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Keywords: amphiphilic, catalysis, surfactant

MS31.P18

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Potential Pt-complexes for catalytic water splitting

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To meet the ever-growing demand for green and carbon neutral energy, water splitting for the generation of hydrogen fuel represents an appealing strategy. Platinum is currently being investigated to mediate mono-nuclear water splitting reactions in an effort to understand the fundamental steps of O-H and O-O bond activation. This research is directed at synthesizing and studying plausible organometallic intermediates (Pt-OH and Pt-H species) in order to determine what role they play in the water activation process. The crystal structures of the following complexes will be presented:

(I) $C_{79}H_{88}N_2$; MW = 1065.51; T = 100 K; $\lambda = 1.54178 \text{ \AA}$; triclinic; P 1; a = 10.4847(2), b = 10.8571(3), c = 14.8431(3) \AA , $\alpha = 77.447(1)$, $\beta = 82.283(1)$, $\gamma = 85.908(1)^\circ$, V = 1632.76(6) \AA^3 ; Z = 1; $D_c = 1.084 \text{ Mg/m}^3$; u = 0.460 mm^{-1} ; F(000) = 576; R [$I > 2\sigma(I)$] = 0.0589; twin fraction = 0.46(10).

(II) $C_{92}H_{102}ClN_3O_3Pt$; MW = 1528.31; T = 173 K; $\lambda = 0.71073 \text{ \AA}$; triclinic; P -1; a = 11.9160(4), b = 17.2432(4), c = 21.2196(7) \AA , $\alpha = 77.787(2)$, $\beta = 87.935(1)$, $\gamma = 74.098(2)^\circ$; V = 4097.1(2) \AA^3 ; Z = 2; $D_c = 1.239 \text{ Mg/m}^3$; u = 1.794 mm^{-1} ; F(000) = 1588; R [$I > 2\sigma(I)$] = 0.0761.

(III) $C_{85}H_{101}ClN_2O_4Pt$; MW = 1445.22; T = 173 K; $\lambda = 0.71073 \text{ \AA}$; triclinic; P -1; a = 10.8290(1), b = 19.6712(4), c = 20.7832(4) \AA , $\alpha = 63.472(1)$, $\beta = 77.109(1)$, $\gamma = 74.190(1)^\circ$; V = 3784.73(11) \AA^3 ; Z = 2; $D_c = 1.268 \text{ Mg/m}^3$; u = 1.939 mm^{-1} ; F(000) = 1504; R [$I > 2\sigma(I)$] = 0.0382.

(IV) $C_{83}H_{96}N_4O_8Pt$; MW = 1472.73; T = 173 K; $\lambda = 0.71073 \text{ \AA}$; triclinic; P -1; a = 11.0942(6), b = 11.0872(5), c = 16.7892(7) \AA , $\alpha = 98.593(3)$, $\beta = 99.870(3)$, $\gamma = 110.025(2)^\circ$; V = 1862.6(2) \AA^3 ; Z = 1; $D_c = 1.313 \text{ Mg/m}^3$; u = 1.941 mm^{-1} ; F(000) = 764; R [$I > 2\sigma(I)$] = 0.0670; Flack parameter = 0.100(11).

The ligand was made to be "super" bulky to prevent dimerization (in an attempt to study mono-nuclear water splitting). The nitro and chloro complexes were made as precursors to making the hydroxide compound.

Keywords: organometallic, intermediates, catalysts

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XRD, SAXS and XANES studies of mesoporous zirconia-based materials

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The synthesis of ordered mesoporous zirconia based structures

for catalytic applications is a research area under development. These systems are also potential candidates as anodes in intermediate temperature solid oxide fuel cells [1-3]. Ordered mesoporous zirconia can be formed with a polymeric template, but during the calcination process the amorphous walls crystallize, causing the collapse of the ordered network [3]. Nevertheless, many synthesis strategies can be explored in order to attain high surface areas (50-100 m^2/g), even in disordered porous networks. In this work the zirconia based materials were prepared with ZrCl₄, Pluronic P123, ethanol and water, varying some synthesis parameters. SAXS, XRD, and XANES at Zr L₂ and L₃ edges were performed to characterize the samples.

For samples heated in water vapor, the SAXS results showed that the ordered mesoporous structure vanished after calcination. The XRD data revealed a single tetragonal zirconia crystalline wall, free of chloride species after a 400°C calcination process. On the other hand, the SAXS data related to the sample that remained in an autoclave for 48 hours, showed a partially ordered structure after calcination. The XRD results showed a mixture of tetragonal and monoclinic phases, besides chloride species that did not decompose at 540°C. The use of a less acidic precursor solution overcame this problem.

In order to study probable changes on the Zr first shell in pure ZrO₂ samples prepared by different synthesis processes, XANES data were collected by TEY at Zr L_{2,3} edges at the D04A/SXS beamline of LNLS (Brazil). ZrO₂ monoclinic standard (coordination number, CN=7), BaZrO₃ and ZrSiO₄ standards (CN equal to 6 and 8, respectively) were measured. A calibration curve was built, fitting each spectrum of the Zr L₃ edge and taking the energy split of the molecular orbitals. The sample synthesized with hydrothermal treatment in water vapor and calcinated at 400°C should present a CN close to 8, since its XRD data revealed a tetragonal structure, but the XANES analysis showed a CN close to 7. Previous XAS results of nanocrystalline tetragonal zirconia at Zr K edge showed a lower coordination number, related to the high disorder of the O atoms in Zr first shell [4,5], in agreement with the present work. For the samples calcinated at 540°C the mixture of crystalline phases detected by XRD are in agreement with the obtained CN close to 7.

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Keywords: zirconia, porous, XANES.

MS31.P20

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Structure/activity relationships: pre-catalysts for alkene methoxycarbonylation

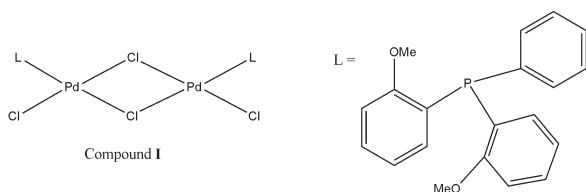
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Catalytic reactions in which the elements of carbon monoxide (CO) and water / alcohols are added to the double bond of alkenes are referred to as hydrocarbonylations / alkoxy carbonylations [1]. Palladium / phosphine systems are generally the preferred catalysts in these reactions since they work under relatively mild conditions [1]. The regioselectivity (linear to branched ratio) of these Pd-catalyzed reactions has been extensively investigated for styrene and related vinylarenes aimed at the synthesis of non-steroidal anti-inflammatory

agents [2]. However, the information on the regioselectivity of the corresponding reaction of simple α -olefins is fragmentary, particularly with regard to branched chain selectivity.

Our approach to the synthesis of methyl methacrylate [3], an important monomer in the polymer industry, requires the efficient conversion of propene into methyl-2-methylpropionate as a key step. This has been achieved as part of an ongoing study [4] of the methoxycarbonylation of α -olefins. A detailed kinetic study indicated the dependence of reaction rate on pressure, temperature, solvent polarity, acidity, etc. In addition the results indicated the separation of the rate determining step and the step in which the regioselectivity is established. This selectivity appears to depend on the competition between Markovnikov and anti-Markovnikov addition of Pd-H to α -olefins [5], which is critically dependent on solvent polarity and ligand (triarylphosphine) structure (both steric and electronic).

Structure determination by single-crystal X-ray diffraction of several catalytic precursors [6 – 9] (one such example is compound **1**) has been carried out and has provided much insight into the relationship between reaction mechanism and selectivity and this work focuses on these structure/activity relationships.



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Keywords: carbonylation catalysis, α -olefins, single-crystal X-ray diffraction

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Hydrothermal synthesis of 3D mixed sulfate-succinate MOFs

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In previous works, the synthesis of succinates of rare- earth has been carried out to find 2- and 3D MOFs with different properties such as catalytic activity, optical and magnetic properties [1].

Here we report four novel compounds [$\text{Ln}_2(\text{C}_2\text{H}_4\text{C}_2\text{O}_4)_2(\text{SO}_4)(\text{H}_2\text{O})_2$] [$\text{Ln} = \text{La}$ (1), Pr (2), Nd (3) and Sm (4)] hydrothermally synthesized and characterised by single crystal X-ray diffraction, powder X-ray diffraction, IR spectroscopy and thermal analysis (TGA). The crystalline products are a series of isostructural 3D polymeric compounds that crystallize in the monoclinic system, space group P2(1)/n. The compounds are formed by dimeric building blocks of trivalent lanthanide cations nona-coordinated linked by the succinate ligand, which acts as oxo-carboxylate bridge in *b* direction and links the metallic chains in *c* direction. The layers are linked in *a* direction by the sulfate anion and a slightly twisted succinate ligand. The use of

the sulfate anion as tetradentate ligand ($\mu_4 \eta^2$) allows the formation of a mixed compound with 3D structure. The presence of the sulfate ligand and strong intramolecular hydrogen bonds contribute to stability of these compounds in comparison with analogues hydrates, as may be seen in the thermal analysis.

1-4 were tested in the hydrogenation of nitro group in aryl derivatives obtaining excellent activity and selectivity.

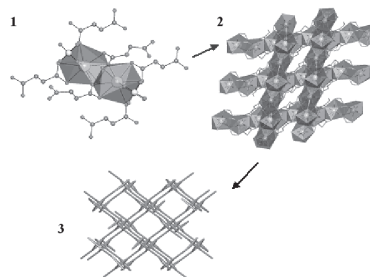


Fig 1. Building block of the isostructural compounds (1) and tridimensional representations (2, 3).

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Keywords: lanthanide MOFs, Sulfate-succinate, Heterogeneous catalysis

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A rod packing Zn MOF: acid catalyst in multicomponent reaction (MCR) and topology

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Following the previous studies of our group we used 4,4'-(hexafluoroisopropylidene)diphthalic anhydride as a flexible ligand in order to achieve new topologies in MOFs. By hydrothermal synthesis we have obtained a new Zn MOF with composition $[\text{Zn}_3(\text{H}_2\text{O})(\text{C}_{19}\text{O}_8\text{H}_7\text{F}_6)](\text{H}_2\text{O})_{0.33}$ (**1**). Its structure has been solved from single crystal X-Ray diffraction data. According with rod packing classification, the topological type for the net of (**1**) is **eta**. It is a chiral and uninodal 3-connected net. The final topology is characterized by the Schläfli symbol: $\{8^3\}$, vertex symbol with circuits: $[8.8.8(2)]$. Topological classification was done with TOPOS¹ and optimized with SYSTRE².

This Zn MOF has been tested as acid catalyst in a multicomponent reaction, and its activity is compared with the corresponding for different Zn MOFs with the same ligand [3,4].

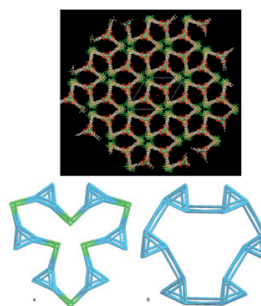


Figure 1 up: Crystal Structure of $[\text{Zn}_3(\text{H}_2\text{O})(\text{C}_{19}\text{O}_8\text{H}_7\text{F}_6)](\text{H}_2\text{O})_{0.33}$, **down:** topology of decorated net (a), not decorated net (b).