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Synthesis and characterization of lanthanum acetate for application as a catalyst

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Abstract

The use of precursors based upon the rare earths is of considerable interest for the manufacture of catalysts. Starting with a rare earths fraction depleted in cerium (a low cerium carbonate, LCC) produced locally by the industrial processing of monazite sand as raw material, a very pure concentrate of lanthanum was prepared. The rare earth chloride solution was loaded into a strong cationic ion-exchange resin and then eluted using the ammonium salt of EDTA. No barrier ion was used. The lanthanum fraction was separated from the EDTA and then precipitated as oxalate and fired to lanthanum oxide. The lanthanum oxide was fairly easily dissolved using only acetic acid from which lanthanum acetate was crystallized. The solid salt was characterized via thermal analysis, chemical analysis, X-ray diffraction, inductively coupled plasma optical emission spectrometry and infrared spectroscopy. An aqueous solution of lanthanum acetate was prepared to be added to alumina microspheres support, especially sinthesized by the sol–gel process for use as a catalyst. Further work will involve the preparation of a highly specific surface lanthanum oxide via lanthanum acetate to be used as a catalyst and to be compared with the alumina–lanthanum oxide catalyst.

Keywords: Precursors; Rare earths; Lanthanum acetate; Catalysts

1. Introduction

Lanthanum and its compounds are being increasingly applied in the manufacture of new materials such as special glasses, lenses, lasers, semiconductors, metallic alloys, special ceramic materials and catalysts for use in petroleum cracking and car exhaust gas treatment. The Instituto de Pesquisas Energeticas e Nucleares (IPEN), São Paulo, has in operation an experimental production facility for the preparation and purification of rare earth compounds.

In the present work the separation of lanthanum from a rare earth chloride solution prepared from a low cerium carbonate fraction is discussed. Very pure lanthanum acetate and oxide fractions are obtained via an ion-exchange technique. Lanthanum acetate solution was prepared aiming towards its use for the impregnation alumina spheres specially fabricated as support for the lanthanum salt and its conversion to oxide over the alumina. On the other hand, from crystallized lanthanum acetate was prepared lanthanum oxide to serve as a catalyst and as a support for metallic ions that can be converted to oxides. Further work is scheduled for testing both preparations as catalysts.

2. Experimental

2.1. Dissolution of the low cerium carbonate (LCC)

This rare earth concentrate produced by the monazite sand local industrialization whose average concentration is depicted in Table 1 was treated with hydrochloric acid to dissolve it and obtain the corresponding chlorides. The LCC was slurried slowly over the hot acid, under constant

Table 1
Average composition of the low cerium carbonate (LCC)

Constituent	Content (%)	Constituent	Content (%)
La_2O_3	45.9	Tb_4O_7	0.1
CeO_2	3.7	Dy_2O_3	0.3
Pr_6O_{11}	8.4	Ho_2O_3	<0.05
Nd_2O_3	33.6	Er_2O_3	<0.05
Sm_2O_3	4.6	Yb_2O_3	<0.05
Eu_2O_3	0.1	Y_2O_3	1.1
Gd_2O_3	2.2		

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agitation.The solution was filtered to remove some insolubles and then made up to volume. The total rare earth concentration was determined via oxalic acid precipitation and calcination to the oxides [1]. The final rare earth stock solution was 100 g l^{-1} in R_2O_3 (total oxide) and pH 6.0.

2.2. Separation of cerium

The separation of cerium was accomplished directly by a fractional precipitation technique in the $RECl_3$–NH_3–air–H_2O_2 system from the mixed rare earth chlorides using the stock solution by a hydrolytic–oxidation process. Cerium(III) was oxidized to cerium(IV) by the controlled introduction of 30% volume hydrogen peroxide. The acidity liberated by the hydrolytic process was continuously neutralized by the NH_3 stream generated by compressed air injected into the 1 mol l^{-1} NH_4OH solution and bubbled directly into the solution of rare earth chlorides. During the cerium precipitation the temperature was maintained at 60 °C. After the cerium precipitation reaction was complete, the precipitate was separated by filtration. The filtrate was then used for the separation and enrichment of lanthanum.

2.3. Separation of lanthanum from the other rare earths

The filtrate from the cerium separation was treated the same way but without use of hydrogen peroxide. The bubbling of NH_3 was done slowly and the precipitation lasted from 2 to 4 h. With this treatment some rare earth fractions free from lanthanum were obtained. After the precipitation of almost the total of other rare earths, lanthanum was precipitated by raising the pH with NH_3. This final precipitate enriched in lanthanum was separated by filtration and then dissolved with hydrochloric acid. The lanthanum chloride was used as the feeding solution to a strong cationic ion exchanger. After the loading the column was rinsed with water and eluted with ammonium salt of EDTA, several eluted fractions being collected. Finally lanthanum was eluted. Free EDTA acid was precipitated by addition of HCl acid and separated by filtration. The ultimate lanthanum chloride solution was treated with oxalic acid and the lanthanum oxalate separated, dried and fired to lanthanum oxide. This highly pure oxide (>99.9%) was directly dissolved with hot concentrated acetic acid. There was no difficulty in this operation aimed at the preparation of the lanthanum acetate.

2.4. Lanthanum acetate crystallization

The lanthanum acetate solution, prepared as above, was evaporated using low temperature heating treatment. The lanthanum acetate crystals were collected, dried overnight using an oven at 65 °C. This first batch of crystals was sent to be analyzed. In a second experiment using the same procedure the solution was crystallized once and then dissolved with a little water in the same beaker and crystallized again. This treatment was repeated again. The crystals prepared in this second batch were dried overnight at 65 °C and sent to be analyzed. In a third experiment, the lanthanum crystals were prepared the same way as the second batch but after the second crystallization the crystals were washed with acetone and dried at room temperature in air atmosphere. Finally the crystals were dried at 65 °C and sent to be analyzed.

3. Results and discussion

3.1. Analytical characterization and purity determination

When necessary, fractions of pure lanthanum solution were analyzed by gravimetry via oxalate precipitation and weighing after the preparation of the oxides by thermal decomposition. For the identification and determination of traces of other rare earths as impurities in the lanthanum oxide extensive use of inductively coupled plasma optical emission spectrometry (ICP-OES) was made based on IPEN/CNEN/SP standard procedures [2].The main rare earth impurities, namely Ce, Nd, Sm, Eu, Tb and Yb were analyzed by neutron activation analysis as well. The results were compared with those obtained by the analysis of international standard (BDH), as can be seen in Table 2.

Minor quantities of rare earth elements as impurities in highly pure lanthanum oxide were analyzed by ICP-MS spectrometry with the plasma source technique [2].

Table 3 shows the results of RE determination in several representatives samples compared with one certified imported RE oxide standard (Johnson Mattey).

3.2. Characterization of the lanthanum acetate by thermal analysis (TG)

Samples of highy pure lanthanum acetate were submited to thermal analysis for characterization. The equipment used in this work was a Shimadzu TGA-50H consisting of a microbalance with continuous recording, an oven and a device for gas work. The samples were analyzed under dynamic atmosphere of synthetic air with a flow of 50

Table 2
Determination of RE impurities in highly pure lanthanum oxide sample by neutron activation analysis

Element	La_2O_3 IPEN	La_2O_3 BDH
Ce	6±1	478±48
Pr	N.a.	N.a.
Nd	15±3	135±52
Sm	N.a.	103±19
Eu	<0.1	8.8±0.1
Tb	1.3±0.1	5.5±0.2
Yb	<1.1	N.a.

N.a., not analyzed.

Table 3
Results of RE impurities determination in the lanthanum oxide

Sample	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Imported	131	68	1130	125	5	475	0.86
La-9	12	21	145	24	0.5	600	93
La-16	17	5	95	24	0.3	415	0.1
La-18	15	5	109	36	0.1	427	0.05
La-19	25	4.7	410	16	0.1	381	0.08
La-21	50	3.2	–	10	0.3	434	0.35
La-23	33	1.3	509	11	0.3	425	0.58
La-25	45	0.8	426	19	0.3	433	0.07
La-29	19	19	–	6	0.1	430	2.03
La-30	253	2	34	16	0.1	485	1.06
La-31	167	1.3	25	12	0.1	397	0.08
	Dy	Ho	Er	Tm	Yb	Lu	Y
Imported	80	12.4	18.5	0.34	61.7	0.3	4
La-9	0.6	0.06	0.5	0.1	22.6	0.08	0
La-16	2.1	0.05	0.6	0	6.6	0	0.6
La-18	2.2	0.06	0.9	0	8.6	0	0
La-19	0.8	0.02	1	0	9.3	0	0.5
La-21	2.8	0.04	0.8	0	9.4	0	0
La-23	3.2	0.07	0.8	0	8.1	0	2.7
La-25	0.4	0.04	0.6	0.04	8.8	0	0.03
La-29	21	0.09	1	0.09	8.8	0.05	0.07
La-30	1.8	0.1	1.4	0.1	10.6	0.05	0
La-31	1.1	0.06	1.4	0.06	11	0.04	0

ml/min and heating rate of 10 °C min^{-1} and the temperature program rate was from 25 to 900 °C.

The data collected using representative lanthanum acetate samples prepared as described in this paper are depicted in Figs. 1–3.

3.3. Characterization by infrared spectroscopy (IR)

IR spectroscopy is a technique used in catalysis, and it provides information in a simple way on the nature of the catalyst according to interactions between absorbate and absorvent. Figs. 4 and 5 depict the IR spectra of two

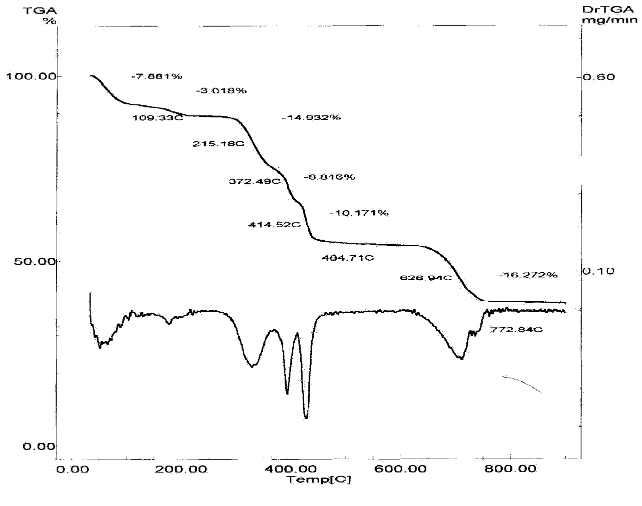

Fig. 1. TG/DTG curves of lanthanum acetate (sample 1) at the heating rates indicated, in a dynamic (50 ml min^{-1}) air atmosphere.

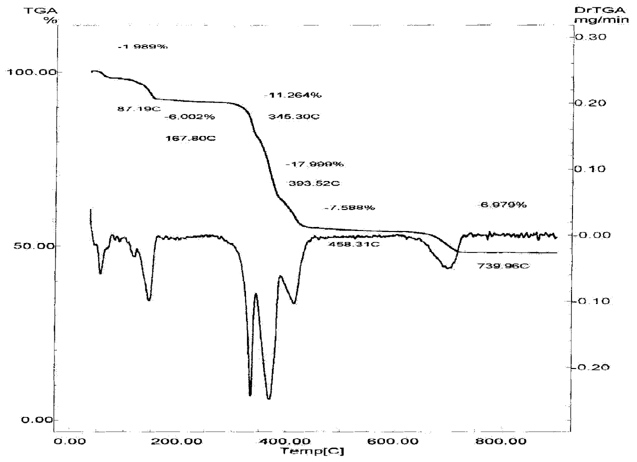

Fig. 2. TG/DTG curves of lanthanum acetate (sample 2) at the heating rates indicated, in a dynamic (50 ml min^{-1}) air atmosphere.

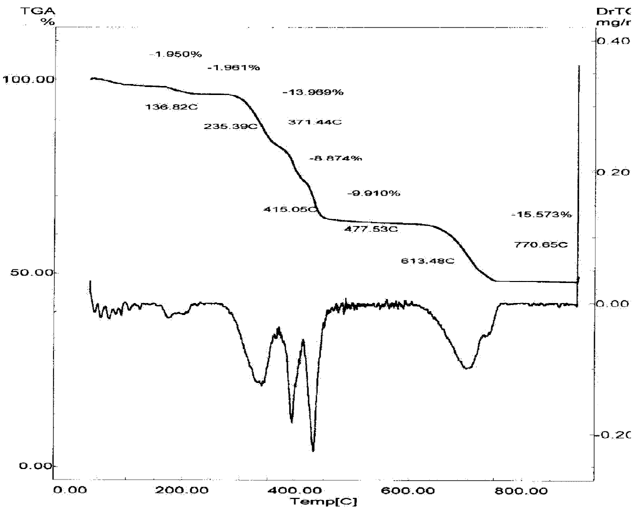

Fig. 3. TG/DTG curves of lanthanum acetate (sample 3) at the heating rates indicated, in a dynamic air atmosphere.

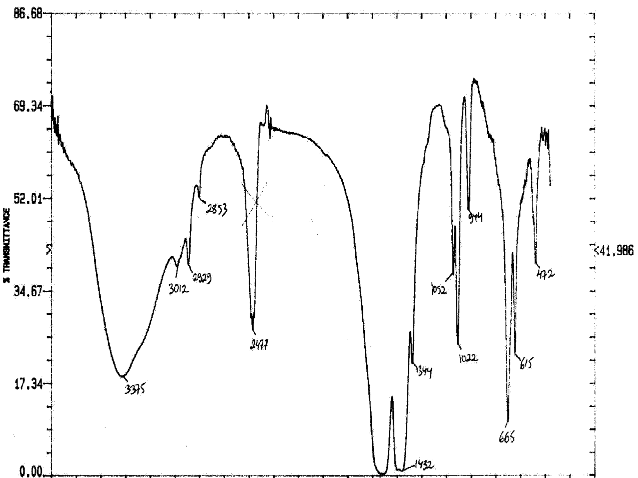

Fig. 4. Infrared spectra; lanthanum acetate (sample 1).

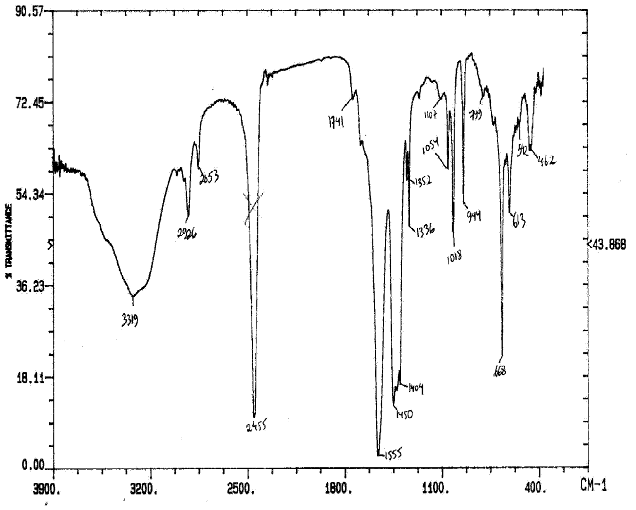

Fig. 5. Infrared spectra; lanthanum acetate (sample 2).

representative lanthanum acetate samples. In Table 4 are the IR absorption bands of the lanthanum acetate samples. The equipment used in this work consists of a Bomem spectrophotometer, model MB-100. The samples were analyzed in the form of tablets containing KBr and the frequency strip varying from 4000 to 200 cm^{-1}.

3.4. X-ray characterization of lanthanum acetate samples

In this study the powder method was used, at room temperature, using a Phillips diffractometer, model PW37610 with copper anode and Ni filter, radiation Kα. The results for the analyzed samples were compared with records patterns of the database JCPDS.

The X-ray analysis identification of the lanthanum acetate samples prepared in this work exhibit three crystalline structures, as indicated by the literature [3]. As a general behaviour the anhydrous lanthanum acetate does not present a reproducible standard when studied by X-ray analysis.

Table 4
Infrared absorption bands of lanthanum acetates frequency cm^{-1}

Sample 1	Sample 2	Band assignments
3375	3319	ν(O–H)
3012		νas(C–H)
2929	2926	νs(C–H)
2853	2853	
	1741	δOH
1566	1555	νas (COO−)
1432	1450	νs(COO−)
	1404	δas(CH3)
1344	1336	δs(CH3)
	1352	
	1107	
1052	1054	ρ(CH3)
1022	1018	
944	944	ν(C–C)
665	668	δ(COO−)
615	613	ρ(COO−)
472	542	π(COO−)
	462	

4. Conclusion

The analytical data collected in this paper for crystallized lanthanum acetate samples led to the conclusion that the representative samples of this compound synthesized at IPEN/São Paulo exhibited the analogous chemical compositilon published by the technical literature [3–6]. The lanthanum acetate prepared in this work has the stoichiometric compostion of $La(CH_3COO)_3 \cdot 1.5H_2O$. Considering the results of the thermal analyses the following steps were identificed:

$$La(CH_3COO)_3 \cdot 1.5H_2O \rightarrow La(CH_3COO)_3 \cdot H_2O + 0.5H_2O \qquad (a)$$

$$La(CH_3COO)_3 \cdot H_2O \rightarrow La(CH_3COO)_3 + H_2O \qquad (b)$$

$$2La(CH_3COO)_3 \rightarrow La_2O_2CO_3 + 3CH_3COCH_3 + 2CO_2 \qquad (c)$$

$$2La_2O_2CO_3 \rightarrow La_2O_3 + CO_2 \qquad (d)$$

The X-ray analysis and infrared identification of the lanthanum acetate samples prepared in this work exhibit three crystalline structures, as indicated by the literature [3]. As a general behaviour the anhydrous lanthanum acetate does not present reproducible standards when studied by X-ray analysis. In this work it was possible to observe that the samples are isomorphous and their crystalline structure belong to the type A.

The catalytic precursor, lanthanum acetate, presents several possibilities of coordination of the anion acetate [3–6]. The representation in those coordination ways is the following: ionic, monodentate, bidentate and polymeric. The nature of the connections in metal acetate is similar. As an exception, in sample 2, at 1741 cm^{-1} the salt was obtained in the hydrated form, due to a deformation in the angle of the molecules of coordinated water (OH).

The next step of this work will be the performance of catalytic tests to verify the efficiency of the synthesized catalytic precursor.

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