High catalytic efficiency of a layered Coordination Polymer for simultaneous desulfurization and denitrogenation of fuels

by

Fátima Mirante [a], Ricardo F. Mendes [b], Filipe A. Almeida Paz [b]*, Salete S. Balula [a]*

[a] *REQUIMTE/LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal*

[b] *CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*

Electronic Supporting Information

* Corresponding authors.

E-mail addresses: filipe.paz@ua.pt (Filipe A. Almeida Paz); sbalula@fc.up.pt (S.S. Balula).

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1. Experimental Sections

1.1. Materials and methods

The following chemicals and reagents were purchased from Sigma-Aldrich (unless otherwise indicated) and used as received: dibenzothiophene (98%), 4,6-dimethyldibenzothiophene (97%), 4-methyldibenzothiophene (96%), 1-benzothiophere (98%), quinoline (98%), indole (≥99%), *n*-octane (98%), 1-butyl-3-methylimidazolium hexafluorophosphate (97%), tetradecane (99%), acetonitrile (Fisher Chemical), 1-butyl-3-methylimidazolium tetrafluoroborate (≥98%) and 30 wt.% hydrogen peroxide. Gadolinium(III) oxide (at least 99.99%, Jinan Henghua Sci. & Tec. Co. Ltd); nitrilotris(methylenephosphonic acid) [H_6nmp, $N(CH_2PO_3H_2)_3$, 97%, Fluka]; hydrochloric acid (HCl, 37% Analytical Reagent Grade, Fisher Chemical)

Fourier-transformed Infrared (FTIR) spectra were acquired on the attenuated total reflectance (ATR) operation mode of a Perkin Elmer FTIR System Spectrum BX spectrometer and all the representations are shown in arbitrary unities of transmittance. Inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis were registered with a spectrometer Optima 4300 DV (Perkin Elmer) with plasma source (RF generator of 40 Hz), and automatic sampler (PerkinElmer AS93-plus). ICP-OES analysis were performed at "*Centro de Apoyo Científico-Tecnológico (CACTUS) de la Universidad de Santiago de Compostela, USC (Galicia, Spain)*".

SEM (Scanning Electron Microscopy) images were acquired using either a high-resolution Hitachi SU-70 working at 4 kV. or performed in a FEI Quanta 400 FEG ESEM high resolution scanning electron microscope equipped with an EDAX Genesis X4M spectrometer working at 15 kV. Samples were prepared by deposition on aluminium sample holders followed by carbon coating using an Emitech K950X carbon evaporator or coated with a Au/Pd thin film by sputtering using a SPI Module Sputter Coater equipment.

Routine Powder X-Ray Diffraction (PXRD) data for all materials were collected at ambient temperature on a Empyrean PANalytical diffractometer (Cu $K\alpha_{1,2}$X-radiation, $\lambda_1 = 1.540598$ Å; $\lambda_2 = 1.544426$ Å), equipped with an PIXcel 1D detector and a flat-plate sample holder in a Bragg-Brentano para-focusing optics configuration (45 kV, 40 mA). Intensity data were collected by the step-counting method (step 0.04°), in continuous mode, in the *ca*. $5 \leq 2\theta \leq 50^{\circ}$ range.

Catalytic reactions were periodically monitored by GC-FID analysis carried out in a Bruker 430-GC-FID chromatograph. Hydrogen was used as carrier gas (55 $cm.s^{-1}$) and fused silica Supelco capillary columns SPB-5 (30 m x 0.25 mm i. d.; 25 μm film thickness) were used.

1.2. Preparation of MOF $[Gd(H_4nmp)(H_2O)_2]Cl \cdot 2H_2O$

One-pot Synthesis (**1op**): Layered MOF $[Gd(H_4nmp)(H_2O)_2]Cl \cdot 2H_2O$ was prepared following procedures described previously [REF]. In a typical synthesis, a mixture containing H_6nmp (0.1425 g, 0.477 mmol) and Gd_2O_3 (0.1587 g, 0.438 mmol) in *ca*. 10.0 mL of distilled water and 10.0 mL of HCl 6 M was stirred thoroughly in a round bottom flask. The resulting solution was kept at 120 ℃ for 18h in an oil bath, after which time the vessel was allowed to cool slowly to room temperature at ambient conditions. Crystals of $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ (**1**) were readily obtained after *ca.* 15 min, and a few days later individual crystals could be harvested manually from the vessels and their structure investigated using single-crystal X-ray diffraction (see Section 4.6 for further details on the crystal harvest).

Microwave-Assisted Synthesis (**1mw**): A reactive mixture composed of 0.1545 g (0.518 mmol) of H_6nmp and 0.1622 g (0.495 mmol) of La_2O_3 in *ca.* 3 mL of distilled water and 3 mL of hydrochloric acid 6M was prepared at ambient temperature inside a 10 mL IntelliVent microwave reactor. Reaction took place inside a CEM Focused Microwave Synthesis System Discover S-Class equipment, under constant magnetic stirring (controlled by the microwave equipment) using an irradiation power of 50 W at 90 ℃ for a 20 minutes. A constant flow of air (*ca.* 20-30 psi of pressure) ensured a close control of the temperature inside the reactor. The resulting product, $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ (**2mw**), was isolated as a white microcrystalline powder and it was recovered by vacuum filtration, washed with copious amounts of distilled water and then air-dried at ambient temperature.

Hydrothermal Synthesis (**1ht**): A reactive mixture containing H_6nmp (0.1671 g, 0.558 mmol) and La_2O_3 (0.0888 g, 0.272 mmol) in *ca.* 3 mL of distilled water and 3 mL of Hydrochloric acid 6M, was placed inside an adapted Teflon-lined Parr Instruments reaction vessel (autoclave with internal volume of *ca.* 10 mL). The vessel was then placed inside a pre-heated oven at 100 ℃ for a period of 18 hours. After this period, the vessel was allowed to cool to ambient temperature. The resulting white powder, identified as $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ (**2h**), was recovered by vacuum filtration, washed with copious amounts of distilled water and then air-dried at ambient temperature.

1.3. Desulfurization Process

The desulfurization studies were performed using a model diesel containing the most refractory sulfur-compounds present in real diesel, namely: 1-benzothiophene (1-BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimehtyldibenzothiophene (4,6-DMDBT) in *n*-octane (Figure S1). All the experiments were carried out under air (atmospheric pressure) in a closed borosilicate 5 mL reaction vessel, equipped with a magnetic stirrer and immersed in a thermostatically controlled liquid paraffin bath (50, 70, 80 ℃). The catalytic oxidative step was performed in the presence of an immiscible polar solvent, with equal volume of diesel and polar solvent. Different extraction solvents were used, as the ionic liquids (ILs), 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM]PF_6$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM]BF_4$) and acetonitrile.

The oxidation of the sulfur compounds only occurred in the presence of a catalyst and an oxidant, where H_2O_2 (aq. 30%) was used as oxidant and $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ as catalyst (20 mg was used). In a typical experiment, 0.75 mL of model diesel (containing a total sulfur concentration of 2350 ppm) and the extraction solvent (0.75, 0.37, 0.19 mL) were added to the catalyst. An initial extraction of sulfur compounds from model diesel to the IL phase occurred by only stirring the both immiscible phases for 10 min, inside the thermostated bath. The oxidative catalytic step of the process is then initiated by the addition of H_2O_2 oxidant (75, 50, 25 μL). The sulfur content in the model diesel phase was periodically quantified by GC analysis using tetradecane as standard. The recycle capacity of the heterogeneous catalyst was investigated using the same solid in consecutive desulfurization cycles. New portions of model diesel, oxidant and extraction solvent was added to the used catalyst at the end of each desulfurization cycle. Between cycles the solid catalyst was washed with MeCN. Furthermore, a reusing process was also performed, where the extraction phase containing the catalyst was either reused without any further treatment. All reused and recycled cycles were performed under the same initial experimental conditions by the addition of fresh portions of model diesel and 30% aq. H_2O_2 and, for the recycling process, also extraction solvent.

1.4. Denitrogenation Process

The denitrogenation studies were performed using a model diesel containing 400 ppm of nitrogen compounds known to be present in fuel compositions: quinoline (200 ppm) and indole (200 ppm) dissolved in *n*-octane (Figure S1). The reaction conditions used were the previously optimized for the desulfurization process: 20 mg of layered $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ catalyst, 0.43 mmol of H_2O_2 oxidant and 1:0.5 model diesel/$[BMIM]PF_6$, at 70 °C.

1.5. Simultaneous Desulfurization and Denitrogenation Processes

The desulfurization and denitrogenation of a multicomponent model diesel was performed using an *n*-octane solution containing sulfur (1-BT, DBT, 4-MDBT and 4,6-DMDBT) and nitrogen (200 ppm of N from quinoline and 200 ppm of N from indole, Figure S1). Contents of 2350 and 400 ppm of S and N, respectively, which gives a S/N ratio in accordance with the approximate value present in real diesel. The reaction conditions used were: 20 mg of layered $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ catalyst, 0.43 and 0.64 mmol of H_2O_2 oxidant, 1:0.5 and 1:1 model diesel/$[BMIM]PF_6$, at 70 °C. The catalytic stability of $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ was tested for several reusing cycles, following the methods described in section 2.3.

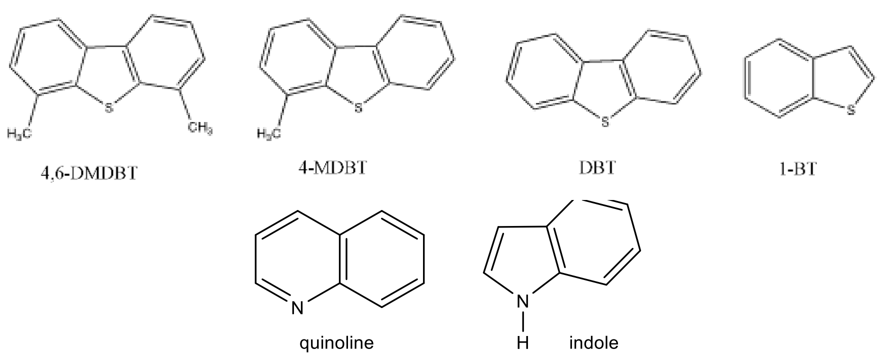

Figure S1. The representative sulfur and nitrogen compounds used in this work to prepare model diesels. 1-benzothiophene (1-BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT).

2. Structural Characterization

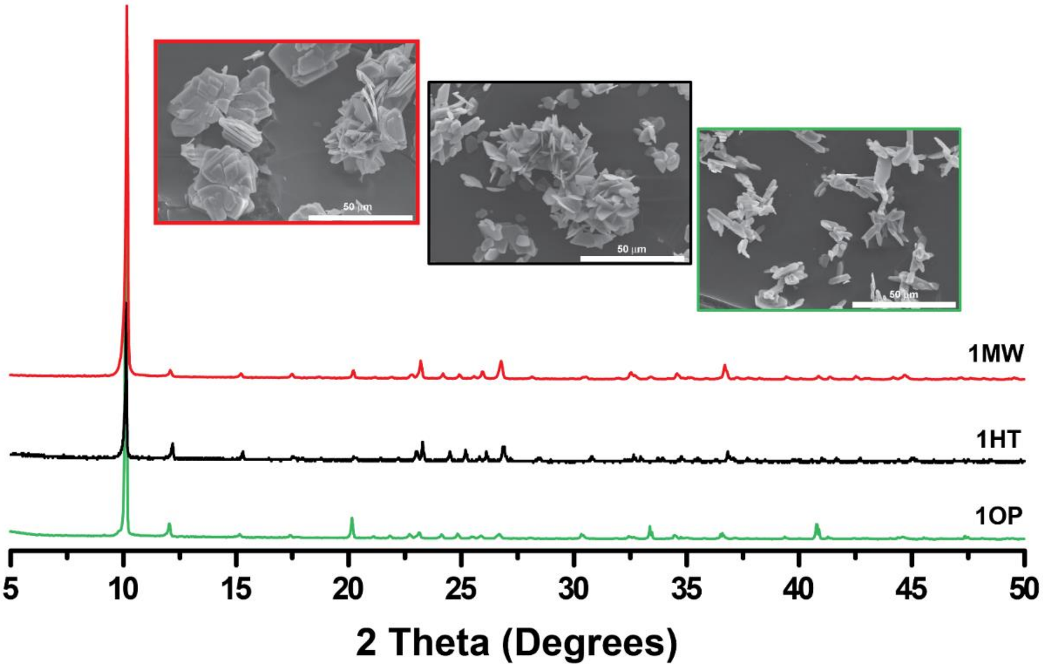

Figure S2. Powder X-ray diffraction and SEM images of $[Gd(H_4nmp)(H_2O)_2]Cl \cdot 2H_2O$ (**1**) obtained using different experimental methods (**op** – one-pot; **mw** – Microwave Assisted; **ht** – Hydrothermal).

3. Additional Catalytic Studies

The desulfurization process conciliates extraction of the sulfur compounds from the diesel phase to the extraction solvent phase and an oxidative catalytic step. The extractive and catalytic oxidative desulfurization system (ECODS) used in this work started by an initial extraction step by stirring the biphasic diesel/extraction solvent system for 10 min at 70 ◦C. During this period occurs the transfer of sulfur compounds from the model diesel to the extraction solvent. After 10 min of stirring, an equilibrium in the sulfur transfer between the two phases was achieved, and the removal of more sulfur compounds from model diesel only occurred after the addition of H_2O_2 oxidant that initiates the oxidative catalytic stage of the process. At this point, the sulfur compounds in the extraction solvent are oxidized to sulfoxides and/or sulfones. This leads to a continuous transfer of non-oxidized sulfur compounds from the model diesel to the extraction phase. The oxidant chosen was 30% aq. H_2O_2 due to its environmental friendliness, stability and availability.

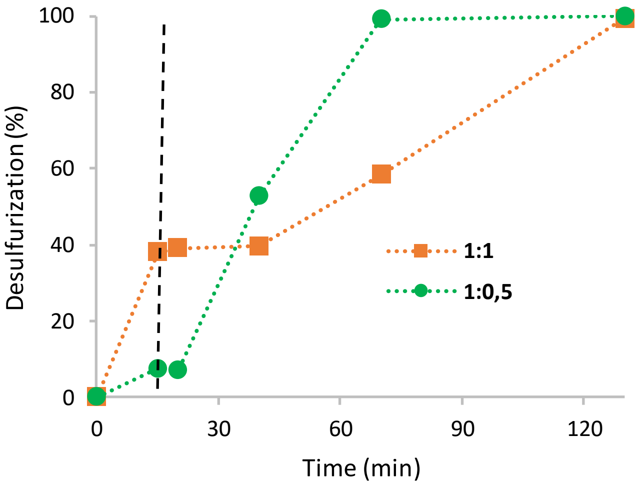

Figure S3. Desulfurization of a multicomponent model diesel (2350 ppm S) catalyzed by layered MOF [Gd(H_4nmp)(H_2O)$_2$]Cl·2H_2O (20 mg), using 0.43 mmol of H_2O_2 oxidant and different volume of [BMIM]PF_6 extraction solvent (1:1 and 1:0.5 model diesel/[BMIM]PF_6), at 70 °C. The vertical dashed line indicates the instant that oxidative catalytic reaction was started by addition of oxidant.

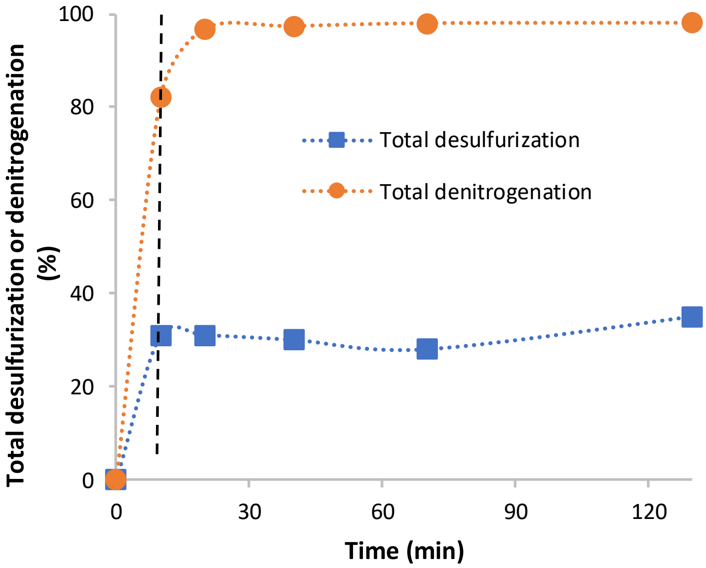

Figure S4. Denitrogenation and desulfurization profile of a model diesel containing approximately 400 ppm N and 2200 ppm of S, catalysed by layered MOF $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ (20 mg), 0.43 mmol of H_2O_2 oxidant and 1:0.5 model diesel/$[BMIM]PF_6$, at 70 ℃. The vertical dashed line indicates the instant that oxidative catalytic reaction was started by addition of oxidant.

3.2. Structural Stability of [Gd(H_4nmp)(H_2O)$_2$]Cl $2H_2O$

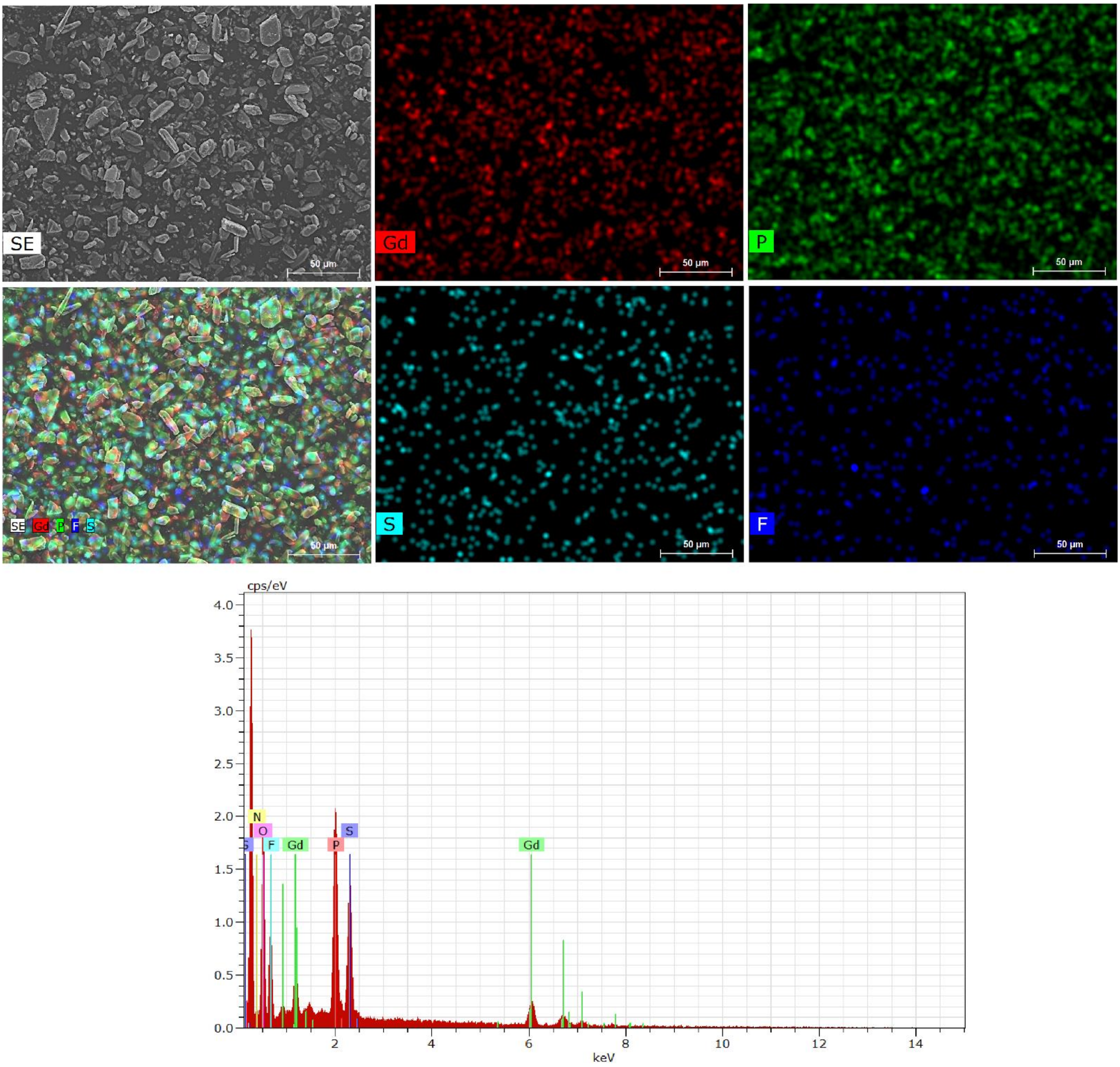

Figure S5. SEM, mapping and EDS spectra of compound [Gd(H_4nmp)(H_2O)$_2$]Cl $2H_2O$ (**1**) after catalytic use for one cycle of ECODS, with a P:Gd ratio of 3:1.

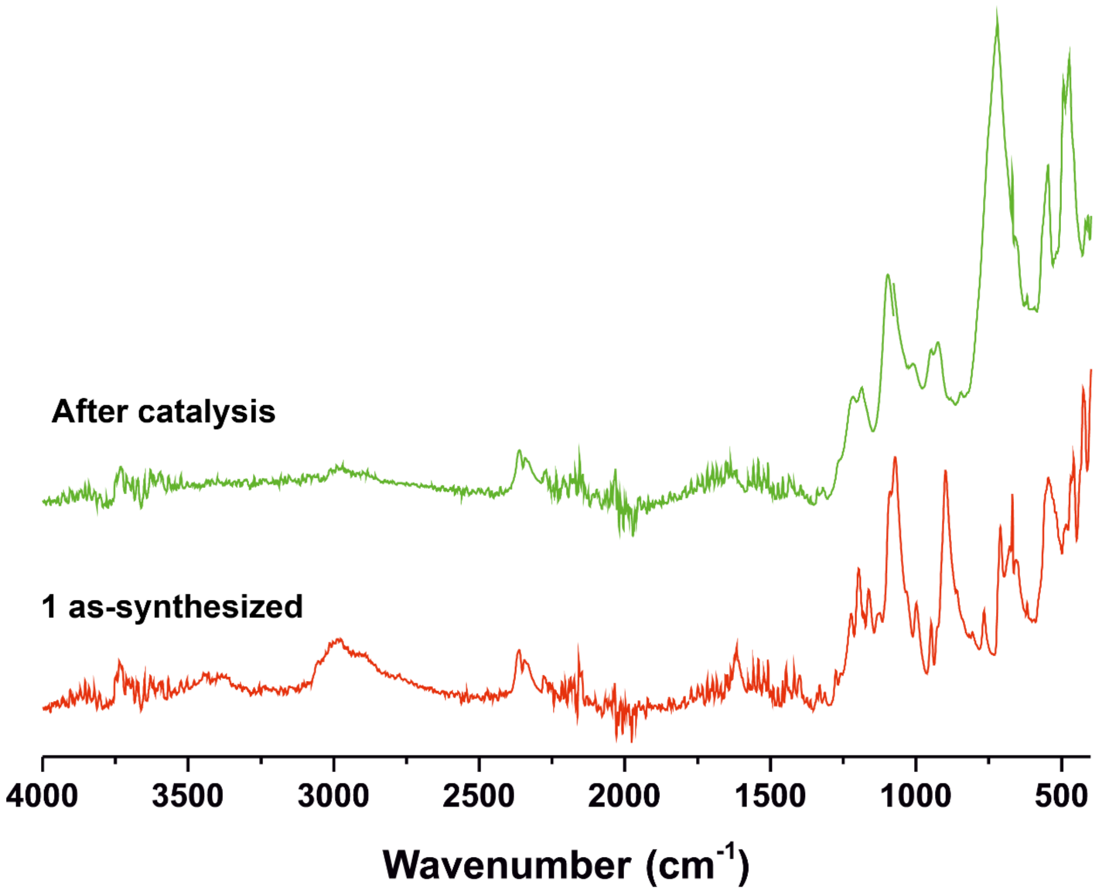

Figure S6. FT-IR spectra of layered [Gd(H_4nmp)(H_2O)$_2$]Cl·2H_2O before and after catalytic use for one ECODS cycle.