in the oxidation reaction. The substrates with methyl groups are the most actives and in the cases of thymol and carvacrol with isopropyl groups, the conversion is lower.

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1. Introduction

It is now widely accepted that there is an urgent need for more environmentally acceptable processes in the chemical industry [1]. This trend is been known as Green Chemistry [2,3] or sustainable technology.

A primary cause of waste production in the fine chemicals industry is the widespread use of stoichiometric reagents. Classical 'stoichiometric' technologies that generate copious quantities of inorganic salts are rampant in fine chemicals manufacture, primarily the domain of the synthetic organic chemist. Examples that readily come to mind are stoichiometric oxidations with permanganate, manganese dioxide, and chromium (VI) reagents, stoichiometric reductions with metal hydrides (NaBH₄, LiAlH₄, and

variants thereof). The solution to this waste problem is evident: the widespread substitution of antiquated stoichiometric technologies with cleaner catalytic alternatives [4].

In the drive towards cleaner methodologies, the entire arsenal of catalytic methodologies—homogeneous, heterogeneous and enzymatic catalysis will be brought to bear on organic synthesis. All three approaches have their advantages and limitations. Homogeneous catalysis by organometallic complexes [5] is finding wide application in both bulk and fine chemicals and is the method of choice in e.g. carbonylations and hydroformylations. Similarly, biocatalysis [6], which has the advantage of mild reaction conditions and high chemo-, regio-, and enantioselectivity, will be increasingly used in fine chemicals manufacture. Solid, heterogeneous catalysts have the advantages of ease of recovery and recycling and are readily amenable to continuous processing.

Recently, the sol-gel technique has offered new approaches for the synthesis of porous materials, simple and mixed oxides [7,8].

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