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OXIDATIVE DEHYDROGENATION OF ETHANE OVER LANTHANA: ACTUAL NATURE OF THE ACTIVE PHASE

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Characterization studies of lanthana before and after running the oxidative dehydrogenation of ethane (OXDE) on lanthana show the "in situ" transformation of La_2O_3 in hexagonal $La_2O_2CO_3$. Thermodynamic considerations, as well as the results of the catalytic activity essays carried out on an intentionally prepared $La_2O_2CO_3$ sample demonstrate that, under the experimental conditions used, type II lanthanum mono-carbonate dioxide phase constitutes the actual active phase. This may explain the differences of catalytic activity observed between lanthana and several other rare earth sesquioxides.

1. Introduction

The rare earth sesquioxides are considered to be highly active oxides towards H_2O and CO_2 [1,2]. In particular, lanthana, the most basic term of the series, can strongly react with atmospheric H_2O and CO_2 even at room temperature [3].

Nowadays, it is well known that basic oxides, and particularly the rare earth sesquioxides, are interesting catalysts for the methane dimerization [4–9] and closely related reactions like oxidative dehydrogenation of ethane (OXDE) [10,11]. Under catalytic conditions, these processes lead to the formation of significant amounts of H_2O and CO_2, which can modify the actual nature of the catalysts, and consequently their behaviour.

This work reports on the OXDE reaction over lanthana. According to the results of our characterisation studies, under catalytic conditions, the starting catalyst transforms into a monocarbonate dioxide, $La_2O_2CO_3$. The catalytic properties exhibited by an intentionally prepared $La_2O_2CO_3$ sample, as well as thermodynamic considerations regarding the stability of this phase corroborates with our proposal that lanthanum monocarbonate dioxide is the actual active phase in the OXDE on lanthana.

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2. Experimental

The lanthanum oxide investigated was obtained from Rhône-Poulenc Minérale Fine, with a 99.9% purity. Before testing its catalytic behaviour, the sample had been stabilized in air at room temperature. The BET surface area was 5.1 m^2/g. No significant modification of the S_{BET} was observed after the catalytic tests.

The monocarbonate dioxide phase, $La_2O_2CO_3$, was prepared by heating, in flowing CO_2 (101.3 kPa) the aged-in-air lanthana sample mentioned above. The heating rate was 0.1 $K.s.^{-1}$. The sample was held at 773 K for 4 h, and then cooled down to 473 K, always in a flow of CO_2.

The X-ray powder diffraction (XRD) diagrams were recorded with a Philips Instrument, model PW 1710 diffractometer. The radiation was $CuK\alpha$, and a Ni filter was used. The IR spectra were obtained with a Perkin Elmer model 580 spectrometer. The sample disks were prepared in a KBr matrix (95% KBr and 5% sample).

The catalytic activity experiments were performed in a fixed bed reactor at atmospheric pressure. The catalyst (ca. 100 mg) was deposited on a quartz wool bed allocated in the middle of a quartz tube (40 cm × 0.35 cm I.D.). The reaction conditions were: $P_{C_2H_6}$: 8.0 kPa; P_{O_2}: 3.1 kPa; P_{He}: 90.2 kPa; the total flow rate being 1 $cm^3 \cdot s^{-1}$ (HSV : 36000 h^{-1}). The reaction temperature ranged from 673 K to 923 K. Blank experiments with quartz wool were performed before and after running the reaction in the presence of the catalysts. No significant contribution from the homogeneous reaction was observed below 923 K. The products gases were analysed by a double gas chromatographic system using a Katharometer and a flame ionization detector. The separation of the gaseous mixtures was carried out with PORAPAK Q and PORAPAK R columns, respectively.

3. Results and discussion

It is well known [2,3] that, upon exposure to air, at 298 K, for a few hours, lanthana completely disappears with formation of a partially carbonated hydroxide. In accordance with this, our lanthana sample, which as usual had been stored and manipulated in air with no special precautions, shows an XRD diagram and an IR spectrum, figs. 1a and 2a, which are in complete agreement with those reported in the literature for an aged-in-air lanthanum oxide [2,3].

It is also known [2], that the carbonation in air of La_2O_3 is much less strong than its hydration, the intensity of the former process depending on the surface area of the sample. In the present case, since the lanthana sample has a low surface area, the initial CO_2 uptake is small, which is qualitatively confirmed by the weak intensity of the IR bands appearing in fig. 2a between 1300 cm^{-1} and 1600 cm^{-1}, typically due to carbonate species [12,13], compared to the intensity of the band observed at 3600 cm^{-1}, corresponding to $La(OH)_3$ [3,14].

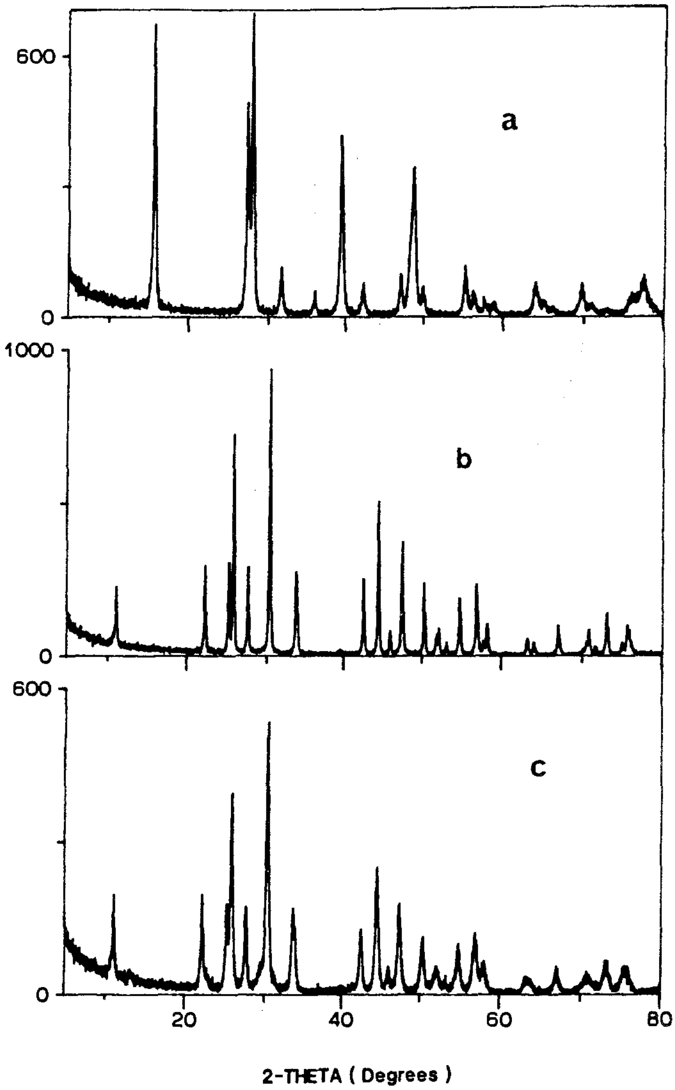

Fig. 1. X-ray powder diffraction diagrams corresponding to: a) aged-in-air lanthanum oxide; b) lanthana catalyst after OXDE reaction; c) hexagonal $La_2O_2CO_3$ prepared in the present work.

The study of the catalytic activity of lanthana for the oxidative dehydrogenation of ethane has revealed that the main reaction products are C_2H_4, CO_2 and CO. Small amounts of CH_4 and higher, C_3 and C_4, hydrocarbons have also been observed, the latter ones being detected only at the highest temperatures of the experimental range investigated here. The activity was measured step by step, by increasing and then decreasing temperatures. An hysteresis in the conversion curve was observed indicating a deactivation of the lanthane catalyst. For example, at 773 K, the conversion was lowered by a factor higher than 5.

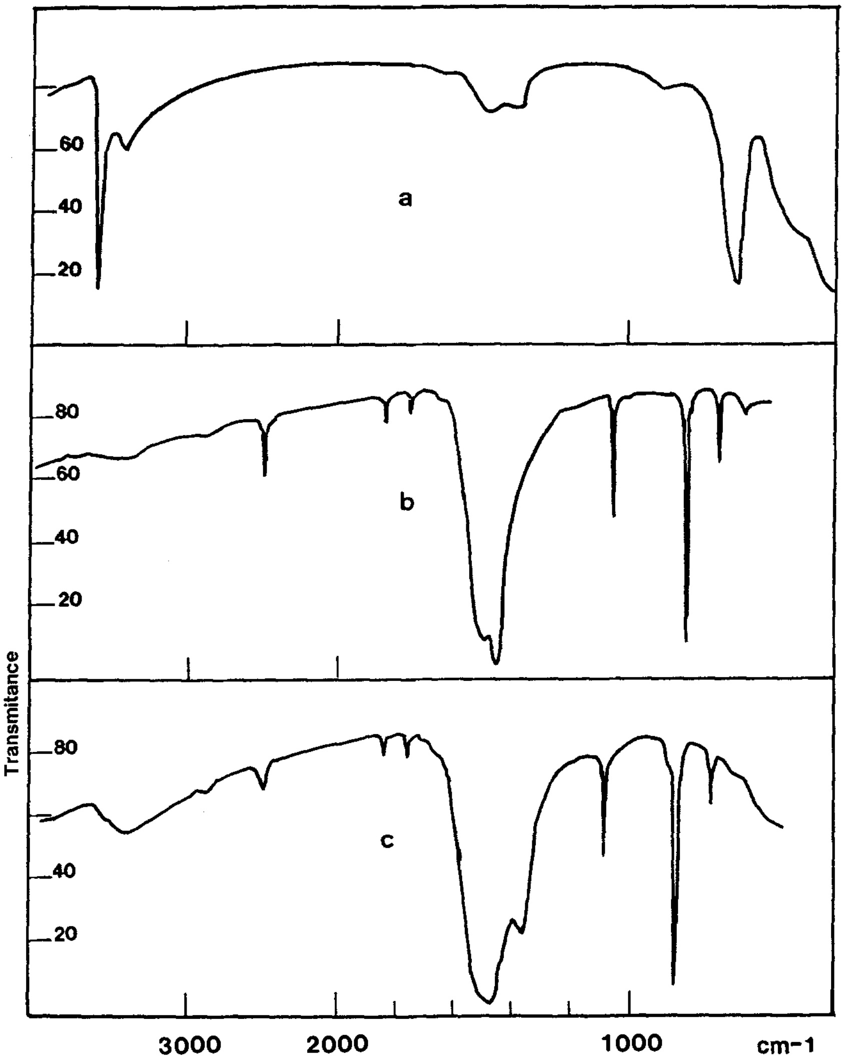

Fig. 2. IR spectra of: a) aged-in-air lanthanum oxide; b) lanthana catalyst after OXDE reaction; c) hexagonal $La_2O_2CO_3$ prepared in the present work.

Consequently the data on lanthana were obtained on a stabilized sample after reaction at 923 K. The results at 773 K are summarized in table 1 together with those related to Sm_2O_3 and Gd_2O_3, for which no significant aging was observed. The selectivity values for lanthana are similar to those found for samaria and gadolinia [15]. However, it should be noted that its activity is approximatively one order of magnitude lower.

In contrast with Sm_2O_3 and Gd_2O_3, the characterization studies carried out on lanthana show that after reaction, the actual catalyst differs from the initial one. Figs. 1b and 2b depict, respectively, the XPD diagram and IR spectrum recorded.

Table 1
Activity and selectivity data for OXDE reaction over several rare earth oxides and $La_2O_2CO_3$

Catal.	$V_{C_2H_4}$ [a]	V_{CO_2} [a]	V_{CO} [a]	$S_{C_2H_4}$ [b]	S_{CO_2} [b]	S_{CO} [b]
$La_2O_3$1.2	14.1	12.6	8.2	48.2	43.0	
$La_2O_2CO_3$	1.1	16.6	13.0	6.7	52.1	40.8
$Sm_2O_3$9.9	121.1	82.9	8.9	54.0	37.0	
$Gd_2O_3$15.5	129.0	117.0	9.7	46.1	43.5	

T_R: 773 K, $P_{C_2H_6}$: 8.0 kPa; P_{O_2}: 3.1 kPa; P_{He}: 90.2 kPa.
Total flow rate: 1 $cm^3 \cdot s^{-1}$ (HSV: 36.000 h^{-1}).
[a] Rate of reaction ($\times 10^8$) in $mole \cdot m^{-2} \cdot s^{-1}$.
[b] Selectivity (%) referred to ethane transformed.

The XPD diagram, fig. 1b, fits very well with that reported in the JCPDS file for the hexagonal variety, type II, of the lanthanum monocarbonate dioxide, $La_2O_2CO_3$. Likewise, the IR spectrum, fig. 2b, agrees well with that reported in the literature for this phase [16]. Neither XPD nor IR spectroscopy indicate the coexistence of $La_2O_2CO_3$ with any other lanthanum containing phase like La_2O_3, $La(OH)_3$ or $La(OH)(CO)_3$.

It can be concluded from these results that, under the conditions existing during the OXDE reaction on lanthana, strong chemical and structural modifications of the starting catalytic phase occur. The characterization data here reported show that the process above lead to the "in situ" formation of a monocarbonate dioxide phase, which accordingly would constitute the actual active phase. Considering the deactivation process observed on lanthana, it can be deduced that the monocarbonate dioxide phase is less active than the oxide.

Table 2 lists the equilibrium pressures corresponding to the decomposition of $La_2O_2CO_3$-II into La_2O_3 and CO_2 at several temperatures within the range of the catalytic tests. These values were calculated from the thermodynamic data reported in ref. [17]. Also, table 2 includes the experimental partial pressures of CO_2 as measured during the catalytic essays. The equilibrium CO_2 pressures are always higher than the experimental values under catalytic reaction conditions.

Table 2
Comparison between the equilibrium P_{CO_2} for the decomposition of hexagonal $La_2O_2CO_3$ and P_{CO_2} values observed during OXDE reaction over lanthana.

T(K)	P_{CO_2} [a]	P_{CO_2} [b]
673	1×10^{-3}	2×10^{-2}
773	3×10^{-2}	0.3
873	0.4	1.5

[a] Equilibrium pressures, in kPa, as determined from the thermodynamic data reported in ref. [17].
[b] Experimental pressures in kPa as measured during the catalytic essays
Reactions conditions: $P_{C_2H_6}$: 8.0 kPa; P_{O_2}: 3.1 kPa; P_{He}: 90.2 kPa; HSV: 36.000 h^{-1}.

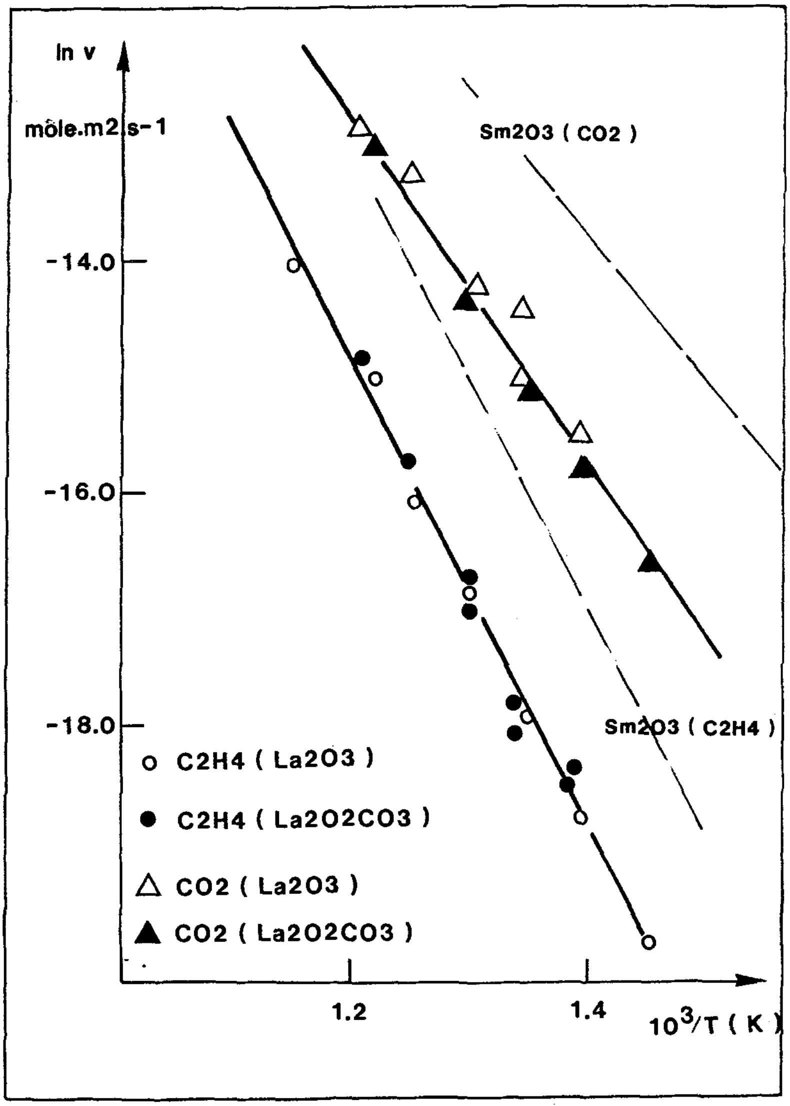

Fig. 3. OXDE reaction over lanthana (open points) and $La_2O_2CO_3$ (filled points). Arrhenius plots corresponding to the formation of C_2H_4 and CO_2.

Therefore, the monocarbonate dioxide phase rather than the oxides constitutes the stable phase under the reaction conditions used in the present work.

We also prepared a sample of $La_2O_2CO_3$-II and tested its catalytic properties. This sample, which was obtained as described in the experimental section, has been characterized by XPD and IR. In figs. 1c and 2c, the XPD diagram and the IR spectrum of the prepared $La_2O_2CO_3$ are shown.

Fig. 3 summarizes the catalytic activity results. Data concerning both stabilized lanthana and the monocarbonate dioxide phase, are shown in this figure. For comparative purposes, fig. 3 also includes Arrhenius-like plots obtained for Sm_2O_3, which resemble those corresponding to gadolinia closely.

It is obvious from fig. 3 that the two lanthanum containing catalysts show essentially similar behaviours. This lend further support to the proposal already advanced in the sense that under the conditions investigated here, $La_2O_2CO_3$-II constitutes the true active phase in the oxidative dehydrogenation of C_2H_6 over lanthana.

Since no parallel carbonation phenomena could be observed over Sm_2O_3 and Gd_2O_3 [15], it may be concluded that the differences of activity observed between lanthana and the two sesquioxides mentioned above are due to the different nature of the actual catalytic phase participating in either case, the monocarbonate dioxide being less active than the oxide.

The results presented here show that the occurrence of "in situ" deep carbonation phenomena can play an important role in determining the catalytic behaviour of the rare earth oxides for reactions like the oxidative dehydrogenation of hydrocarbons, where significant amounts of CO_2 are produced. Our results also suggest that the conditions required for the formation of the carbonated phase are different from one 4f oxide to the other. Accordingly, attention must be paid when comparing the catalytic properties of the rare earth oxides. Otherwise, the behaviour of phases other than the oxides could be compared with that of true 4f sesquioxides.

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