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

Guido Trautwein<sup>a</sup>, Bouchra El Bakkali<sup>a</sup>, Juan Alcañiz-Monge<sup>a,\*</sup>, Beñat Artetxe<sup>b</sup>, Santiago Reinoso<sup>b</sup>, Juan M. Gutiérrez-Zorrilla<sup>b,c</sup>

<sup>a</sup> Departamento de Química Inorgánica, Universidad de Alicante, E-03080 Alicante, Spain

<sup>b</sup> Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, P.O. Box 644, E-48080 Bilbao, Spain

<sup>c</sup> BCMaterials, Parque Científico y Tecnológico de Bizkaia, Edificio 500, 48160 Derio, Spain

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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<sub>2</sub>O<sub>2</sub> itself, and therefore, different Lewis acid catalysts such as AlCl<sub>3</sub>, ZnCl<sub>2</sub>, BF<sub>3</sub>, TiCl<sub>4</sub>, SnCl<sub>4</sub>, and BF<sub>3</sub>·OEt<sub>2</sub> 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,

#### ABSTRACT

In this work we demonstrate the efficiency of some dimeric  $[Ln_4(H_2O)_6(\beta-GeW_{10}O_{38})_2]^{12-}$  anions composed of lanthanide-stabilised dilacunary Keggin tungstogermanate fragments  $(\beta\beta-Ln_4, Ln = Dy,$ 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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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<sub>2</sub>) 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<sub>3</sub>) 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





JOURNAL OF CATALYSIS

<sup>\*</sup> Corresponding author. Fax: +34 965909419. *E-mail address: jalcaniz@ua.es* (J. Alcañiz-Monge).

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 catalvst [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 oximation 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 H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> of the sodium salts of four isomorphic dimeric anions composed of lanthanidestabilised dilacunary Keggin subunits with  $\beta$ -type skeletons,  $Na_{12}[Ln_4(H_2O)_6(\beta-GeW_{10}O_{38})_2] \sim 44H_2O$ namely (Na-BB-Ln<sub>4</sub>) 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 Na<sub>12</sub>[Ln<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>( $\beta$ -GeW<sub>10</sub>O<sub>38</sub>)<sub>2</sub>]-~44H<sub>2</sub>O (**Na**- $\beta\beta$ -**Ln**<sub>4</sub>, 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; DyCl<sub>3</sub>·6H<sub>2</sub>O, 0.369 g; HoCl<sub>3</sub>·6H<sub>2</sub>O, 0.372 g; ErCl<sub>3</sub>·6H<sub>2</sub>O, 0.374 g; TmCl<sub>3</sub>·6H<sub>2</sub>O, 0.376 g) in aqueous 0.5 M NaOAc buffer (40 mL) solid GeO<sub>2</sub> (0.093 g, 0.89 mmol) and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (2.640 g, 8.00 mmol) were successively added. The reaction mixture was stirred at room temperature for 1 h. Compounds **Na**- $\beta\beta$ -**Ln**<sub>4</sub> 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 µL of aniline, 85 µL of hydrogen peroxide (30%), 4.9 mL of dichloroethane and 2 µmol of the corresponding catalyst previously dried at 100 °C (15 mg of Na- $\beta\beta$ -Ln<sub>4</sub>; 4 mg of the heteropolyacids  $H_3PMo_{12}O_{40}$  or  $H_3PW_{12}O_{40}$ ). 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 vields 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**- $\beta\beta$ -**Ln**<sub>4</sub> compounds, powder X-ray diffraction (PXRD) patterns were collected from  $2\theta$  = 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  $\theta$ - $\theta$  configuration with monochromated Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) and a PIXcel solid state detector (3.347° active length in 2 $\theta$ ). Infrared spectra between 400 and 4000 cm<sup>-1</sup> were obtained on a SHIMADZU FTIR-8400S spectrometer operating in transmittance mode using KBr pellets (20 scans per spectrum, resolution of 4 cm<sup>-1</sup>).

The results of the elemental analyses for the title **Na**- $\beta\beta$ -**Ln**<sub>4</sub> 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<sup>-1</sup> using a TA Instruments 2960 SDT thermobalance under a 100 cm<sup>3</sup> min<sup>-1</sup> flow of air (Fig. A.3 in the Supplementary Information). The experimental and calculated mass losses ( $\Delta m$ ) 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



**Scheme 1.** Aniline-to-nitrosobenzene selective oxidation process and molecular structure of the  $\beta\beta$ -**Ln**<sub>4</sub> catalysts, Ln = Dy, Ho, Er, Tm (colour code: WO<sub>6</sub>, white octahedra or dark grey for the 60°-rotated {W<sub>3</sub>O<sub>13</sub>} trimers; GeO<sub>4</sub>, green tetrahedra; Ln, violet spheres; O, red spheres; N, green spheres; C, dark grey spheres; H, light grey spheres). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

DRIFT experiments, the **Na**- $\beta\beta$ -**Ln**<sub>4</sub> samples were dried at 40 °C under a 30 cm<sup>3</sup> min<sup>-1</sup> flow of He for 1 h. Then, they were heated at a rate of 5 °C min<sup>-1</sup> up to 300 °C in He atmosphere and DRIFT spectra were collected each 4 min at room temperature. The evolved gas during the heating treatment was analysed with a ThermoStar TM GSD 301 T mass spectrometer (Fig. A.4 in the Supplementary Information).

To determine whether the structures or chemical properties of the catalysts were modified after the reaction, fresh and used catalysts were analysed by DRIFT and UV–Vis spectroscopy. It is worth to mention that other characterisation techniques such as elemental analysis, powder X-ray diffraction (XRD) and TG were also used, but did not provide any significant differences among fresh and used samples. The UV–Vis spectra were conducted in the 190–800 nm range using a Jasco V-670 UV–Vis/NIR spectrophotometer.

The identification of the reaction products was performed by gas chromatography (GC) on an Agilent 6890 equipment provided with an HP-1 column of size 30 m  $\times$  250  $\mu$ m  $\times$  0.25  $\mu$ m and coupled to an Agilent 5975 mass spectrometer. The reaction progress was followed by extracting aliquots of the reaction mixture at regular time periods. All the reaction products were quantitatively estimated from linear calibration methods using standard solutions of the pure compounds.

#### 3. Results and discussion

#### 3.1. Brief description of the $\beta\beta$ -Ln<sub>4</sub> anions

The synthesis, TG and IR spectroscopic analyses, crystal structures and stability in aqueous solution of compounds Na<sub>12</sub>[Ln<sub>4</sub>(H<sub>2</sub>-O)<sub>6</sub>( $\beta$ -GeW<sub>10</sub>O<sub>38</sub>)<sub>2</sub>]·~44H<sub>2</sub>O (**Na**- $\beta\beta$ -**Ln**<sub>4</sub>, Ln = Dy, Ho, Er, Tm) have been previously reported elsewhere by some of us [22]. The molecular structure of the  $\beta\beta$ -**Ln**<sub>4</sub> POMs is represented within Scheme 1. The title POMs consist of two [Ln<sub>2</sub>( $\beta$ -GeW<sub>10</sub>O<sub>38</sub>)]<sup>6-</sup> subunits associated in a face-to-face manner via two pairs of Ln–O(WO<sub>5</sub>)-Ln

bridges to lead to a chiral dimeric assembly with ideal  $C_2$  symmetry where the bridges arrange in either left- or right-handed orientations. Each subunit contains a dilacunary {GeW<sub>10</sub>O<sub>38</sub>} skeleton derived from the  $\beta$ -Keggin cluster, which is formed by a 60°-rotated {M<sub>3</sub>O<sub>13</sub>} cap, a central hexameric belt and a bottom {M<sub>3</sub>O<sub>15</sub>} triad. For the  $\beta\beta$ -Ln<sub>4</sub> anions, the vacant sites are located in non-adjacent positions of the belt and the bottom triad. The lanthanide atoms show in-pocket coordination modes and are inserted into the vacant sites of the  $\beta$ -Keggin framework with three external coordination sites occupied by a bridging O atom from a neighbouring subunit and two aqua ligands. All Na- $\beta\beta$ -Ln<sub>4</sub> solid samples are mixtures of two triclinic *P*-1 crystalline phases that consist in racemic crystals containing equal amounts of both right- and left-handed  $\beta\beta$ -Ln<sub>4</sub> forms regardless of the phase.

#### 3.2. Catalytic activity tests

One basic requirement to be fulfilled by Ln-POM species to act as heterogeneous catalysts is the insolubility in the reaction media and this fact led us to carry out our reactions in an organic medium such as dichloroethane. However, a minimum amount of catalyst might be solubilised in the course of the reaction because of the water content of the hydrogen peroxide solution. The cumulative percentage of catalyst mass transferred to the solution is highly dependent on its nature. For example, Keggin-type heteropolyacids (HPAs) such as  $H_3PMo_{12}O_{40}$  or  $H_3PW_{12}O_{40}$  (from now on referred as HPMo and HPW, respectively) were completely soluble in our reaction medium as expected, whereas the **Na**- $\beta\beta$ -**Ln**<sub>4</sub> samples remained virtually insoluble. This fact is of great importance because it allows the catalyst to be recovered and reused for several consecutive reaction runs.

The miscibility of hydrogen peroxide represents also a key point in this type of reactions. This oxidant is not miscible with most of the organic solvents, and therefore, the use of phase transfer compounds (PTCs) is frequently required [23]. Despite the fact that PTCs increase the yields of oxidation reactions involving organic substrates, they are relatively expensive and harmful for industrial applications because huge amounts are required. The use of an effective catalyst under a biphasic medium is thus needed. It is worth mentioning in this context the peroxotungstate Venturello catalysts for which a high efficiency towards the PTC-assisted epoxidation of alkenes with  $H_2O_2$  in a liquid biphasic system has been reported [24]. Several other POMs have also been used as effective catalysts for homogeneous oxidation reactions with hydrogen peroxide [25–27]. In contrast, no PTCs have been used in this study, and hence, the first point to analyse is whether the selected **Na**- $\beta\beta$ -**Ln**<sub>4</sub> POMs show catalytic activity for heterogeneous oxidation in our experimental conditions.

Fig. 1 displays the evolution of the aniline conversion over the time for the **Na**- $\beta\beta$ -**Dy**<sub>4</sub> catalyst as an illustrative example for the whole series of Ln-POMs tested. It should be first indicated that the reaction does not take place in the absence of any Ln-POM under our experimental conditions and that the **Na**-*BB*-**Ln**<sub>4</sub> samples selected showed to be fully inefficient to oxidise aniline by themselves when no H<sub>2</sub>O<sub>2</sub> was added to the reaction mixture even if the amount of catalyst employed was one order of magnitude higher than that used in the presence of H<sub>2</sub>O<sub>2</sub>. These two facts evidence that compounds **Na**- $\beta\beta$ -**Ln**<sub>4</sub> have high catalytic activity towards the oxidation of aniline. The evolution of the aniline conversion shows a sigmoid curve tendency, which is typical of catalysts that require an induction period. This suggests that the interaction between the catalyst and  $H_2O_2$  is essential for the reaction to take place. Previous catalytic studies on the oxidation of different organic compounds by Ti, V, Zr, Mo or W complexes have demonstrated that these reactions are based on intermediary peroxometallic species originated from the interaction between the oxidant  $H_2O_2$  and the complex [28,29]. Moreover, it has been generally observed that high nuclearity species, as well as POMs, need an induction period for being able to catalyse the oxidation with H<sub>2</sub>O<sub>2</sub>. Therefore, it seems reasonable that the induction period observed in our reaction is related to the development of intermediary species on the surface of the solid catalyst. To validate this hypothesis an analogous experiment with the Na- $\beta\beta$ -Dv<sub>4</sub> catalyst but pre-treated with  $H_2O_2$  for 1.5 h was performed (Fig. 1). The induction period disappeared by following this approach and this behaviour supports the hypothesis above involving the existence of peroxometallic intermediaries on the Na- $\beta\beta$ -Ln<sub>4</sub> catalyst surface that originate upon reaction with H<sub>2</sub>O<sub>2</sub> and act as the real active centres in the aniline oxidation reaction. To confirm this assump-



**Fig. 1.** Evolution of the aniline conversion versus time using  $Na-\beta\beta$ -Dy<sub>4</sub> as catalyst (fresh and pre-treated with H<sub>2</sub>O<sub>2</sub>).

tion, the solution was monitored by means of UV–Vis absorption spectroscopy at different reaction times (Fig. 2).

The UV-Vis spectrum of the fresh catalyst shows one absorption band at ca. 215 nm and a shoulder around 265 nm. These signals are related to a charge transfer band from the oxo ligands to the tungsten(VI) centres and they correspond to the W-O<sub>d</sub> and W–O<sub>b</sub>/O<sub>c</sub> bonds, respectively [30,31]. After 3 h of reaction, an additional broad band emerges in the 250-320 nm range. Similar observations have also been reported by other authors [30,32]. The correct identification of these bands is difficult based on the different interpretations given in the literature [33-37]. While some authors relate the electronic transitions in the 250-300 nm range to the existence of surface tetrahedral M–O complexes, others assign bands found at 300-320 nm to M<sub>7</sub>O<sub>24</sub> type species and those at 320-340 nm to isolated MO<sub>3</sub> particles. Our observations could then suggest a possible modification of the dilacunary Keggin structure in the fresh catalyst by the  $H_2O_2$  action, thus becoming a mixture of peroxoanions and/or other Keggin-type derivatives (or even products of degradation) that coexist both in solution and on the surface of the solid. However, the fact that the inspection of the fresh and reused **Na**- $\beta\beta$ -**Dy**<sub>4</sub> samples by elemental analyses and powder XRD afforded similar results unequivocally reveals that peroxoanion species reside only on the surface of the solid catalyst, and hence that the reused and fresh **Na**- $\beta\beta$ -**Dy**<sub>4</sub> samples are virtually identical from the chemical and structural point of view.

# 3.3. Influence of the type of lanthanide atom on the extent of conversion

Four isomorphic  $\beta\beta$ -**Ln**<sub>4</sub> dimeric POMs composed of lanthanidestabilised dilacunary Keggin subunits with  $\beta$ -type skeletons were selected to evaluate the influence of the type of rare-earth metal on the reaction in heterogeneous phase. More specifically, anions with the following lanthanides were employed: Dy, Ho, Er, and Tm. To compare our results with those previously reported in the literature, the same reaction was also performed in homogeneous phase with the two HPAs that have been most widely used by other authors, i.e. HPMo and HPW.

As shown in Fig. 3, the **Na**- $\beta\beta$ -**Ln**<sub>4</sub> salts show conversion yields comparable to or even higher than those of the commercial HPAs. The selectivity of our Ln-POMs towards nitrosobenzene is 100%, whereas HPMo and HPW show lower selectivity towards this compound (80%) and even lead to other overoxidised by-products (see Table B.3 in the Supplementary Information). This can be well explained after taking into account the strong oxidising power of the HPMo and HPW acids. In relation to these observations, it is worth mentioning that heterogeneous catalysts other than POMs



**Fig. 2.** UV–Vis spectrum of the fresh **Na**- $\beta\beta$ -**Dy**<sub>4</sub> catalyst compared to that obtained after 3 h of reaction.



**Fig. 3.** Aniline conversion using different  $Na-\beta\beta-Ln_4$  catalysts and the two commercial heteropolyacids HPMo and HPW.

have also been used in the oxidation of aniline, resulting in product distributions different from those afforded by our **Na**- $\beta\beta$ -**Ln**<sub>4</sub> compounds and the selected HPAs [6,7]. For example, azoxybenzene is obtained instead of nitrosobenzene with a catalyst such as TS-1 (titanium silicalite) [38] and this fact is most likely due to the higher acidity of the latter compared to the **Na**- $\beta\beta$ -**Ln**<sub>4</sub> series (Ti<sup>4+</sup> vs. Ln<sup>3+</sup>). The **Na**- $\beta\beta$ -**Ln**<sub>4</sub> catalysts require shorter reaction times than those associated with the selected HPAs under the same reaction conditions in spite of the fact that it is made in heterogeneous phase. Additional experiments with these **Na**- $\beta\beta$ -**Ln**<sub>4</sub> catalysts demonstrate that increasing the temperature decreases the reaction time slightly with no effect over the selectivity of the aniline-to-nitrosobenzene oxidation.

Although all  $\beta\beta$ -**Ln**<sub>4</sub> POMs reached full conversion after 9 h of experiment, the kinetics showed to be significantly different for each specific anion. Initially, all POMs tested show similar reaction rates up to the first two hours with the exception of the  $\beta\beta$ -**Tm**<sub>4</sub> derivative, which systematically displays the lowest reaction rates within the **Na**- $\beta\beta$ -**Ln**<sub>4</sub> series as indicated by its lowest conversions reached at any reaction time. The reaction rates decrease at experimental times above two hours and this decrease becomes more pronounced as the atomic number of the lanthanide centre



Fig. 4. DRIFT spectra of the Na- $\beta\beta$ -Ln<sub>4</sub> catalysts (Ln = Dy, Ho, Er, Tm).

increases. To analyse this feature, the **Na**- $\beta\beta$ -**Ln**<sub>4</sub> salts were characterised by DRIFT measurements (Fig. 4). The DRIFT spectra display four characteristic peaks that originate from antisymmetric stretching vibrations in the dilacunary Keggin-type framework. These are  $v_{as}(W-O_t)$  at 943–947 cm<sup>-1</sup>,  $v_{as}(W-O_b-W)$  at 875–910 cm<sup>-1</sup>,  $v_{as}(W-O_c-W)$  at 776–783 cm<sup>-1</sup> and  $v_{as}(Ge-O_a)$  at 814–876 cm<sup>-1</sup> [39–41].

The bands observed at wave numbers above 1100 cm<sup>-1</sup> do not correspond to any vibrational mode calculated theoretically for a Keggin-type POM framework [41], and hence their assignment is not as straightforward. Taking into account that our solid samples are highly hydrated (see Table B.2 in the Supplementary Information), these bands most likely associate with vibrational modes of the different types of water molecules present in the structures of the Na- $\beta\beta$ -Ln<sub>4</sub> salts. Thus, the broad band in the 3600-2600 cm<sup>-1</sup> range is characteristic of the stretching vibration in the O-H bonds and should be attributed to disordered, interstitial water molecules of crystallisation in the four  $Na-\beta\beta-Ln_4$  samples. The peak at c.a. 1640  $\text{cm}^{-1}$  can be assigned to the H–O–H bending on the basis of the in-plane bending observed for the  $H_5O_2^+$  ion [42]. This peak is virtually identical in all four DRIFT spectra, but in contrast, that located near 1550 cm<sup>-1</sup> and those signals observed around 1455 cm<sup>-1</sup> differ significantly in intensity within the Na- $\beta\beta$ -Ln<sub>4</sub> series, in such a way that they become weaker when going from  $\beta\beta$ -**Dy**<sub>4</sub> to  $\beta\beta$ -**Tm**<sub>4</sub>. These intensity-variable signals observed in the spectral region associated with the H-O-H bending might originate from the presence of water clusters in the vicinity of the lanthanide centres in our structures. The existence of welldefined water clusters with different sizes has been recently assessed for porous MOF-POM type composites [43], as well as in the structure of a hybrid compound based on Wells-Dawson POMs and dicopper metal-organic moieties [44]. Taking into account the report by Sato et al. on the fact that Ln<sub>2</sub>O<sub>3</sub> oxides become more basic as Ln varies from Dy to Tm [45], a similar trend could be expected for our **Na**- $\beta\beta$ -**Ln**<sub>4</sub> compounds in which the lanthanides are confined in the pockets of an oxotungstate framework. Thus, the differences in the relative intensities of the DRIFT signals could be related to the acidity of the lanthanide atom. and more specifically, with the more acidic Dy atom favouring the clustering of water molecules in its close vicinity over the more basic Tm through stronger hydrogen bonding.

#### 3.4. Recyclability of the **Na-** $\beta\beta$ -**Ln<sub>4</sub>** catalysts

To reuse a given catalyst in several successive reaction runs is of great interest from an economical and operational point of view [46]. To explore the recyclability of our **Na**- $\beta\beta$ -**Ln**<sub>4</sub> catalysts, we selected the Ho derivative as illustrative example and performed several successive experiments using the same **Na**- $\beta\beta$ -**Ho**<sub>4</sub> sample, which was added to the corresponding fresh solution without any intermediate regeneration step. The conversion results obtained over nine consecutive runs are shown in Fig. 5.

Our results show that the selectivity of the catalyst towards nitrosobenzene remains constant (100%) even after nine reaction runs, but it is more interesting the fact that the time required to obtain 100% conversion decreases in the successive reactions (Fig. 5), that is, the catalytic activity of the **Na**- $\beta\beta$ -**Ho**<sub>4</sub> sample increases over the runs. This aspect is evidenced by a remarkable increase on the slope of the conversion curves, which is closely related to the reaction rate. Thus, the slope increases after successive runs up to the fifth and then remains nearly constant even after nine runs. Taking into account that the catalytic centres should be peroxometallic intermediates at the surface of the catalyst as commented in Section 3.2, the observed increase in the reaction rate appears to be related to a higher amount of peroxo groups developed on the surface of the solid sample after each



**Fig. 5.** Aniline conversion at room temperature using  $2 \times 10^{-3}$  mmol of the **Na**- $\beta\beta$ -**Ho**<sub>4</sub> catalyst throughout nine consecutive runs.

reaction, in such a way that the maximum number of surface peroxo groups possible is reached during the fifth run. To analyse this point, we also inspected the catalyst by DRIFT spectroscopy after the fourth run (Fig. 6).

The DRIFT spectrum of the reused catalyst after four consecutive runs exhibits a weak band near 880 cm<sup>-1</sup> that can be attributed to O–O peroxo bonds [47]. This value is very similar to that corresponding to the stretching O–O vibration in hydrogen peroxide (877 cm<sup>-1</sup>) [48] and strongly suggests that the dimeric  $\beta\beta$ -**Ln**<sub>4</sub> anions are converted into peroxo-POM derivatives after each run. Similar behaviour was previously observed by other authors [49] and confirmed using other techniques such as Raman spectroscopy [25,39]. This fact could be well related to the development of peroxo groups on the Keggin framework because the increase in the number of highly electronegative O atoms around the addenda metal centres reduces the electronic density of the W atoms, which in turn enhances the electron withdrawing from the Ln centres and increases their Lewis acidity in this way.

#### 3.5. Effect of the thermal treatment on the catalytic activity

Addition of aqueous hydrogen peroxide to the reaction mixture can lead to partial dissolution of Ln-POM catalysts in the organic



**Fig. 6.** Comparison between the DRIFT spectra of a fresh  $Na-\beta\beta$ -Ho<sub>4</sub> catalyst and that reused after four runs.

medium, but this might be overcome with a thermal pretreatment, which has been shown to be able to decrease the solubility of POM salts in polar media such as  $H_2O_2$  (aq) according to a previous work reported by some of us [50]. To explore whether thermal treatments improve the heterogeneous catalytic activity of compounds **Na**- $\beta\beta$ -**Ln**<sub>4</sub> by hindering any partial solubilisation, the catalysts were calcined at 200 °C in air and subsequently applied in a reaction process with the same experimental conditions than those used for the fresh catalysts. The parameters for the thermal treatment were selected on the basis of previous thermogravimetric results to avoid any structural decomposition (Fig. A.3 and Table B.2 in the Supplementary Information). The results obtained from these studies on the solubility and catalytic activities of our Ln-POMs compared to those of commercial HPAs are shown in Table 1 and Fig. 7, respectively.

As expected, the selected HPAs are completely soluble in the organic reaction medium (dichloroethane), whereas fresh Na- $\beta\beta$ -Ln<sub>4</sub> compounds (Ln = Dy, Tm) showed subtle solubility in the reaction conditions that tended to increase throughout the runs. Our **Na**- $\beta\beta$ -**Ln**<sub>4</sub> samples are alkaline Ln-POM salts, i.e. sodium salts, and hence they do not show solubility in organic solvents such as dichloroethane in the strict sense. The observed transfer of a minimum amount of mass to the reaction medium only takes place as a result of the reaction with H<sub>2</sub>O<sub>2</sub>. As mentioned in Section 3.2, the interaction with  $H_2O_2$  results in the development of peroxometallic intermediates at the POM surface as the catalytically active sites and these species might undergo partial decomposition to lead to molecular, soluble complexes with time. It is also worth mentioning that compounds **Na-** $\beta\beta$ **-Ln<sub>4</sub>** become more insoluble as the atomic number of the lanthanide atom increases. The thermal treatment applied to the **Na-** $\beta\beta$ -**Ln**<sub>4</sub> salts increases their insolubility, and this fact could be related to a tighter packing and stronger interaction of  $\beta\beta$ -Ln<sub>4</sub> anions and Na<sup>+</sup> cations in the solid state upon release of both interstitial and Na-coordinated water molecules.

In regard to the catalytic performance (Fig. 7), thermally treated samples show higher activity than the corresponding fresh catalysts throughout the first four runs, whereas the slope of the conversion curves becomes nearly equal from the fifth run on. In the case of the Er derivative for example, the slope of the conversion curve for the calcined sample in the first run is very close to that obtained with the fresh catalyst after the third run. This higher activity displayed by the thermally treated catalysts could originate from a larger concentration of oxo species on the surface when compared to that shown by fresh catalysts and this feature might be associated with a modification on the acidic sites promoted by the thermal treatment. To analyse this aspect, DRIFT spectra were recorded in situ during the thermal treatment of compound Na- $\beta\beta$ -Er<sub>4</sub> (Fig. 8) and evolved gases were analysed by MS coupled to the IR instrument (Fig. A.4 in the Supplementary Information).

Fig. 8 shows the amplification of the  $1700-1300 \text{ cm}^{-1}$  region, while the full spectra from 600 to 4000 cm<sup>-1</sup> are given in the inset.

Table 1

Cumulative percentage of catalyst mass (referred to the initial amount) that is transferred to the solution after several runs.

Catalyst	Run		
	1	2	5
НРМо	100	-	-
HPW	100	-	-
$Na-\beta\beta-Dy_4$	10	15	25
<b>Na</b> -ββ- <b>Dy</b> <sub>4</sub> (cal. 200 °C)	4	8	10
Na-ββ-Tm₄	8	13	20
<b>Na</b> - <i>ββ</i> - <b>Tm</b> <sub>4</sub> (cal. 200 °C)	3	5	8



**Fig. 7.** Catalytic activity of **Na**- $\beta\beta$ -**Er**<sub>4</sub> throughout several runs at room temperature using 2 × 10<sup>-3</sup> mmol of fresh ( $\bigcirc$ ) and calcined ( $\Box$ ) catalyst.

An inspection of the latter reveals that the vibration peaks originating from the dilacunary Keggin framework (1000–600 cm<sup>-1</sup>) remain unchanged during the calcination process, which is in agreement with the fact that the Keggin structure is thermally stable up to at least 300 °C [51]. The main modifications take place in the spectral region corresponding to the bonding water on the  $\beta\beta$ -**Er**<sub>4</sub> POM. This is in agreement with the analysis of the evolved gases, which consist in exclusively water. More specifically, the relative intensities of the bands located in the 3600–2600 cm<sup>-1</sup> range and at c.a. 1640 cm<sup>-1</sup> are significantly modified during the thermal treatment, whereas variations for those close to 1550 cm<sup>-1</sup> and 1455 cm<sup>-1</sup> are almost negligible. All signals maintain their original intensity up to 168 °C, but at higher temperatures the intensity of the former group of bands undergoes remarkable decrease, while those forming the latter group remain nearly constant up to 260 °C and start becoming weaker only at higher temperatures. This behaviour is indicative of two types of water molecules present in the structures of compounds **Na**- $\beta\beta$ -**Ln**<sub>4</sub>: one type (associated with the 3600–2600  $\text{cm}^{-1}$  and 1640  $\text{cm}^{-1}$  signals) must be loosely bound water of crystallisation easy to be lost, whereas

the second type corresponds to molecules involved in stronger interactions that make their release to be slower by taking place at higher temperatures. This second type must encompass the aqua ligands coordinated to the Ln centres, and possibly, some other water molecules clustered in the close vicinity via strong hydrogen bonding.

These observations show good correlation with the TG analysis (Fig. A.3 in the Supplementary Information), which reveals a single mass loss step between room temperature and ca. 280 °C that involves the release of all water molecules in Na- $\beta\beta$ -Er<sub>4</sub>. The TG curves reproduce accurately those previously obtained by some of us [22]. In fact, 10.75% of the total mass is lost at 170 °C and this value nicely corresponds to 41 water molecules per  $\beta\beta$ -**Er**<sub>4</sub> anion. Considering that the molecular formula of compound Na- $\beta\beta$ -Er<sub>4</sub> contains approximately 44 water molecules of hydration per dimeric POM, the results above strongly suggest that the increase of the catalyst acidity with the temperature is mainly due to the loss of interstitial water that could result in a better accessibility to the Ln atoms. In this way, the acidity reaches its highest peak when only water molecules coordinated to the Ln centres remain in the solid sample and diminishes when the latter are also released.

#### 4. Conclusions

Compounds  $Na_{12}[Ln_4(H_2O)_6(\beta-GeW_{10}O_{38})_2] \sim 44H_2O$  (Na- $\beta\beta$ -Ln<sub>4</sub>, Ln = Dy, Ho, Er, Tm) are excellent heterogeneous catalysts for the oxidation of aniline with hydrogen peroxide in organic phase. These dimeric POMs composed of lanthanide-containing dilacunary Keggin subunits of the  $\beta$ -type act as Lewis acids leading to full conversion of the substrate and total selectivity towards nitrosobenzene. The exact nature of the lanthanide centres affects not only the catalytic activity, but also the solubility of the catalyst during the reaction. Reaction rates decrease as the atomic number of the lanthanide increases, but at the same time, less catalyst is transferred to the solution. Thermal pre-treatment of Na- $\beta\beta$ -Ln<sub>4</sub> samples increases their insolubility and acidity to lead to higher catalytic activities. Peroxometallic intermediates formed on the surface of the solid catalysts have been identified as the real active sites for the reaction by UV-Vis and DRIFT spectroscopic techniques. The rare-earth containing POM catalysts were separated



Fig. 8. DRIFT spectra of Na-ββ-Er<sub>4</sub> at different temperatures recorded during the thermal treatment in He atmosphere up to 300 °C.

from the heterogeneous system with ease simply by filtration and were reused with increasing catalytic activity over consecutive runs.

In conclusion, an eco-friendly, clean, and cheap heterogeneous catalytic protocol for the oxidation of aniline under mild reaction conditions has been described.

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#### Appendix A. Supplementary material

Appendix A includes: powder XRD patterns, FT-IR spectra and TG curves for the catalysts; a graphical representation of the effect of the amount of catalyst on the anile conversion; and a mass spectrometric analysis of the evolved gases during the thermal treatment of the catalysts. Appendix B includes tables with the following data: elemental and thermogravimetric analyses for the catalysts; and distribution of the products obtained from the aniline oxidation. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. jcat.2015.09.004.

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