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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.

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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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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