



Well-defined lanthanum ethylenediaminetetraacetates as the precursors of catalysts for the oxidative coupling of methane



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ABSTRACT

Water-soluble metal organic framework (MOF) complex $[\text{La}_5\text{Cl}_2(\text{edta})_3(\text{H}_2\text{O})_{18}]_n\text{Cl}_n \cdot 8n\text{H}_2\text{O}$ (**1**) is converted to its nitrate or sulfate derivatives $[\text{La}_2(\text{NO}_3)_2(\text{edta})(\text{H}_2\text{O})_5]_n \cdot 3n\text{H}_2\text{O}$ (**2**), $[\text{La}_2(\text{SO}_4)(\text{edta})(\text{H}_2\text{O})_3]_n$ (**3**) ($\text{H}_4\text{edta} = \text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, ethylenediaminetetraacetic acid). The three well-defined complexes are further calcinated for the preparations of pure lanthanum oxides LaOCl , $\text{La}_2\text{O}_2\text{CO}_3$ and $\text{La}_2\text{O}_2\text{SO}_4$ or their mixtures respectively. The oxides from **1** to **2** show good catalytic performances for the oxidative coupling reaction of methane (OCM). Their conversions of methane and the selectivities to C_2 achieved 24.5%, 39.2% and 28.0%, 47.4% respectively at low temperature 550 °C, while the pure $\text{La}_2\text{O}_2\text{SO}_4$ from **3** is not active at low temperature. The latter is contradict to the result by simple treatment of $\text{La}_2(\text{SO}_4)_3$ reported previously.

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1. Introduction

The construction of lanthanide complexes is an interesting topic due to its attractive chemical properties of luminescence [1–3], magnetic [4,5], and application in catalysis [6–10], precursors for the syntheses of nanoparticles [11–17] and so on. On account of the high affinity to hard donor atoms of lanthanides, aminopolycarboxylates are widely exploited for their capability of bridging metal centers in various coordination modes [18–21]. However, as a widely used multidentate ligand, ethylenediaminetetraacetic acid shows limited coordination modes with lanthanides, such as a mononuclear or oligomer species $\text{Ln}(\text{edta}) \cdot n\text{H}_2\text{O}$ or $\text{MLn}(\text{edta}) \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Na}, \text{K}, \text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Er}$) [22–25], $\text{Na}_2\text{K}_2[\text{Ce}_2(\text{O}_2)_2(\text{edta})_2] \cdot 13\text{H}_2\text{O}$ [26], $\text{Na}_{10}[\text{La}_4(\mu_3\text{-OH})_4(\text{edta})_4] \cdot 2\text{ClO}_4 \cdot 27\text{H}_2\text{O}$ [27]. Most of the insoluble coordination polymers are formed in hydrothermal condition with general formula $\{[\text{Ln}(\text{Hedta})(\text{H}_2\text{O})_2]_n$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Er}$) [28–31], and one $[\text{Ce}_3(\text{Hedta})_2(\text{H}_2\text{O})_9]_n[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]_n \cdot n\text{H}_2\text{O}$ was reported [32]. Here, a novel 2-D water-soluble MOF of lanthanum ethylenediaminetetraacetate $[\text{La}_5\text{Cl}_2(\text{edta})_3(\text{H}_2\text{O})_{18}]_n\text{Cl}_n \cdot 8n\text{H}_2\text{O}$ (**1**) was obtained in mild condition with excess metal salt and converted to its nitrate or sulfate derivative $[\text{La}_2(\text{NO}_3)_2(\text{edta})(\text{H}_2\text{O})_5]_n \cdot 3n\text{H}_2\text{O}$ (**2**), $[\text{La}_2(\text{SO}_4)(\text{edta})(\text{H}_2\text{O})_3]_n$ (**3**) by the addition of nitrate or sulfate.

The three novel lanthanum ethylenediaminetetraacetates **1–3** are synthesized with different coordinated anions, which are used as the precursors after thermal treatment to obtain the catalysts of lanthanum oxides. Usually, the metal oxides can be synthesized in several ways, such as sol–gel [33–36], carbonate [37], templates [38–40], homogeneous precipitation [41,42] et al. Thermal treatment of well-defined polymeric precursor method is attractive, since it decomposes to high purity oxides at a moderate calcinating temperature with explicit composition [43]. Besides that, there is template effect of precursor morphology during the syntheses of oxide through thermal decomposition method [44,45]. It is noted that the catalytic performances of lanthanum oxides [46–49] are influenced by their anion species for the selectivity to C_2 in oxidative coupling reaction of methane (OCM) [50]. Several lanthanum catalysts such as halide-containing lanthanum oxide, lanthanum carbonate and sulfate have been investigated and shown good OCM performances [51–53]. Much information is needed for the lanthanum catalysts. Here the thermal decomposition of lanthanides **1–3** were assigned as pure LaOCl , $\text{La}_2\text{O}_2\text{CO}_3$ and $\text{La}_2\text{O}_2\text{SO}_4$ or their mixtures respectively, and their catalytic performances for OCM were investigated.

2. Experimental

2.1. Materials and instrumentation

All chemicals were of analytical or reagent grade purity and used as received. The pH value was measured by potentiometric

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method with a digital PHB-8 pH meter. Infrared spectra were recorded as Nujol mulls between KBr plates on a Nicolet 200 FT-IR spectrometer. Elemental analyses were carried out using an EA 1110 elemental analyzer. Solution $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded in D_2O on a Bruker AV 400/500 MHz NMR spectrometer using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an internal reference. Solid state ^{13}C NMR spectra were recorded on a Bruker AV 400 MHz NMR spectrometer using cross polarization, magic angle spinning (13 kHz) and adamantane as reference. Thermogravimetric analysis were recorded on a SQT-Q600 and TG 209F1 thermal analyzers, under an air flow of 100 mL/min at a heating rate of 10 °C/min. X-ray powder diffraction (XRD) analysis was carried out on a Rigaku Ultima IV X-ray diffractometer with scanning 2θ from 20° to 80°. Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) obtained at 40 kV and 30 mA was used as the X-ray source.

2.2. Synthesis

Synthesis of $[\text{La}_5\text{Cl}_2(\text{edta})_3(\text{H}_2\text{O})_{18}]_n\text{Cl}_n \cdot 8n\text{H}_2\text{O}$ (**1**)

Ethylenediaminetetraacetic acid (3.0 g, 10 mmol) was added to a stirred solution of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (11.1 g, 30 mmol) in water (50 mL). The mixture was stirred for two hours at room temperature, and the pH value was adjusted to 6.5 by imidazole (1.0 mol L^{-1}). Colorless crystalline product was obtained after several days and isolated by filtration. Yield: 5.8 g (81.6%) (with respect to H_4edta). IR (KBr, cm^{-1}): $\nu_s(\text{CO}_2)$ 1582_{vs}, $\nu_{as}(\text{CO}_2)$ 1439_m, 1414_s, 1329_m; Anal. Calc. for $\text{C}_{30}\text{H}_{88}\text{N}_6\text{O}_{50}\text{La}_5\text{Cl}_3$: C, 16.9; H, 4.2; N, 3.9. Found: C, 16.5; H, 4.2; N, 3.9%.

Synthesis of $[\text{La}_2(\text{NO}_3)_2(\text{edta})(\text{H}_2\text{O})_5]_n \cdot 3n\text{H}_2\text{O}$ (**2**)

The above chloride **1** (2.1 g, 1.0 mmol) and excess ammonium nitrate (0.26 g, 3.0 mmol) were added in water (10 mL) and stirred. The pH value of the solution was adjusted to 6.5 by imidazole (1.0 mol L^{-1}). Colorless crystalline product was obtained after several days and isolated by filtration. Yield: 0.54 g (64.7%) (with respect to chloride **1**). IR (KBr, cm^{-1}): $\nu_s(\text{CO}_2)$ 1583_{vs}, $\nu_{as}(\text{CO}_2)$ 1490_w, 1441_s, 1419_s, 1384_{vs}, 1327_s; Anal. Calc. for $\text{C}_{10}\text{H}_{28}\text{N}_4\text{O}_{22}\text{La}_2$: C, 14.4; H, 3.4; N, 6.7. Found: C, 14.1; H, 3.3; N, 6.7%.

Synthesis of $[\text{La}_2(\text{SO}_4)(\text{edta})(\text{H}_2\text{O})_3]_n$ (**3**)

Similarly, chloride **1** (2.1 g, 1.0 mmol) and excess ammonium sulfate (0.43 g, 3.0 mmol) were added in water (10 mL) and stirred.

The pH value of the solution was adjusted to 6.5 by imidazole (1.0 mol L^{-1}) and heated at 70 °C for four days to obtain the colorless crystalline product. Yield: 0.45 g (62.8%) (with respect to chloride **1**). IR (KBr, cm^{-1}): $\nu_s(\text{CO}_2)$ 1644_m, 1581_{vs}, $\nu_{as}(\text{CO}_2)$ 1443_w, 1408_m, 1338_w, 1325_w; Anal. Calc. for $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_{15}\text{S}_1\text{La}_2$: C, 16.8; H, 2.5; N, 3.9. Found: C, 16.4; H, 2.3; N, 3.7%.

2.3. Catalytic reaction

The catalytic performances of the catalysts were investigated using a $\text{CH}_4/\text{O}_2 = 3/1$ mixture (molar ratio) as a reaction feed. The OCM reaction for the investigated samples was carried out in a fixed-bed quartz tubular reactor (internal diameter 5 mm) at atmospheric pressure and a total flow rate of 50 mL/min. The reactor was packed with 0.10 g samples (40–60 mesh size) between quartz wool plugs. The reactor was heated with a furnace connected to a temperature controller (Yudian AI-708PFKSL2). The performances of the catalysts were evaluated over 550–750 °C with a gas hourly space velocity (GHSV) of 15,000 mL/(g h).

2.4. X-ray crystallography

Complexes **1–3** were measured at 173(2) K on an Oxford Gemini S Ultra CCD diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The initial model was obtained through direct methods and the completion of the rest of the structure achieved by difference Fourier strategies. The structures were refined by least squares on F^2 , with anisotropic displacement parameters for non-H atoms. For **1**, the unit cell includes a large region of disordered solvent water molecules and chlorides, which could not be modelled as discrete atomic sites. PLATON/SQUEEZE [54] was employed to calculate the diffraction contribution of the solvent molecules and chloride counteranions, in order to produce a set of solvent-free diffraction intensities. The SQUEEZE calculations showed a total solvent accessible area volume of 745 \AA^3 in **1** and the residual electron density amounted to 195 e per unit cell, considering the charge balance, it is assigned to nearly 16 water molecules and 2 chlorides (H_2O : 10e, Cl^- : 18e). All calculations to solve and refine the structures were carried out with SHELXS 97 and SHELXL 97 programs [55,56]. Crystallographic data for **1–3** were listed in Table 1.

Table 1

Crystallographic data for $[\text{La}_5\text{Cl}_2(\text{edta})_3(\text{H}_2\text{O})_{18}]_n\text{Cl}_n \cdot 8n\text{H}_2\text{O}$ (**1**), $[\text{La}_2(\text{NO}_3)_2(\text{edta})(\text{H}_2\text{O})_5]_n \cdot 3n\text{H}_2\text{O}$ (**2**) and $[\text{La}_2(\text{SO}_4)(\text{edta})(\text{H}_2\text{O})_3]_n$ (**3**).

Compound reference	1	2	3
Empirical formula	$\text{C}_{30}\text{H}_{88}\text{Cl}_3\text{La}_5\text{N}_6\text{O}_{50}$	$\text{C}_{10}\text{H}_{28}\text{La}_2\text{N}_4\text{O}_{22}$	$\text{C}_{10}\text{H}_{18}\text{La}_2\text{N}_2\text{O}_{15}\text{S}$
Formula weight	2133.92	834.18	716.14
Crystal system	trigonal	monoclinic	monoclinic
<i>a</i> (Å)	17.242(1)	12.7623(4)	8.1727(2)
<i>b</i> (Å)	17.242(1)	8.3831(2)	9.2832(2)
<i>c</i> (Å)	17.242(1)	23.9610(7)	24.6545(7)
α (°)	61.04		
β (°)	61.04	104.924(3)	90.535(3)
γ (°)	61.04		
Unit cell volume (Å ³)	3709.4(5)	2477.1(1)	1870.43(8)
<i>T</i> (K)		173(2)	
Space group	<i>R</i> -3 <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
No. of formula units per unit cell, <i>Z</i>	2	4	4
No. of reflections measured	13,524	21,005	6417
No. of independent reflections	2303	5490	3765
<i>R</i> _{int}	0.0674	0.0488	0.0253
Final <i>R</i> ₁ values ($I > 2\sigma(I)$) ^a	0.0792	0.0330	0.0303
Final <i>wR</i> (<i>F</i> ²) values ($I > 2\sigma(I)$)	0.2184	0.0714	0.1028
Final <i>R</i> ₁ values (all data) ^b	0.0897	0.0407	0.0342
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.2295	0.0747	0.1075
Goodness-of-fit (GOF) on <i>F</i> ²	0.790	1.156	0.840

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]^{1/2}$.

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