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### PAPER

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# Synthesis of glycerol carbonate over 2D coordination polymer building with Nd<sup>3+</sup> ions and organic ligand<sup>+</sup>

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In this work, a two-dimensional coordination polymer was synthesized and the structure was determined by single-crystal X-ray diffraction. The crystal structure belongs to space group *Pna2*<sub>1</sub> and was characterized by Raman and FT-infrared spectroscopy, powder X-ray diffraction and Brunauer-Emmett-Teller surface area analysis. Catalyst activities were evaluated though the synthesis of glycerol carbonate from glycerol and urea using a batch reactor. After the optimization of both, reaction and reactor conditions, the activity results showed that the coordination polymer used as a heterogeneous catalyst has good values of conversions and selectivity to the manufacturing of glycerol carbonate in a fine-chemical process. The analysis of powder X-ray diffraction and spectroscopic for the coordination polymer employed, before and after reaction show that some changes have taken place in the crystal structure during the process, in spite of recovering at the end of the reaction. The advantages and limitations of coordination polymer were discussed and compared with previous heterogeneous catalysts in the literature.

#### **1** Introduction

In the last years, a rapid growth has been observed in the building of uni- (1D), bi- (2D) or three-dimensional (3D) coordination polymers<sup>1, 2</sup>, not only due to their structural properties, which support both, academic and industrial studies, but also to a great interest in its potential applications in several areas, such as, absorption<sup>3</sup> and gas storage<sup>4, 5</sup>, separation processes<sup>6</sup>, <sup>7</sup>, nonlinear optics<sup>8-10</sup>, magnetic properties<sup>11-13</sup> and catalysts<sup>14-16</sup>. In this context, different coordination polymers have been widely used for the production of materials with pores that have different shapes and sizes<sup>17-19</sup>. The possibility of the incorporation of the active metals or distinct functional groups inside the pores allows the applications in heterogeneous catalysis<sup>20</sup>. So, the metal sites available in these coordination polymers can be used as Lewis acid to catalyze organic reactions<sup>16, 21</sup>. The catalytic activities may still be provided by functional groups added by postsynthetic modification of the organic ligands<sup>20</sup> or may be introduced by the incorporation of metal nanoparticles, such as Pd, Au, Ru, Cu, Pt, Ni and Ag<sup>17, 22-24</sup>. On the other hand, the low thermal stability when compared to oxides represents the major disadvantage and limitation in industrial processes using such coordination polymers<sup>25, 26</sup>.

A large number of different coordination polymers referred to in the literature as metal–organic frameworks (MOFs) are known and can be used in a wide-ranging for a variety of heterogeneous catalytic reactions<sup>27-29</sup>. For example, the MIL-101 can be applicate in heterogeneous catalysis due to a pseudo-octahedral coordination sphere around chromium ions in the crystalline structure constructed by oxygen atoms from benzene-1,4-dicarboxylate and water molecules or a hydroxyl group in some cases. The coordinated water molecules can be easily removed with increasing temperature and chromium ions may be available for use as catalytic sites in organic reactions such as cyanosilylation of aldehydes<sup>30</sup>, phenol hydrogenation<sup>31</sup>, hydrogenation of CO<sub>2</sub> to formic acid<sup>24</sup> and hydrogenation of furfural to tetrahydrofurfuryl alcohol<sup>32</sup>.

Many processes for obtaining and synthesizing new materials in the chemical industry are based on catalytic processes derived from Zeolites<sup>33-36</sup>; consequently, the research for new materials with catalytic properties is important and represents a promising field for further investigation. However, the development of an efficient catalyst with an easy synthesis process, easy recovery and reuse without loss of the catalytic activities has been major practical challenge in the industry; most of the recent successful developments are basically restricted to the employment of supported oxides. Several coordination



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polymers described in the literature have potentials for catalytic activities in an extensive variety of organic reactions<sup>37-39</sup>; for example, for the conversion of benzyl alcohol to benzaldehyde with hydrogen peroxide in aqueous solution<sup>40, 41</sup>, isomerization of terpene derivatives<sup>33, 42</sup> benzaldehyde cyanosilylation<sup>43, 44</sup> and among others reactions<sup>16, 41, 45</sup>. The improvement of catalysts and new materials for applications in chemical reactions is very positive; currently, 90% of all processes in the chemical industry have employed at least one catalytic process to obtain the manufactured product<sup>46, 47</sup>. Various catalytic processes have emerged in recent years due to a need, in most cases economic, such as the use of many compounds in the cracking<sup>48</sup> petroleum and gasoline desulphurization processes<sup>49</sup>. Thus, the economic need of a given process and/or product drives research in different areas and materials. In recent decades, the rise in the price of oil barrel in conjecture with a demand for an alternative to less polluting fuels has strongly improved the biofuels industry worldwide. The large development of the biodiesel industry from biomass leads to the formation of glycerol as a low-value by-product of the reaction. The increasing abundance of glycerol in the market has led to a drastic reduction in prices since 2016, and in 2014, the price of the tonne of crude glycerol was estimated at US\$ 240<sup>50</sup> and when it is imported from China can reach values from 50 to 70 US\$/Ton<sup>51, 52</sup>.

In this context, the conversion of glycerol to higher valueadded products has attracted the attention of different researchers who are trying to explore the possibilities of conversion to different products, such as, 1,3-propanediol, acrolein and gasoline additives<sup>53</sup>. However, the product which has attracted most attention in recent years is glycerol carbonate; it can be used in fine chemicals industry to find reaction intermediates, it can also be used as bio-lubricants, plastic, semiconductor, polymer, petrochemical and cosmetic industries<sup>54, 55</sup>. This great versatility transforms glycerol carbonate into a high value-added product, with a market price of up to \$ 8141/ton. Due to the high cost of production, until now, despite the different applications, the use is quite limited to a production of few Kilotons per year <sup>55</sup>. Different routes using commercial glycerol have been used for the production of glycerol carbonate in the last years, among them are reactions with phosgene, dimethyl carbonate, ethylene carbonate, carbon dioxide<sup>55, 56</sup> and reactions with urea<sup>57</sup>. All reactions generally have routes involving both, homogeneous and heterogeneous catalysts derived from acids, bases, carbonates, ionic liquids, enzymes in addition to metal oxides and hydrotalcites doped with transition metals 55, 57-59. The use of polymeric materials is very limited and is restricted only to the use of some resins<sup>60</sup> and a use of transition metal polymers for condensation of glycerol with acetone can still be seen<sup>61</sup>. The compact literature in the field of coordination polymers for application in the route of glycerol carbonate production makes evident, at first, a limitation of the use of these materials, therefore, represents a great challenge in both academic and industrial areas.

This work shows the synthesis, characterization and evaluation of the catalytic properties of a coordination polymer derived from a neodymium ion and sulphocarboxylic ligand, in addition to describing the structural properties and shows a relationship with the potential of application of this material in conversion reactions of commercial glycerol in higher value-added products when compared with other catalyst materials existent in the literature.

#### 2 Experimental

#### 2.1. Syntheses of compound Nd-5sis:

A solution of 10 mmol (2.682 g) of 5-sulfoisophthalic acid monosodium salt and 10 mmol (3.214 mg) of hydrated neodymium acetate was prepared in 80 mL of water and transferred to a Teflon vessel where 80 mL of ethanol was added. The solution was placed in an autoclave under hydrothermal conditions at 160 °C for 20 hours accompanied by a cooling rate of 1.5 °C h<sup>-1</sup> until room temperature. At the end, it was observed the formation of pink single-crystal suitable for analysis by single-crystal X-ray diffraction. Yield 85% relative to the weight of all reagents. CHN Anal. Calcd. for NdC<sub>8</sub>H<sub>11</sub>O<sub>11</sub>S (%): C, 20.91; H, 2.41. Found: C, 20.96; H, 2.63.

#### 2.2. Characterization

Single-crystal data was collected using an Oxford GEMINI A-Ultra diffractometer with MoK $\alpha$  ( $\lambda$  = 0.71073 Å) radiation at room temperature (298 K). The data collection, cell refinements and data reduction were performed using the CRYSALISPRO software<sup>62</sup> and the structure was resolved by direct methods and refined by SHELXL-2014 program<sup>63</sup>. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms connected to carbon were placed in idealized positions and treated by rigid model, with Uiso(H) = 1.2Ueq(C) and H atoms from water molecules were refined with O-H = 0.85 Å and Uiso(H) = 1.5Ueq(O). The figures were drawn using ORTEP-3 for Windows<sup>64</sup>, Mercury<sup>65</sup> and Topos4.0<sup>66</sup> programs. X-ray diffraction patterns of the compound were recorded on an Advance DaVinci D8 diffractometer with Bragg-Brentano  $\theta$ - $\theta$  geometry using CuK $\alpha$  (1.54056 Å) at 40 kV and 40 mA and LynxEye linear detector. The measurements were collected in the 2 $\theta$  range from 5° to 60°, in steps of 0.02° and accumulation time ranging from 0.5s to 1s by steps with a divergence slit of 0.6 mm and primary and secondary Soller slits of 2.5°. X-ray diffraction patterns performed with temperature variation were collected under the same conditions, using the MRI temperature module coupled to the diffractometer with temperature ranging from 25 °C to 700 °C and a heating rate of 10 °  $\min^{-1}$ .

Elemental analysis for C, H and N were carried out on Perkin– Elmer 2400 CHN analyzer. Fourier-transform Raman spectroscopy was performed using a Bruker RFS 100 spectrometer with  $Nd^{3+}/YAG$ laser operating at 1064 nm excitation line in the near infrared region using an N<sub>2</sub> liquid and CCD detector with a spectral resolution of 4 cm<sup>-1</sup>.

The infrared spectra were recorded on an FT-IR Perkin-Elmer FRONTIER spectrometer using KBr pellets in the range 4000–400

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cm<sup>-1</sup> with an average of 128 scans and 4 cm<sup>-1</sup> of spectral resolution. The thermogravimetric data were recorded in a Shimadzu DTG60 thermobalance with a heating rate of 10 °C min<sup>-1</sup> to a temperature of 700 °C in a dynamic atmosphere of air and atmosphere of N<sub>2</sub> with a flow of 100 mL min<sup>-1</sup>.

The specific apparent area data were estimated by the B.E.T method (Brunauer, Emmett and Teller)<sup>67, 68</sup> and were acquired from a Quantachrome Autosorb1 equipment. The measurements were performed using nitrogen gas at 78 K, where the compound *Nd-5sis* was degassed at 130 °C for 24 hours before analysis.

The surface proprieties were estimated by a model of reaction which involves the reaction of the water molecules on the surface and hydrogen peroxide in a solution of acetonitrile. These studies were performed using a system with a fixed temperature (T=25.7 °C), a pressure of approximately 0.899 atm, 1.0 mL of hydrogen peroxide 30% (v/v) and a fixed volume of 15.0 mL for the system. The use of acetonitrile (V = 14.0 mL) as a solvent allows contact over the entire surface of *Nd-5sis*, thus avoiding limitations related to mass diffusion effects.

#### 2.3. Catalytic testing

A schematic illustration of the experimental apparatus is shown in Fig. 1. Catalytic tests were performed in a batch reactor 1 (150 mL) which has a controlled rotation system 2 (130 rpm) for better distribution of heat between reagents and catalyst inside reactor, a tank 3 (500 mL) with temperature control and containing a heating oil bath, a thermometer 4, a trap system 5 with hydrochloric acid (1 mol  $L^{-1}$ ) to capture ammonia produced in the reaction and a vacuum pump 6 for removing ammonia with a pressure value at 10 kPa. Compound Nd-5sis was used as a heterogeneous catalyst and commercial glycerol, urea and solvents were purchased from Aldrich. In a typical experiment glycerol (12.61 g), urea (8.225 g) and compound Nd-5sis (0.250 g) were placed in a batch reactor and heated in bath oil at 140 °C with constant stirring (130 rpm) under a reduced pressure. After 90 minutes of reaction, methanol was added and the resulting solution was centrifuged at 3500 rpm for 15 minutes. Then, the compound Nd-5sis (catalyst) was separated by filtration. The method used was reproduced; however, a heat pre-treatment was performed for the compound Nd-5sis. 250 mg of Nd-5sis was left in a muffle with a heating rate of 10 ° min<sup>-1</sup> to a temperature of 160 °C for 2 hours. After this time, the dehydrated compound, as denoted Nd-5sis-desh, was added to the reaction mixture.



Fig. 1 Schematic illustration experimental system.

In order to compare the activities of catalyst, reactions were carried out in the absence of a catalyst and using ZnSO₄ calcined at 300 °C for 3 hours. The products were analyzed using a gas chromatograph-mass spectrometer Agilent 7190-5975 system. The samples were diluted in methanol 1:250 and a 0,1 µL was injected at 250 °C of temperature and 10:1 split ratio. The temperature program was 80 °C for 5 min and then 3 °C min<sup>-1</sup> until 110 °C, with a capillary column HP-5MS. The area of glycerol was integrated with the T.I.C. signal and a 5 steps calibration curve was used to determine the glycerol conversion. The Linalool and cyclohexanol were used as internal standard for quantitative conversion results. Selectivity results were obtained with the relative area of products formed. The <sup>13</sup>C spectra were collected on an Avance DRX400 NMR spectrometer at 300 K, 400 MHz as specified. The Nd-5sis leaching study was performed on a Ray Ny EDX-800 Shimatzu X-Ray Fluorescence equipment.

#### **3** Results and Discussion

#### 3.1. Structural description

The crystallographic data for compound *Nd-5sis* are shown in Table 1. The compound *Nd-5sis* was crystallized in the orthorhombic crystalline system and a non-centrosymmetric space group *Pna2*<sub>1</sub> and presents a deprotonated *5sis* ligand and an Nd<sup>3+</sup> ion in the crystal structure, Fig 2. The Flack parameter is at 0.18(5), showing that the absolute structure is correct for this compound<sup>69</sup>. It is observed that Nd<sup>3+</sup> ion is coordinated to nine oxygen atoms, four of which are derived from water molecules (Nd1-O8, Nd1-O9, Nd1-O10 and Nd1-O11) with average distance Nd-O of 2.498(11) Å

Table 1 Crystal data and refinement parameters for compound *Nd-5sis*.

Compound	Nd-5sis			
Formula	$C_8H_{11}NdO_{11}S$			
Formula weight (g mol <sup>-1</sup> )	459.47			
Crystal system	Orthorhombic			
Space group	Pna2 <sub>1</sub>			
a(Å)	7.3216(5)			
b(Å)	16.6789(9)			
c(Å)	10.4430(5)			
$\alpha = \beta = \gamma(^{\circ})$	90			
V(Å <sup>3</sup> )	1275.26(13)			
Z	4			
Crystal size (mm)	0.20 x 0.18 x 0.11			
μ (Mo-Kα) (mm <sup>-1</sup> )	0.71073			
Flack parameter	0.18(2)			
Refl. measured/independt	9010 / 3089			
Observed refl.[ $F_{obs}^2 > 2\sigma(F_{obs}^2)$ ]	2622			
No.of parameters refined	137			
R(F <sub>0</sub> ), WR (F <sub>0</sub> <sup>2</sup> ), S	0.035, 0.140, 1.14			
$\Delta \rho_{max}$ , $\Delta \rho_{min}$ (e Å <sup>-3</sup> )	1.72, -0.72			

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**Fig. 2** The crystal structure for **Nd-5sis**. Symmetry code: (i) x, y, z-1 e (ii) -1/2-x, 1/2 + y, z-1/2. Some hydrogen atoms were omitted for more clarity and the ellipsoids were drawn with 50% probability.



**Fig. 3** Packing for *Nd-5sis*. (a) Extension of the 2D polymer along of *bc*-plane. Colour code: C: gray, O: red, S: yellow, Nd: light pink. (b) Formation of the 3D supramolecular arrangement of polymer along of *a*-axis. Some atoms have been omitted for better visualization.

and other atoms from the carboxylate (Nd1-O1", Nd1-O2", Nd1-O3 Nd1-O4<sup>i</sup>) and sulfonate groups present in the organic ligand (Nd1-O6). The crystalline structure of Nd-5sis leads to the building of a two-dimensional polymer (2D) extending along the crystallographic bc-plane, are as shown in Fig 3(a). Thus, the structure of Nd-5sis is defined as a uni-nodal (3)-connected and can be described as a point symbol  $6^3$  and is deposited in RCSR as a net of type *hcb*, with hexagonal symmetry P6mm<sup>70</sup>. Three-dimensional (3D) supramolecular arrangement in the compound is formed mainly by moderate hydrogen bonds between the 2D sheets along of the crystallographic *a*-axis with an average distance of 2.915(13) Å, Fig. 3(b). In Fig. S1<sup>+</sup> and S2<sup>+</sup> (supplementary material), it is possible to observe the electron density map  $(e^{A^{-3}})$  neighboring of Nd<sup>3+</sup> ion and the plane of the aromatic ring of **5sis** ligand.

By the map, it is possible to see that Nd<sup>3+</sup> ion presents a much greater contribution when compared with the carbon, oxygen and sulfur atoms present in the structure, data coherent with the number of electrons of the atoms. In this sense, the intensity of the reflections in the crystal is attenuated by the absorption effect of  $\mathrm{Nd}^{\mathrm{3+}}$  ions in the structure. If the absorption correction is not applied, it is possible observed high levels of anisotropic displacement or negative (physically impossible) to different atoms and with a high residual electron density near the  $Nd^{3+}$  ions. Furthermore, even if the atomic positions of the heavy atoms (Nd<sup>3+</sup>) are not affected during the refinement, it is noted that the position of the light atoms such as carbon, oxygen and sulfur is compromised due to the formation of several scattered electron density peaks in the electron density map around these atoms. Fig. S3<sup>+</sup> shows the residual electronic density map of *Nd-5sis* after refinement process. The correction of empirical absorption using spherical harmonics<sup>71</sup> and considering strong absorption centers were fundamental for the determination of the crystalline structure in the compound *Nd-5sis*. Although it is still possible to verify a marked residual value of untreated electron density around the  $Nd^{3+}$  atom (1.72 eÅ<sup>-3</sup>), thus indicating that, even with the absorption treatment in the reflections, the model is not yet the most appropriate for the structure. The compound Nd-5sis is isostructural to a series of compounds which were synthesized in the literature by Liu and co-workers with Ho, Dy, Tb, Sm, Pr ions and 5sis ligand<sup>72</sup>. By crystallographic data of the compounds, it can be seen that the crystalline structures, in spite of presenting statistical data acceptable to the International Union of Crystallography (IUCr), show some limitations, mainly in the anisotropic parameters of some carbon and oxygen atoms that have been refined isotropically due to negative values of atomic displacement, or even the various restrictions applied in order to minimize such problems in the refinement. All structures have high values of the absorption coefficient and, mainly, high values of residual electronic density, except for Ho (0.615  $e^{A^{-3}}$ ) and Pr (0.754  $e^{A^{-3}}$ ), indicating that the effect of absorption is very evident in these type of compounds involving lanthanide atoms. However, the electron density accumulation enveloped by these ions in different materials represents a potential for the application of these compounds in the catalysis area and may be exploited in some organic reactions, such as Diels-Alder reactions<sup>73</sup> and  $\pi$ -allyl bond formation<sup>74, 75</sup> where the products of reactions depend on the kind of added rare earth element<sup>76-81</sup>.

#### 3.2. Thermal stability studies

The results of the thermogravimetric analysis for compound *Nd-Ssis* are displayed in Fig. S4<sup>+</sup> and S5<sup>+</sup>. When the compound *Nd-Ssis* was heated in air at a rate of 10 °C min<sup>-1</sup>, two events of weight loss are presented. The first event occurs in the temperature range from 110 to 160 °C accompanied by an endothermic event at 150 °C. The weight decrease (15%) observed is in good agreement with the removal of four mols of water with a relative deviation of approximately 5%, and it is in agreement with CHN elemental analysis. The compound *Nd-Ssis* shows thermal stability between 160-550 °C; however, an oxidative process is observed which origins a slight weight increase in this temperature range. The second

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weight loss event may be attributed to a thermodecomposition that causes the collapse of the crystal structure. The DTA curve shows an exothermic event at 604 °C, where the calculation of weight loss of 40% indicates that the residue is related to oxidation of the products with the formation of 1/2 mol of neodymium oxysulphate,  $Nd_2O(SO_4)_2$ , with a relative deviation approximately of 6%. In Fig S5<sup>+</sup>, it is observed that the thermodecomposition curve in nitrogen atmosphere has two events of weight loss. The first event of 15% in the temperature range from 110 °C to 180 °C accompanied by an endothermic event at 155 °C may be attributed to the loss of four mols of water molecules (relative deviation of 5%). No weight change was observed in the range from 180 °C to 550 °C. The second stage of weight loss of 35% with a slightly exothermic event at 622 °C refers to the formation of 1/2 mol of neodymium oxysulphate, Nd<sub>2</sub>O(SO<sub>4</sub>)<sub>2</sub>, (relative deviation 2%). Comparative results of the thermogravimetric analysis in air and nitrogen atmosphere show that the thermodecomposition occurs in a similar way in which the compound Nd-5sis is thermally stable at approximately 550 °C. But, it is noted that the two thermodecomposition patterns are quite different in the temperature range of 180 °C to 550 °C due to an oxidation process which results in a slight weight increase. Oxidation process in air atmosphere is related to the formation of carbonates and oxycarbonates of neodymium with dehydration of the crystal structure.

According to the X-ray analysis, the thermodecomposition of the compound *Nd-5sis* can also be separated into three steps which are related to the formation of the different intermediate crystalline phases of carbonates and oxycarbonates of neodymium after the loss of the water molecules. Polycrystalline diffraction patterns of Nd-5sis at different temperatures (heating rate of 10 ° C min<sup>-1</sup>) are shown in Fig 4 and indicates that the compound exhibits a stable crystalline phase at 130 °C. The increase in temperature allows the removal of the water molecules and a reduction of the crystallinity of the compound with the formation of intermediate crystalline phases as shown in Fig 5. Phases of Neodymium carbonate intermediates,  $Nd_2(CO_3)_3$  (orthorhombic, Pccn) and  $Nd_2O_2CO_3$  (hexagonal,  $P6_3/mmc)^{82,\ 83}$  with different initial ratios appear in 160 °C. The thermal treatment of the compound up to 300 °C allows a gradual reduction of neodymium carbonate phase, which can be accompanied by a reduction of the intensity of diffraction peak at  $2\theta = 19.42^{\circ}$  (CuK $\alpha$ ) besides a slight increase of the neodymium oxycarbonate phase ( $2\theta = 11.09^\circ$ ,  $2\theta = 23.41^\circ$  and  $2\theta$  = 26.80°, CuKa). It should be noted that the formation of oxycarbonate phase from Nd-5sis occurs much more softly (160 °C-200 °C) when compared to previous reports found in the literature (450 °C) for thermodecomposition of carbonate phases of rare earth<sup>82</sup>. At 350 °C, the formation of a neodymium oxysulphate phase is observed ( $2\theta = 17,65^\circ$ ,  $2\theta = 34,50^\circ$  and  $2\theta = 36,20^\circ$ , CuK $\alpha$ ) and it is possible to observe that the crystal structure of Nd-5sis remains partially crystalline up to 400 °C (peak at  $2\theta = 13.07^{\circ}$ ) and above 450 ° C, only the neodymium oxysulfate phase is observed. The decomposition of neodymium oxysulphate to neodymium oxide was not detected during the experiments and it is consistent with data found in the literature  $^{84}$ , in which the formation of  $\rm Nd_2O_3$ is observed at temperatures between 900 °C and 1100 °C depending on the crystalline phase. These results are in agreement with thermal analysis data in an air atmosphere, where the oxidation processes are observed in the region of 160 °C to 500 °C. However, a heating and thermodecomposition of the sample lead to the overlap of different diffraction peaks. In order to check the overlaps, a CHN elemental analysis of the sample was made during the formation of the different crystalline phases. The chemical composition of the products formed during sample, heating together with the experimental observations of X-ray and thermal analysis, suggests coherence in relation to crystalline phases formed, results are shown in Table 2.

#### 3.3. Structure and surface effects

One of the complications in working with the heterogeneous catalyst is a need to increase and stabilize the surface acidity, so a study of the quantification of the sites that cover the internal and/or external surface of the solid is usually necessary<sup>85, 86</sup>. Several methods are used to characterize and quantify the acid-base sites, some of these used for site density determination and others for site nature characterization, such as programmed thermal desorption<sup>87, 88</sup> and spectroscopy in the infrared region<sup>89-91</sup>. Both techniques are well established for the characterization of inorganic materials and oxides used as catalysts<sup>92-94</sup>. However, for coordination polymers, these techniques generally show a lot of limitations, since the use of high temperatures are required or the formation of numerous adsorption bands occurs which overlaps the marker bands of the probe molecules used. In this sense, a model of reaction might be used to determine and quantify more exactly the superficial properties of coordination polymers such as Nd-5sis.



**Fig. 4** Diffraction patterns for the compound *Nd-5sis* with a temperature range of 30 to 650 °C.

$$Nd(5sis).4H_{2}O \xrightarrow{O_{2}(atm)} \left\{ \begin{array}{c} Nd(5sis) \\ Nd_{2}(CO_{3})_{3} \\ \hline \\ -H_{2}O \end{array} \right\} \xrightarrow{450^{\circ}C} Nd_{2}O(SO_{4})$$

Fig. 5 Scheme of formation of different crystalline phases with the heating of the compound *Nd-5sis*.

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Heating temperature / °C	Composition	Water of hydration in the sample		С%	Н%	Crystalline phase* (%)
30	Nd(5sis).4H <sub>2</sub> O		Experimental	20.96	2.63	100
			Calculated	20.91	2.41	
			Relative error / %	2	8	
160	Nd(5sis)		Experimental	21.24	2.63	98
	Nd <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	3	Calculated	21.41	2.03	2
			Relative error / %	1	22	
200 Nd(55 <i>i</i> s) Nd <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> Nd <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>		Experimental	23.19	1.51	90	
	Nd <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	1	Calculated	21.72	1.16	5
	Nd <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>		Relative error / %	6	23	5

Table 2 Chemical analysis of the products formed with the thermodecomposition of Nd-5sis.

The quantification of Nd<sup>3+</sup> sites acting as Lewis acid on the surface of Nd-5sis can be determined by considering a chemical reaction between water molecules on the surface of Nd-5sis and  $H_2O_2$  species, which allows the formation of OOH and  $H_3O^+$  ions, as shown in Fig 6. Based on empirical observations, a model was proposed and a mathematical equation was obtained that describes the number of active sites in the relation to the amount of Nd-5sis, considering some limitations. A plot of pH versus the amount of Nd-5sis was constructed and it is shown in Fig 7(a). For a constant value of the H<sub>2</sub>O<sub>2</sub> solution (1 mL), it is observed that, when the amount of Nd-5sis increases, pH of the solution is reduced, and after 50 mg of Nd-5sis, the pH remains practically constant and suffers small oscillations. It is known that hydrogen peroxide solution employed in the experiment is commercially acidified  $(2 \le pH \le 4)$  so that there is a chemical equilibrium, Fig 7(b), in order to maintain a constant concentration of  $H_2O_2$  species in the system.

Thus, it is experimentally observed that increasing the concentration of  $Nd^{3+}$  sites (weight of *Nd-5sis*) on the surface leads to a higher consumption of  $H_2O_2$  species and a formation of  $H_3O^+$  ions. At the moment that an excess of  $H_3O^+$  ions occurs in the system, the chemical equilibrium in solution is displaced in order to restore the concentration of  $H_2O_2$  species in the system, attenuating variation of pH of the solution, Fig 7(b). Thus, after addition of 50 mg of *Nd-5sis*, it is possible to see that the equilibrium works as a buffer effect in the system avoiding pH variations in the solution. So, a linear function of the surface can be obtained considering the number of  $H_3O^+$  ions formed in the system in the range of 5 to 35 mg of *Nd-5sis*, as a shown in Fig 8.



Fig. 6 Reaction model for the reaction between water molecules and hydrogen peroxide on the surface of compound *Nd-5sis*.

Based on crystallographic data together with the elemental analysis data, it is possible to calculate the amount of  $Nd^{3+}$  sites noting that there is a proportion of 4 molecules of water per  $Nd^{3+}$  site in the crystal structure and consequently 4 molecules of  $H_3O^+$  formed in the system per  $Nd^{3+}$ . As a consequence of the use of this model of reaction, when *Nd-5sis* weight is equal to zero, the pH assumes pH value of the solution, pH = 3.35, and this initial value must be considered to obtain the mathematical equation 1 (eq.1).

$$Nd^{3+}_{surf} = (5 \pm 4).10^{-8} + (40 \pm 2).10^{-6}.w$$
 (eq. 1)

Where  $Nd^{3+}_{surf}$  represents the number of Nd<sup>3+</sup> sites on the surface of **Nd-5sis** in mols and *w* the amount of compound in grams. It is also perceived that at the limit where the weight tends to zero, the comportment of the reaction assumes values close to real values and there was not restoring effect of the H<sub>2</sub>O<sub>2</sub> species. As a result, considering the equation obtained by fit linear analyses of the graph in Fig 8, the compound **Nd-5sis** has a number of Nd<sup>3+</sup> sites in the range of 38.01 to 42.09 µmol per one gram.



**Fig. 7** (a) Graph of the variation of pH in relation to the amount of *Nd-5sis* and (b) chemical equilibrium in peroxide solution 30% (v/v).

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**Fig. 8** Graph of the amount of *Nd-5sis* and number of  $Nd^{34}$  sites on the surface in the range of 5 to 35 mg.

Therefore, using this data, it is possible to determine the rate of reaction per active site (TOF - Turnover frequencies) from consumption values of glycerol in the catalytic tests performed.

#### 3.4. Catalytic activity

The catalyst tests were made with commercial glycerol, urea and Nd-5sis as a catalyst, Fig 9. Incorporation of a weak Lewis acid, such as Nd<sup>3+</sup> ions, can favor the reaction, in addition to decreasing significantly the interaction of reactants and products formed avoiding surface contamination of the solid by the slight adsorption of all species in the system. It has been different from what occurs in the literature that basically uses Lewis acids derived from transition metals<sup>60</sup>. The conversion and selectivity of glycerol to glycerol carbonate are affected by different parameters of the reaction conditions, such as temperature and pressure. Then, for a reduced pressure of 20 Pa and a temperature of 25 °C, the equilibrium constant has a value of 0.516 x 10<sup>2</sup> while for a temperature of 140 °C, it has a value of  $3.658 \times 10^{7-95}$ . Indeed, the increase in temperature favors the formation of glycerol carbonate, however, a degradation effect of the product was considered with a drastic increase in temperature, as well as excessive energy costs. In order to favor the thermodynamic conditions of the reaction, the temperature of 140 °C was established as well as a reduced pressure, based also on what it has been done in literature<sup>57, 96</sup>. The experimental results for the catalytic tests obtained in the absence of catalyst, ZnSO4 and with Nd-5sis were compared with the conversion and selectivity data of a series of compounds which have been prepared and employed as a heterogeneous catalyst for synthesis of glycerol carbonate<sup>57, 59, 96</sup>



Fig. 9 Scheme of reaction between commercial glycerol and urea.

To support a chemical reaction with a catalyst, the desired requirement is that the step controlling the reaction is the chemical kinetics. However, during the process several other physical and chemical phenomena may occur, in addition to phenomena of diffusion and mass transfer from bulk phase to active site. A great difficulty in determining of kinetic data in heterogeneous catalysis is the external effect of heat and mass transfer, especially into the pores of catalysts with high specific area. At first, it is important that initially, to define the conversion values of glycerol, it is necessary to estimate these catalytic phenomena involved in the process and consequently specify how much these terms are significant or not to estimate the real conversion values. As previously mentioned, reaction temperature is an important factor affecting the conversion values and reaction rate by increasing the equilibrium constant in addition to contributing to the alteration of the viscosity of the mixture, decreasing the diffusion process and increasing the contact between the reactants and the catalyst particles. An increase in temperature for such a reaction above 140 °C may result in a loss of thermal stability of the Nd-5sis catalyst.

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However, in this case, a number of kinetic analysis experiments were performed in the range of 80-280 rpm to find suitable speed of agitation on percentage of conversion values. The results are show in Fig S6<sup>+</sup>. Based on the kinetic analysis results, it is possible to confirm that the agitation speed does not directly influence the conversion values, on the other hand, plays an important role in controlling the process of diffusion and mass transfer combined with a temperature at 140°C, thus securing the chemical kinetics of the reaction. For experimental facilities the stirring speed of 130 rpm was selected for the reaction.

The effect of catalyst amount of the reaction was investigated in a range from 0.25% to 2.4% of the catalyst weight percentage and at 90 minutes for reaction time (Fig S7<sup>+</sup>). The increase of *Nd-5sis* catalyst amount promotes an increase of glycerol conversion; on the other hand, further increasing on the catalyst amount to above 1.2% w/w cannot improve the conversion values. Fig 10 shows glycerol conversion and selectivity values in the absence of catalyst of 37% and 73%, respectively. It is emphasized that it is not possible to compare real conversion values in a quantitative and rigorous way for different catalysts under similar conditions. However, Fig 10 can be useful for understanding the maximum potential of the catalysts under their optimized conditions current in the literature. Catalyst derived from Zeolites and hydrotalcites doped with Mg<sup>2+</sup>, Zn<sup>2+</sup>, Zn<sup>2+</sup>/Li<sup>+</sup> and  $Fe^{2+}/Mg^{2+59}$  assume values ranging from 70% to 93% for conversion and in the range from 5% to 88% in terms of selectivity. Moreover, it is also possible to note that for neodymium oxide,  $Nd_2O_3$  <sup>96</sup>, the conversion and selectivity results are approximately 30% and 93%, respectively, and despite the high selectivity, conversion value is comparable to reaction in the absence of the catalyst and it is indication of a low catalytic activity, with a yield of 27.5%.



**Fig. 10** Catalyst performance for the synthesis of glycerol carbonate over different catalyst. Reaction conditions for absence of catalyst: Molar ratio Glycerol/Urea = 1, 1.5 h, 140°C, 10 KPa. For *Nd-5sis* and *Nd-5sis-desh*: Molar ratio Glycerol/Urea = 1, 1.2wt%, 1.5 h, 140°C, 10 KPa and for ZnSO<sub>4</sub>: Molar ratio Glycerol/Urea = 1, 4wt%, 1.5 h, 140°C, 10 KPa. For Nd<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>-600: Molar ratio Glycerol/Urea = 1, 0.4wt%, 1 h, 140°C, 4 KPa. For the other catalysts: Molar ratio Glycerol/Urea = 1, 5wt%, 5 h, 145°C, 4 KPa.

High conversion and selectivity results are found for the compound  $La_2O_3$ <sup>96</sup>, with values of 68.9% and 98.1%, respectively. For catalyst test using anhydrous zinc sulphate, the experimental results of conversion were of 71 % while of selectivity were of 77%. The process of manufacturing glycerol carbonate by  $ZnSO_4$  and other heterogeneous Zn-derived catalysts has already been described in the literature by Yoo *et al.*<sup>57</sup> and presented an economic viability with a yield of 86% glycerol carbonate. The yield results differing from the theoretical data may indicate that pressure in the batch reactor still need to be adjusted, since the authors use reduced pressure to 4 kPa.

For Nd-5sis, the reaction showed conversion values of 76% and selectivity of 74%, values similar to reaction with ZnSO<sub>4</sub>, When this compound is dehydrated at 160 °C for 2 hours, designated by Nd-5sis-desh (Fig 10), it has values of 74% and 81% for conversion and selectivity, respectively. The slight change in the conversion values might be associated with the dehydration process of Nd-5sis, which allows to formation and disposal of surface active metal sites that work as a Lewis acid favoring the reaction or, in combination with X-ray result, the phases of neodymium oxycarbonate can be found, Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> in Nd-5sis-desh catalyst. It alters the acidity and basicity of the surface approving the selectivity results on the reaction suggesting that these modifications play a significant role in the activity of the catalyst. When comparing the data with Nd<sub>2</sub>O<sub>3</sub>, it is noted that *Nd-5sis* has a more active catalyst and considering the experimental data obtained for conversion and selectivity of the catalyst tests with Nd-5sis and Nd-5sis-desh it can be observed that these catalysts have similar values with several systems described in the literature and presented in this work.

However, when comparing the reaction rate (mmol  $g_{catalyst}^{-1}$  h<sup>-1</sup>), Fig 11, the compound *Nd-5sis* has a reaction rate with reasonable values, thus favoring its application. Wang *et al* reports the use of calcined lanthanum oxide, denoted as La<sub>2</sub>O<sub>3</sub>-600, at 600 °C to catalyze the synthesis of glycerol carbonate from glycerol and urea with a yield of 67.6 % <sup>96</sup>. The experimental data suggests a reaction rate of 1149 mmol  $g_{catalyst}^{-1}$  h<sup>-1</sup>, initially given much higher when compared to *Nd-5sis* (278 mmol <sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>).

The reaction rate results show that the reaction with *Nd-5sis* may contain several reactive molecules per active site ( $\mu$ mol g<sup>-1</sup>), which are much larger than the series of catalyst which have been tested and employed for synthesis of carbonate of glycerol.

#### 3.5. Resonance magnetic nuclear

The reaction mixture of the glycerol reaction with urea, after separation process of *Nd-5sis* with methanol, was cooled and results of <sup>13</sup>C NMR analysis for the reaction mixture with deuterated acetone solvent are shown in supplementary content, Fig S8<sup>+</sup>. The presence of four chemical shift signals ( $\delta$ ) of <sup>13</sup>C in 63.7; 66.4; 71.0 and 159.0 ppm confirm the reaction of glycerol with urea with the loss of the terminal hydroxyl group of glycerol and formation of glycerol carbonate, chemical shifts are in agreement with data reported in the literature for glycerol carbonate (61, 65 and 70 ppm, deuterated methanol)<sup>53</sup>. The presence of urea ( $\delta$  = 162.7 ppm) and small traces of possible by-products in addition to glycerol ( $\delta$  = 64.0 ppm,  $\delta$  =73.4 ppm) were observed.

# 3.6. Glycerol consumption rate and glycerol carbonate production rate in a process

It is possible to calculate the rate of production of glycerol carbonate per unit volume of the catalyst employed, *Nd-5sis*, with experimental data obtained discounting the limitations of the mass and energy transport phenomena in the system during the reaction in a batch reactor.



**Fig 11** Reaction rate results (mmol  $g_{catalyst}$ <sup>-1</sup> h<sup>-1</sup>) for different catalysts. The rates were calculated based on the mole of glycerol converted per gram catalyst per hour of reaction.

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The rate of a chemical reaction using solid-state catalyst depends directly on the number of active sites on the surface of the catalyst and the activity of the catalyst is generally proportional to the area of the active component in the catalyst per weight unit or per volume unit. Since the surface area per volume unit depends on the size of the particles and the bulk density of the material. When it is possible to fill an entire reactor with the catalyst, the bulk density of the material can be calculated, however, when it is not possible, the bulk density is not considered, a situation often used in fine-chemical processes for batch reactors97. With these considerations, TOF can be calculated from the ratio of the glycerol consumption rate at 140 °C, the number of active sites in the catalyst (10  $\mu$ mol) estimated by the formation of OOH on the surface of *Nd-5sis* for the weight of 250 mg and total time of 5400s. It can be noted that the TOF for the catalyst has a value of 1.93 s<sup>-1</sup> and indicates that, approximately, two glycerol molecules are converted to glycerol carbonate per active site per second. The specific surface area of *Nd-5sis* was estimated at  $11 \text{ m}^2 \text{ g}^{-1}$  for calculated particle size of 100 nm by X-ray analyses<sup>98</sup>. The nitrogen adsorption and desorption isotherms, in Fig S9<sup>+</sup>, of *Nd-5sis* presents a typical type IV curves with H3 hysteresis loops. The curve does not exhibit any limiting adsorption at high P/P<sub>0</sub>, suggestive of the existence of non-rigid aggregates of plate-like particles or slit-shaped pores assemblages. This result does not provide a consistent calculation of the pore size distribution.

The weight fraction of the catalyst used is 1.2 wt% and density of the mixture in the batch reactor of 1.30 g cm<sup>-3</sup> (a good approximation since the density of the urea is  $1.32 \text{ g cm}^{-3}$ and commercial glycerol is 1.26 g cm<sup>-3</sup>). Considering the (X-ray) catalyst density of 2.393 g cm<sup>-3</sup>, the volume fraction of the catalyst can be estimated with a value of 6.519 x 10<sup>-3</sup> m<sup>3</sup> m<sup>-3</sup>as well as the surface area in the volume fraction of the catalyst  $(1.716 \times 10^5 \text{ m}^2 \text{ m}^{-3})$  in the reactor with a crystallite size of 100 nm. The number of active atoms available for the reaction is lower than the number of atoms on the surface, which in Nd-5sis is estimated as 2.20 x 10<sup>18</sup> atoms m<sup>-2</sup>, or the number of active atoms per volume of the catalyst has a value of 3.78 x  $10^{23}$  atoms m<sup>-3</sup>. Then, the number of mols of glycerol converted each second per volume of the catalyst utilized can be determined. Considering TOF value and the number of sites active per volume of the catalyst obtains a value of 7.29 x  $10^{23}$ atoms m<sup>-3</sup> s<sup>-1</sup>, or 1.21 mol m<sup>-3</sup> s<sup>-1</sup>.

In summary, the bulk density effect of compounds to catalytic tests and the transport limitations that occur in the batch reactor may be neglected; a reasonable consideration, since the system is maintained with a good distribution of heat, constant density and good agitation. Therefore, the conversion rate of glycerol (mol m<sup>-3</sup> s<sup>-1</sup>) is given approximated by equation 2 (eq.2).

$$R_{c} = \frac{\rho_{mix} (g \ cm^{-3}) x \ w_{i,glycerol}(g) x \ C_{\%}}{mm_{glycerol} (g \ mol^{-1}) x \ w_{t}(g) x \ t_{r}(s)} \ x \ 10^{6} \quad (eq.2)$$

Where  $ho_{mix}$  is the density of the mixture reactional (g cm<sup>3</sup>);  $w_{i,glicerol}$  is the initial weight of glycerol (g),  $C_{\%}$  is the conversion value,  $mm_{glycerol}$  is the molar mass of the glycerol,  $w_t$  is the sum of the weight of reagents (g) used (glycerol and urea) and  $t_r$  is the reaction time (s). The number of active sites on the surface, crystallite size and surface area of the compounds are parameters that directly influence the amount of catalyst and are embedded in equation 2 by the conversion value, at least for the Nd-5sis and ZnSO4. Considering the selectivity values of the reaction, it is possible to determine the rate of production of glycerol carbonate  $(118.09 \text{ g mol}^{-1})$ , in mol m<sup>-3</sup> s<sup>-1</sup>, or Ton m<sup>-3</sup> month<sup>-1</sup>. Thus, for a process of conversion of glycerol to glycerol carbonate occurring over 12 hours, which a good time for the operation of a fine-chemical industry, the production of glycerol carbonate can be determined as 136.2 Ton per cubic meter of Nd-5sis in the period of one month, considering 74% for the selectivity value, with a cost of 189.0 Ton m<sup>-3</sup> month<sup>-1</sup> of glycerol and 123.2 Ton m<sup>-3</sup> month<sup>-1</sup> of urea, or a production of 56.9 kg of glycerol carbonate with consumption of 78.9 kg of glycerol and 51.5 kg of urea per 1 kg of Nd-5sis. Experimental data of different catalyst in the literature 59, 96 were compared and the production of glycerol carbonate per kilogram of the spent catalyst was obtained based on values of conversion and selectivity found by different authors, these results are

summarized in Fig 12.

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From the data, it can be observed that the compound Nd-5sis as well as Nd-5sis-desh have a higher glycerol carbonate production rate, compared to several catalysts used in the literature. On the other hand, it has higher values of glycerol consumption, which is a limiting factor for its application. La2O3-600 shows a better relationship between production of glycerol carbonate and consumption of glycerol, standing out against all catalysts available in the literature to date. Different heterogeneous catalysts have been tested in recent years; although they have advantages and limitations in their use. In addition to the catalysts, which are produced by hydrotalcite (HTC), they have a low reaction rate and require high energy consumption for the calcination process and subsequent recovery of the sites<sup>59</sup>. Catalysts derived from oxides or mixtures of oxides generally have simple methods of synthesis, easy separation and recovery of the compounds in the mixture, besides good regeneration ability, however, they are sensitive and deactivated in the presence of water and their sites are contaminants in the final product. Catalytic reactions in the batch reactor have limitations due to low diffusion in the mixture and, consequently, low catalytic activity  $^{\rm 54,\ 55,\ 97}.$  For calcined zinc sulfate, it is required a higher energy for activation of the sites, besides this, part of the catalyst is soluble in the reaction, which needs a subsequent separation  $^{57}$ . La<sub>2</sub>O<sub>3</sub>-600 is a good candidate for the manufacture of glycerol carbonate, has an excellent reaction rate, easy separation and good recycling, but has high costs for calcination of the material, since it requires high temperatures<sup>96</sup>. The compound *Nd-5sis*, in addition to the reasonable reaction rate, shows a good production of glycerol carbonate, it requires low temperatures for the synthesis with

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a high yield and shows a facility for the separation process. Features which make *Nd-5sis* a good candidate in the manufacturing process. Besides this, the use of the catalyst with Nd<sup>3+</sup> metal site favors the reaction and have been responsible for a good catalytic activity.

#### 3.7. Recyclability of Nd-5sis

The chemical and structural stability of the Nd-5sis catalyst was investigated after the first reaction cycle, the spectroscopic and X-ray data, are presented in Fig S9<sup>+</sup> and S10<sup>+</sup>, respectively. At the end of the reaction, the catalyst was centrifuged and vacuum filtered, then, it was washed with a mixture of water and methanol before the analyses. It is possible to see in Fig S10<sup>+</sup>, in comparison to fresh Nd-5sis catalyst, that the absorption bands at 2944  $\rm cm^{\text{-1}}$  and 2891  $\rm cm^{\text{-1}}$ which are attributed to the stretching modes of CH groups from methyl groups, in conjunction with a band at 1715 cm<sup>-1</sup>, which are related to stretching of C = O group, were associated with the formation of glycerol carbamate, an intermediate of the reaction, adsorbed on the surface of *Nd-5sis*. By Raman scattering spectrum, the bands at 2946 cm<sup>-1</sup> and 2886 cm<sup>-1</sup> in addition to a shoulder at 1719 cm<sup>-1</sup> are correlated to the formation of the intermediate in the reaction.

At the end of the reaction, Nd-5sis exhibited a loss of crystallinity, mainly due to the adsorption of reactants, products and intermediates on its surface, as shown in Fig S11<sup>+</sup>. The *Nd-5sis* recovered was recrystallized using a mixture of water and ethanol at 160 °C for 12 hours and at the end of the process, the crystalline structure is preserved. Recycling of catalyst was investigated until the fourth reaction cycle, as shown in Fig 13. No significant variations in glycerol conversion values were observed even after four consecutive cycles. It is observed that both the catalytic activity and the crystalline structure of the compound are preserved during the recycle tests. The process of recrystallization of the catalyst leads to the removal of impurities adsorbed on the surface of the catalyst and was considered to contribute to a good reuse of the material. It is still verified that after each cycle of reaction a greater time in the process of recrystallization, reaching up to six days at 160 °C to the fourth cycle. The catalyst will maintain catalytic activity after four subsequent cycles, it is according to present in literature for the others catalysts<sup>57, 99</sup>.

One of the possible deactivation mechanisms of *Nd-5sis* in system was investigated by leaching study of  $Nd^{3+}$  ions. The analysis of  $Nd^{3+}$  before and after first cycle of reaction was carried out by X-ray fluorescence semi-quantitative analysis. The results of XRF suggest that after the first reaction cycle, the *Nd-5sis* has an increase of 5% over the initial amount of  $Nd^{3+}$  ions present in the fresh *Nd-5sis*, ensuring the initial catalytic activity for repeated batch reactions. Results are consistent with the catalyst recycling tests up to the fourth reaction cycle, as can be seen in Fig 13. This slight alteration in the amount of  $Nd^{3+}$  ions may probably be related with the leaching process of organic ligand, which may have occurred during the washing, filtration and recrystallization process of *Nd-5sis*. However, this ligand leaching process does not

interfere in the bulk of *Nd-5sis*, i.e., the crystalline structure of the *Nd-5sis*, as shown in Fig S11<sup>+</sup>, indicating that this small increase of metal ions is possibly associated with the formation of an amorphous phase in the system.

From the experimental data it is possible to verify that the reaction of urea with glycerol at 140 ° C under the surface of the Nd-5sis catalyst occurs basically in two steps. In the first stage of the reaction the adsorption of glycerol and urea occurs on the surface of the catalyst, followed by the conversion of the glycerol to the glycerol carbamate (intermediate) and the loss of an ammonia molecule at the surface active sites. Subsequently, a process of cyclization of the structure of the intermediate leads to the desorption of glycerol carbonate and abstraction of another molecule of ammonia. The second stage has a lower kinetic velocity than the first one, due the low conversion value (30%) for reaction in the absence of the catalyst, being, therefore, a determining step of the reaction. The use of the catalyst with the Nd<sup>31</sup> metal site favors the reaction, being responsible for the good catalytic activity. Mechanism similar to that occurring with transition metals present on the surface of hydrotalcites<sup>59</sup> and shown in Fig 14.







Fig. 13. Effects of recycling times on the conversion reaction of glycerol.

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Fig. 14. Mechanism for the reaction of urea with glycerol.

#### Conclusions

Two-dimensional polymer (Nd-5sis) was synthesized by means of a solvothermal reaction, with relatively simple solvents, which guaranteed a better control of the experimental parameters and, therefore, their great reproducibility. The study of thermal stability, when associated with thermodynamic parameters of the conversion reaction of glycerol to glycerol carbonate, allowed establishing a suitable working temperature range for the 2D coordination polymer, denoted as Nd-5sis. With this work it was possible to propose a good methodology for the characterization and quantification of active superficial sites from the study of structure and surface by means of a suitable model reaction using a hydrogen peroxide solution where the structural determination of *Nd-5sis* was fundamental to the proposal.

In addition, a simple mathematical equation was proposed to compare some results in the literature with those calculated in this work, allowing estimating the consumption and formation of glycerol and glycerol carbonate in a process. It noted that Nd-5sis has coordinated water molecules in the metal sites. Based on X-ray diffraction and thermogravimetric experimental data, it is possible verify that Nd-5sis has ability to generate free open-metal sites into structure if the abstraction of coordinated water molecules occurs. This is an important property which allows the application of *Nd-5sis* in the other organic reactions as it allows the molecules adsorbed by different interactions with those metal sites.

The Nd-5sis exhibits a satisfactory catalytic performance in the conversion process when compared to different catalysts in the literature; it can still be easily recovered without significant losses in relation to initial weight, chemical and structural modification. The present work has shown that the coordination polymers can be promising in the conversion process of glycerol, a low-value industrial waste and despite the limitations in the process; the study can help in the competitiveness of biodiesel companies in the market in the near future. But, for the application of these kinds of catalysts in a chemical process, other analyses of variables are required, such as the cost of production, activation and recovery of employed catalyst.

#### **Conflicts of interest**

There are no conflicts to declare.

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#### Notes and references

‡ CCDC 1428527 has the supplementary crystallographic data for this work and it can be obtained free of charge from The Cambridge Crystallographic Data Centre at http://www.ccdc.cam.ac.uk/conts/retrieving.html.

- C. Janiak, Dalton Transactions, 2003, DOI: 10.1039/b305705b, 2781-2804. 2. S. Kitagawa and R. Matsuda, Coordination Chemistry Reviews, 2007, 251, 2490-2509.
  - A. Khutia and C. Janiak, Dalton Transactions, 2014, 43, 1338-1347.
  - L. J. Murray, M. Dinca and J. R. Long, Chemical Society Reviews, 2009, 38,
  - 1294-1314 X. Yang and Q. Xu, Crystal Growth & Design, 2017, 17, 1450-1455.
  - J.-R. Li, R. J. Kuppler and H.-C. Zhou, Chemical Society Reviews, 2009, 38, 1477-1504
  - S. Qiu, M. Xue and G. Zhu, Chemical Society Reviews, 2014, 43, 6116-6140. R. Medishetty, J. K. Zareba, D. Mayer, M. Samoc and R. A. Fischer, Chemical Society Reviews, 2017, 46, 4976-5004.
  - L. R. Mingabudinova, V. V. Vinogradov, V. A. Milichko, E. Hey-Hawkins and A. V. Vinogradov, Chemical Society Reviews, 2016, 45, 5408-5431.
  - L. Li, B. Chen, Y. Song, G. Li, H. Hou, Y. Fan and L. Mi, Inorganica Chimica Acta, 2003, 344, 95-101.
  - X. Wang, G. Gou, D. Wang, H. Xiao, Y. Liu, M. Zhang, B. Dkhil, X. Ren and X. Lou. RSC Advances. 2016. 6. 48779-48787.
  - J.-Q. Liu, J. Wu, Y.-Y. Wang, J.-T. Lin and H. Sakiyama, CrystEngComm, 2014. 16. 3103-3112.
- X.-H. Chang, J.-H. Qin, L.-F. Ma and L.-Y. Wang, Journal of Solid State 13.
  - Chemistry, 2014, 212, 121-127. Y.-B. Huang, J. Liang, X.-S. Wang and R. Cao, Chemical Society Reviews, 2017. 46. 126-157.
  - M. Ranocchiari and J. A. v. Bokhoven, Physical Chemistry Chemical Physics,
  - 2011, 13, 6388-6396. A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov and F. Verpoort,
- Chemical Society Reviews, 2015, 44, 6804-6849. 17 Q. Yang, W. Liu, B. Wang, W. Zhang, X. Zeng, C. Zhang, Y. Qin, X. Sun, T.
  - Wu, J. Liu, F. Huo and J. Lu, Nature Communications, 2017, 8, 14429. R. C. Huxford, J. Della Rocca and W. Lin, Current Opinion in Chemical
  - Biology, 2010, 14, 262-268. P. L. Feng, J. V. Branson, K. Hattar, G. Vizkelethy, M. D. Allendorf and F.
  - Patrick Doty, Nuclear Instruments and Methods in Physics Research Section A: Accelerators. Spectrometers. Detectors and Associated Eauipment. 2011, 652, 295-298.
  - Z. Wang and S. M. Cohen, Chemical Society Reviews, 2009, 38, 1315-1329. S. Horike, M. Dincă, K. Tamaki and J. R. Long, Journal of the American
  - Chemical Society, 2008, 130, 5854-5855. L. Chen, X. Chen, H. Liu and Y. Li, Small, 2015, 11, 2642-2648.
- 22 A. Dhakshinamoorthy and H. Garcia, Chemical Society Reviews, 2012, 41, 23.
  - 5262-5284 S. Wang, S. Hou, C. Wu, Y. Zhao and X. Ma, Chinese Chemical Letters, DOI:
  - https://doi.org/10.1016/j.cclet.2018.06.021.
- D. Farrusseng, S. Aguado and C. Pinel, Angewandte Chemie International 25. Edition. 2009. 48. 7502-7513.
- 26 A. Herbst and C. Janiak, CrystEngComm, 2017, DOI: 10.1039/c6ce01782g. 27. J. G. Flores, E. Sanchez-Gonzalez, A. Gutierrez-Alejandre, J. Aguilar-Pliego, A. Martinez, T. Jurado-Vazquez, E. Lima, E. Gonzalez-Zamora, M. Diaz-Garcia, M. Sanchez-Sanchez and I. A. Ibarra, Dalton Transactions, 2018, 47, 4639-4645
  - E. Sanchez-Gonzalez, A. Lopez-Olvera, O. Monroy, J. Aguilar-Pliego, J. Gabriel Flores, A. Islas-Jacome, M. A. Rincon-Guevara, E. Gonzalez-Zamora, B. Rodriguez-Molina and I. A. Ibarra, CrystEngComm, 2017, 19, 4142-4146.
  - R. Yepez, S. Garcia, P. Schachat, M. Sanchez-Sanchez, J. H. Gonzalez-Estefan, E. Gonzalez-Zamora, I. A. Ibarra and J. Aguilar-Pliego, New Journal of Chemistry, 2015, 39, 5112-5115.

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DOI: 10.1039/C8DT01803K

Journal Name

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Published on 11 July 2018. Downloaded by University of Reading on 7/18/2018 9:16:27 AM

- A. Henschel, K. Gedrich, R. Kraehnert and S. Kaskel, Chemical Communications, 2008, DOI: 10.1039/B718371B, 4192-4194.
- I. E. Ertas, M. Gulcan, A. Bulut, M. Yurderi and M. Zahmakiran, Microporous and Mesoporous Materials, 2016, 226, 94-103.
   73.
- D. Yin, H. Ren, C. Li, J. Liu and C. Liang, *Chinese Journal of Catalysis*, 2018, 39, 319-326.
- M. Schröder, Functional metal-organic frameworks: gas storage, separation and catalysis, Springer, Heidelberg, 2010.
- B. Yilmaz, N. Trukhan and U. MÜLler, Chinese Journal of Catalysis, 2012, 33, 3-10.
- 35. B. Yilmaz and U. Müller, *Topics in Catalysis*, 2009, **52**, 888-895.
- 36. B. M. Weckhuysen and J. Yu, *Chemical Society Reviews*, 2015, **44**, 7022-7024.
- 37. O. A. Kholdeeva, *Catalysis Today*, 2016, **278**, Part 1, 22-29.
- 38. Q. Zhou and G. Shi, *Journal of the American Chemical Society*, 2016, **138**, 2868-2876.
- M. Hatano, E. Takagi, M. Arinobe and K. Ishihara, Journal of Organometallic Chemistry, 2007, 692, 569-578.
- P. Garcia-Garcia, M. Muller and A. Corma, Chemical Science, 2014, DOI: 10.1039/c4sc00265b.
- 41. H. Han, S. Zhang, H. Hou, Y. Fan and Y. Zhu, *European Journal of Inorganic Chemistry*, 2006, **2006**, 1594-1600.
- 42. L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs and D. E. De Vos, *Chemistry A European Journal*, 2006, **12**, 7353-7363.
- 43. H.-F. Yao, Y. Yang, H. Liu, F.-G. Xi and E.-Q. Gao, Journal of Molecular Catalysis A: Chemical, 2014, **394**, 57-65.
- Z. Zhang, J. Chen, Z. Bao, G. Chang, H. Xing and Q. Ren, *RSC Advances*, 2015, 5, 79355-79360.
- N. Snejko, C. Cascales, B. Gomez-Lor, E. Gutierrez-Puebla, M. Iglesias, C. Ruiz-Valero and M. A. Monge, *Chemical Communications*, 2002, DOI: 10.1039/b202639b, 1366-1367.
- 46. I. Fechete, Y. Wang and J. C. Védrine, *Catalysis Today*, 2012, **189**, 2-27.
- 47. C. Duong-Viet, H. Ba, Z. El-Berrichi, J.-M. Nhut, M. J. Ledoux, Y. Liu and C. Pham-Huu, *New Journal of Chemistry*, 2016, **40**, 4285-4299.
- M. Golmohammadi, S. J. Ahmadi and J. Towfighi, *The Journal of Supercritical Fluids*, 2016, **113**, 136-143.
  F.-L. Yu, Q.-Y. Wang, B. Yuan, C.-X. Xie and S.-T. Yu, *Chemical Engineering*
- F.-L. H, Q.-T. Wang, S. Huan, C.-X. Ale and S.-T. Hu, Chennicus Engineering Journal, 2016, DOI: <u>http://dx.doi.org/10.1016/j.cei.2016.10.003</u>.
   R. Cirimina C. D. Pina. M. Rossi and M. Paeliaro. European Journal of Lipid
- R. Ciriminna, C. D. Pina, M. Rossi and M. Pagliaro, European Journal of Lipid Science and Technology, 2014, 116, 1432-1439.
- 51. C. A. G. Quispe, C. J. R. Coronado and J. A. Carvalho Jr, *Renewable and Sustainable Energy Reviews*, 2013, **27**, 475-493.
- 52. O. Valerio, T. Horvath, C. Pond, M. Manjusri and A. Mohanty, *Industrial Crops and Products*, 2015, **78**, 141-147.
- M. Aresta, A. Dibenedetto, F. Nocito and C. Ferragina, *Journal of Catalysis*, 2009, 268, 106-114.
- J. R. Ochoa-Gómez, O. Gómez-Jiménez-Aberasturi, B. Maestro-Madurga, A. Pesquera-Rodríguez, C. Ramírez-López, L. Lorenzo-Ibarreta, J. Torrecilla-Soria and M. C. Villarán-Velasco, Applied Catalysis A: General, 2009, 366, 315-324.
- W. K. Teng, G. C. Ngoh, R. Yusoff and M. K. Aroua, Energy Conversion and Management, 2014, 88, 484-497.
- M. O. Sonnati, S. Amigoni, E. P. Taffin de Givenchy, T. Darmanin, O. Choulet and F. Guittard, *Green Chemistry*, 2013, 15, 283-306.
- J. W. Yoo and Z. Mouloungui, in *Studies in Surface Science and Catalysis*, eds. R. R. W.-S. A. C. W. L. Sang-Eon Park and C. Jong-San, Elsevier, 2003, vol. Volume 146, pp. 757-760.
- 58. C. Chiappe and S. Rajamani, *Journal*, 2011, **84**, 755.
- M. J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty and P. Concepción, *Journal of Catalysis*, 2010, 269, 140-149.
- X. P. Ye and S. Ren, in *Soy-Based Chemicals and Materials*, American Chemical Society, 2014, vol. 1178, ch. 3, pp. 43-80.
- M. N. Timofeeva, V. N. Panchenko, N. A. Khan, Z. Hasan, I. P. Prosvirin, S. V. Tsybulya and S. H. Jhung, *Applied Catalysis A: General*, 2017, 529, 167-174.
- 62. CrysAlisPro, *Rigaku Corporation, Tokyo, Japan.*, 2015.
- 63. G. Sheldrick, Acta Crystallographica Section C, 2015, **71**, 3-8.
- 64. L. Farrugia, *Journal of Applied Crystallography*, 1997, **30**, 565.
- C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *Journal of Applied Crystallography*, 2008, 41, 466-470.
- V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Crystal Growth & Design*, 2014, **14**, 3576-3586.
- S. Tedds, A. Walton, D. P. Broom and D. Book, *Faraday Discussions*, 2011, 151, 75-94.
- K. S. Walton and R. Q. Snurr, Journal of the American Chemical Society, 2007, 129, 8552-8556.
- H. D. Flack and G. Bernardinelli, Acta Crystallographica Section A, 1999, 55, 908-915.
- V. A. Blatov, M. O'Keeffe and D. M. Proserpio, *CrystEngComm*, 2010, 12, 44-48.

- R. Blessing, Acta Crystallographica Section A, 1995, 51, 33-38
- Q.-Y. Liu and L. Xu, European Journal of Inorganic Chemistry, 2005, 2005, 3458-3466.
- Y.-Q. Huang, H.-D. Cheng, H.-Y. Chen, Y. Wan, C.-L. Liu, Y. Zhao, X.-F. Xiao and L.-H. Chen, *CrystEngComm*, 2015, **17**, 5690-5701.
- S. Tobisch, H. Bögel and R. Taube, Organometallics, 1996, 15, 3563-3571.
- C. Lichtenberg, J. Engel, T. P. Spaniol, U. Englert, G. Raabe and J. Okuda, Journal of the American Chemical Society, 2012, **134**, 9805-9811.
- X. Liu, J. Wang, Q. Li, S. Jiang, T. Zhang and S. Ji, *Journal of Rare Earths*, 2014, **32**, 189-194.
- Y. Lei, Y. Wang and Y. Luo, Journal of Organometallic Chemistry, 2013, 738, 24-28.
- E. F. Sousa-Aguiar, F. E. Trigueiro and F. M. Z. Zotin, *Catalysis Today*, 2013, 218–219, 115-122.
- A. Monge, F. Gandara, E. Gutierrez-Puebla and N. Snejko, CrystEngComm, 2011, 13, 5031-5044.
- H. Furuno, T. Kambara, Y. Tanaka, T. Hanamoto, T. Kagawa and J. Inanaga, Tetrahedron Letters, 2003, **44**, 6129-6132.
- S. Kobayashi, M. Sugiura, H. Kitagawa and W. W. L. Lam, *Chemical Reviews*, 2002, **102**, 2227-2302.
- W. Hisanobu, Bulletin of the Chemical Society of Japan, 1978, 51, 2879-2881.
- A. Olafsen, A.-K. Larsson, H. Fjellvåg and B. C. Hauback, Journal of Solid State Chemistry, 2001, 158, 14-24.
- S. S. Batsanov, G. N. Kustova, E. D. Ruchkin and V. S. Grigor'eva, Journal of Structural Chemistry, 1965, 6, 47-53.
- E. L. Moreno and K. Rajagopal, Química Nova, 2009, 32, 538-542.
- A. A. Vedyagin, A. M. Volodin, V. O. Stoyanovskii, R. M. Kenzhin, E. M. Slavinskaya, I. V. Mishakov, P. E. Plyusnin and Y. V. Shubin, *Catalysis Today*, 2014, 238, 80-86.
- E. Selli and L. Forni, *Microporous and Mesoporous Materials*, 1999, **31**, 129-140.
- N.-Y. Topsøe, K. Pedersen and E. G. Derouane, *Journal of Catalysis*, 1981, 70, 41-52.
- N.-Y. Topsøe, Journal of Catalysis, 1991, 128, 499-511.
- Y. T. Kim, K.-D. Jung and E. D. Park, Applied Catalysis B: Environmental, 2011, 107, 177-187.
- G. S. Foo, D. Wei, D. S. Sholl and C. Sievers, ACS Catalysis, 2014, 4, 3180-3192.
- O. A. Anunziata, A. R. Beltramone, Z. Juric, L. B. Pierella and F. G. Requejo, Applied Catalysis A: General, 2004, 264, 93-101.
- V. Fleischer, R. Steuer, S. Parishan and R. Schomäcker, Journal of Catalysis, 2016, 341, 91-103.
- R. Si, J. Liu, K. Yang, X. Chen, W. Dai and X. Fu, *Journal of Catalysis*, 2014, **311**, 71-79.
- J. Li and T. Wang, The Journal of Chemical Thermodynamics, 2011, 43, 731-736.
- L. Wang, Y. Ma, Y. Wang, S. Liu and Y. Deng, *Catalysis Communications*, 2011, **12**, 1458-1462.
  - R. A. Sheldon and H. van Bekkum, Fine Chemicals through Heterogeneous Catalysis, Wiley, 2008.
- A. L. Patterson, *Physical Review*, 1939, **56**, 978-982.
  - M. Aresta, A. Dibenedetto, C. Devita, O. A. Bourova and O. N. Chupakhin, in *Studies in Surface Science and Catalysis*, eds. J.-S. C. Sang-Eon Park and L. Kyu-Wan, Elsevier, 2004, vol. Volume 153, pp. 213-220.

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Production of glycerol carbonate from glycerol and urea using a 2D coordination polymer as the heterogeneous catalyst.