



Dimeric assemblies of lanthanide-stabilised dilacunary Keggin tungstogermanates: A new class of catalysts for the selective oxidation of aniline



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ABSTRACT

In this work we demonstrate the efficiency of some dimeric $[\text{Ln}_4(\text{H}_2\text{O})_6(\beta\text{-GeW}_{10}\text{O}_{38})_2]^{12-}$ anions composed of lanthanide-stabilised dilacunary Keggin tungstogermanate fragments ($\beta\beta\text{-Ln}_4$, Ln = Dy, Ho, Er, Tm) as heterogeneous catalysts for the organic phase oxidation of aniline with hydrogen peroxide. The results obtained evidence total conversion of aniline at room temperature, as well as full selectivity towards nitrosobenzene, and the catalysts are able to retain both their activity and selectivity after several runs. Peroxopolyoxometalate intermediaries have been identified as the catalytically active species during the aniline-to-nitrosobenzene oxidation process.

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1. Introduction

Nowadays, there is a global effort to replace conventional catalysts and current chemical processing by more environmentally benign alternatives. In this context, oxidation reactions are of fundamental importance in the chemical industry. During the last decade, the use of hydrogen peroxide for the oxidation of hazardous organic substrates such as amines to their corresponding oxygen-containing derivatives has become a remarkable goal at the industrial level [1], and hence it has attracted the interest of several research groups worldwide [2]. Many organic compounds cannot be oxidised by H_2O_2 itself, and therefore, different Lewis acid catalysts such as AlCl_3 , ZnCl_2 , BF_3 , TiCl_4 , SnCl_4 , and $\text{BF}_3\cdot\text{OEt}_2$ have been traditionally used for that purpose because of their unique selectivity and the mild reaction conditions they facilitate [3,4]. However, this type of Lewis acids shows some major drawbacks: (i) they are moisture sensitive; (ii) they are often required in more than stoichiometric amounts; and (iii) they cannot be recovered and reused. As a result, large amounts of wastes are produced and this may result in severe environmental problems. Thus,

the search for a new generation of heterogeneous catalysts suitable for overcoming these drawbacks is highly desirable.

Among the most remarkable hazardous organic substrates, aniline released during the manufacturing process of several goods (e.g. dyes, polymers, pesticides, pharmaceuticals) is classified as one of the most persistent pollutants present in wastewater by the US Environmental Protection Agency [5]. Finding a heterogeneous catalyst for the oxidation of this substrate with selectivity towards a single product out of the multiple oxidised derivatives possible (i.e. nitrosobenzene, nitrobenzene, azobenzene and azoxybenzene) constitutes an important task. In this context, Corma et al. have shown that gold nanoparticles supported on titanium dioxide (Au/TiO_2) selectively catalyse the aerobic oxidation of aniline to azobenzene [6]. Moreover, Ghosh et al. reported the selective oxidation of aniline to azoxybenzene (91%) using a silver supported tungsten oxide (Ag/WO_3) nanostructured catalyst [7]. In both cases, expensive noble metals were required. To our knowledge, no reports on heterogeneous catalysts selective towards the nitrosobenzene derivative can be found in the literature at present. These nitroso compounds are extensively used as chemical feedstock for a wide range of materials such as polymers, pharmaceuticals, dyes and perfumes. However, achieving a highly selective catalytic route for their preparation from the oxidation of amines results certainly in challenging due to the existence of competitive

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oxidation reactions and/or to the over-oxidation of the nitroso derivative formed [8].

Polyoxometalates (POMs) are anionic early transition metal-oxo clusters of nanometric size that show several relevant properties to fields such as catalysis, material science, biomedicine and nanotechnology. From the catalytic point of view, POMs can act as both strong Brønsted acids (stronger than mineral acids) and oxidation catalysts showing fast and reversible redox reactions without any structural change [9–12]. In addition, POMs also display good thermal stability and low cost and they are easily recoverable from the reaction media in high amounts. Compared to mineral acids, these well-known clusters offer remarkable environmental and economic advantages derived from their more efficient and cleaner catalytic processes, while they do not decompose or deactivate in the presence of water in contrast to what is commonly observed for the Lewis acidic chloride metals. Among the vast POM family, lanthanide-containing species constitute one of the largest and most active groups at present because combination of POM building blocks with rare-earth metals has been shown to be a powerful tool for designing new architectures and introducing additional properties to the POM system [13–15]. With regard to catalysis, the incorporation of rare-earth metals into the POM framework allows the resulting cluster to act as a Lewis acid catalyst [16–19]. Moreover, combination of Lewis acid lanthanide sites and nucleophilic POM surfaces with Lewis base character can result in bifunctional catalysts suitable for cyanosilylation or oxidation reactions owing to their ability to simultaneously activate complementary substrates [20,21].

Considering the above, we decided to systematically explore the use of lanthanide(III)-containing POMs (Ln-POMs) as heterogeneous catalysts for the selective oxidation of organic substrates with H₂O₂ in place of the traditional mineral or Lewis acids to avoid the acidic waste drain produced by the latter. More specifically, we have first focused our studies on those Ln-POMs showing dilacunary Keggin-type frameworks because, unlike plenary Keggin heteropolyacids or monolacunary Ln-POMs, they have been scarcely applied in catalytic reactions, and hence their potential applications in this area are still to be developed. Hereby, we report our results on the heterogeneous catalytic activity towards the organic phase oxidation of aniline with H₂O₂ of the sodium salts of four isomorphous dimeric anions composed of lanthanide-stabilised dilacunary Keggin subunits with β -type skeletons, namely Na₁₂[Ln₄(H₂O)₆(β -GeW₁₀O₃₈)₂] \cdot ~44H₂O (**Na- $\beta\beta$ -Ln₄**, Ln = Dy, Ho, Er, Tm) [22]. The reaction process is represented in Scheme 1.

2. Experimental

2.1. Materials

All starting materials were purchased from commercial sources and used without further purification. The Na₁₂[Ln₄(H₂O)₆(β -GeW₁₀O₃₈)₂] \cdot ~44H₂O (**Na- $\beta\beta$ -Ln₄**, Ln = Dy, Ho, Er, Tm) POM sodium salts used in this work were prepared according to the literature [22]. The specific synthetic procedure was as follows: to a solution of the corresponding lanthanide chloride salt (0.98 mmol; DyCl₃·6H₂O, 0.369 g; HoCl₃·6H₂O, 0.372 g; ErCl₃·6H₂O, 0.374 g; TmCl₃·6H₂O, 0.376 g) in aqueous 0.5 M NaOAc buffer (40 mL) solid GeO₂ (0.093 g, 0.89 mmol) and Na₂WO₄·2H₂O (2.640 g, 8.00 mmol) were successively added. The reaction mixture was stirred at room temperature for 1 h. Compounds **Na- $\beta\beta$ -Ln₄** were isolated as highly gathered needles from slow evaporation of the resulting in limpid solution at room temperature and identified by powder X-ray diffraction and infrared spectroscopy (Fig. A.1 in the Supplementary Information).

2.2. Catalytic tests: aniline oxidation

The oxidation of aniline was conducted in a 10 mL glass flask. The following chemicals were successively introduced: 35 μ L of aniline, 85 μ L of hydrogen peroxide (30%), 4.9 mL of dichloroethane and 2 μ mol of the corresponding catalyst previously dried at 100 °C (15 mg of **Na- $\beta\beta$ -Ln₄**; 4 mg of the heteropolyacids H₃PMo₁₂O₄₀ or H₃PW₁₂O₄₀). The optimum amount of catalyst was determined as shown in Fig. A.2 in the Supplementary Information. Initial experiments were performed using fresh catalysts; for subsequent tests, the catalysts were previously treated with a hydrogen peroxide solution (30%) for 1.5 h. After adding a small Teflon magnet, the mixture was stirred at room temperature for 9 h. Both shorter (0.5 h) and longer reaction times (up to 24 h) were also tested for comparative purposes. Regarding the solvent, preliminary tests demonstrated that dichloroethane leads to yields higher than those obtained with other conventional solvents such as chloroform, dichloromethane, toluene and dimethylsulphoxide. The solvent seems to play an important role both stabilising the dimeric POM framework against dissociation or decomposition and contributing with protons to the development of the reaction. Polar solvents should also provide protons to the reaction medium, but unfortunately, they work in favour of the catalyst solubilisation, and hence we limited our studies to a non-polar solvent in this work. To determine the performance of the heterogeneous catalysts in consecutive runs, they were recovered from the mixture by filtration upon completion of the reaction time and dried at 100 °C for 24 h before being reused in a new reaction process. The amount of catalyst solubilised during the reaction was estimated from the weight losses between consecutive runs. Analogous experiments were also performed using catalysts previously calcined at 200 °C in air.

2.3. Characterisation

For the preliminary identification of the freshly prepared **Na- $\beta\beta$ -Ln₄** compounds, powder X-ray diffraction (PXRD) patterns were collected from 2 θ = 4 to 60° (0.02606° step size, 30 s per step) using a Philips X'PERT PRO automatic diffractometer operating at 40 kV–40 mA in θ - θ configuration with monochromated Cu K α radiation (λ = 1.5418 Å) and a PIXcel solid state detector (3.347° active length in 2 θ). Infrared spectra between 400 and 4000 cm⁻¹ were obtained on a SHIMADZU FTIR-8400S spectrometer operating in transmittance mode using KBr pellets (20 scans per spectrum, resolution of 4 cm⁻¹).

The results of the elemental analyses for the title **Na- $\beta\beta$ -Ln₄** catalysts are listed in Table B.1 in the Supplementary Information. They show metal contents very close to the expected theoretical values in all cases. The experimental Ge/Ln/Na ratios are in good agreement with the exclusive presence of lanthanide-containing dilacunary Keggin subunits and indicate that no significant decomposition takes place during the oxidation process.

Thermogravimetric (TG) analyses were also performed in order to determine the degree of hydration and thermal stability. They were carried out from room temperature to 700 °C at a rate of 5 °C min⁻¹ using a TA Instruments 2960 SDT thermobalance under a 100 cm³ min⁻¹ flow of air (Fig. A.3 in the Supplementary Information). The experimental and calculated mass losses (Δm) for the dehydration process, together with the decomposition temperatures (T_d) are given in Table B.2 in the Supplementary Information.

Potential modifications of the catalysts during their thermal treatment were analysed in situ by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled to mass spectrometry. A Mattson Infinity MI60 DRIFT spectrophotometer equipped with a chamber of controlled environment and a SpectraTech diffuse reflectance accessory was used. Prior to all

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