

Solid State Equilibria in the System Al₂O₃–La₂O₃–Cr₂O₃: Reactivity Catalyst/Support LaCrO₃/Al₂O₃

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Abstract

The zone of the ternary system Al₂O₃–La₂O₃–Cr₂O₃ delimited by LaCrO₃, LaAlO₃, Al₂O₃ and Cr₂O₃ has been examined. The existence of an extended field of mixed crystals with rhombohedral symmetry LaAl_{1-x}Cr_xO₃ (0 ≤ x ≤ 0.85) has been verified. On the other hand, for x > 0.85, the solids show XR diffraction spectrograms typical of the orthorhombic phase LaCrO₃. It has been found a small isomorphous substitution of Al³⁺ by Cr³⁺ in the β-alumina type phase, leading to the formation of the LaAl_{11-x}Cr_xO₁₈ series (0 ≤ x ≤ 0.75); moreover, the existence of Al_{2-x}Cr_xO₃ (0 ≤ x ≤ 2) mixed crystals field has been confirmed. Finally it has been experimentally verified that catalytic systems formed by mechanical mixtures of LaCrO₃ and Al₂O₃ prepared anyhow (LaCrO₃ dispersed or supported on Al₂O₃) result thermodynamically unstable whatever the composition. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

The mixed oxides like ABO₃ and AO·(ABO₃)_n (A = rare earth and/or alkaline earth metals; B = transition metals) with, respectively, perovskite and layered perovskite structure, have been the subject of special interest, due to their catalytic properties in processes like low temperature combustions, control of NO_x pollutions and combustion of soot particulate in diesel exhaust gases.

The compounds with perovskite structure usually show high structural stability in comparatively wide temperature ranges, with generally possible reversible variations in oxygen content (ABO_{3±δ}), related to temperature and/or oxygen

partial pressure (pO₂) in the gas phase. Unfortunately, the extensive application of these materials is restrained by the low values of B.E.T. areas (max 7–8 m² g⁻¹). This drawback can be get over using suitable supports having large surface area and good mechanical and thermal characteristics. For this purpose, it is advised to use materials like transition aluminas, β-Al₂O₃, MgAl₂O₄.^{1–3} Nevertheless, the possible phenomena of interaction at the catalyst/support interface, can spread to the whole system through diffusion phenomena, with regard to relatively high temperatures, with possible degradation of the catalytic properties.

In order to verify if the conditions of the preparation reported in the note² (impregnations of δ-Al₂O₃ with lanthanum and chromium nitrates and heating up in air to 1000°C for 24 h) correspond to conditions of thermodynamical stability within the ternary system Al₂O₃–La₂O₃–Cr₂O₃, it has been examined the zone of the system delimited by LaCrO₃, LaAlO₃, Al₂O₃ and Cr₂O₃, where all solids of the catalytic system LaCrO₃/Al₂O₃ are supposed to be situated.

It is well known that between the two limit terms of the binary system Al₂O₃–Cr₂O₃ there is, at least for temperatures higher than 1250°C, a complete solid state solubility, which gives rise to mixed crystals Al_{2-x}Cr_xO₃ (0 ≤ x ≤ 2), with rhombohedral α-Al₂O₃ type symmetry.⁴ On the contrary, in the binary system Al₂O₃–La₂O₃ there are the intermediate compounds LaAl₁₁O₁₈ and LaAlO₃.^{5,6} The former owing to a β-Al₂O₃ type structure, shows a slightly variable composition about the atomic ratio Al/La ≈ 11; the latter indeed having a perovskite structure, shows, at room temperature, a lattice with rhombohedral symmetry. At 1070°C the symmetry change to the ideal cubic that persists

until melting point.^{7,8} Recently a new compound $\text{La}_4\text{Al}_2\text{O}_9$, characterized by a monoclinic symmetry,⁹ has been identified in this system; this is a metastable phase, not included in the zone of the system studied in this work, and it transforms into LaAlO_3 and La_2O_3 upon prolonged heating at 1200°C .^a

In the binary $\text{La}_2\text{O}_3\text{--Cr}_2\text{O}_3$ system the LaCrO_3 perovskite-type intermediate compound is only known. At room temperature the orthorhombic symmetry form is stable and changes to rhombohedral at about 260°C . Finally, a further transition to the cubic^{8,10} symmetry occurs at more than 1000°C . The two pointed transitions are perfectly reversible and it is not possible to obtain, at room temperature, the rhombohedral and cubic structures.

The study of the equilibrium relationships among the phases in the already quoted zone of the ternary system $\text{Al}_2\text{O}_3\text{--La}_2\text{O}_3\text{--Cr}_2\text{O}_3$ was carried out examining three series of samples with compositions respectively corresponding to:

- (a) $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$ with $0 \leq x \leq 1$ (solids included between the perovskite structures LaAlO_3 and LaCrO_3);
- (b) $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ with $0 \leq x \leq 2$ (solids included between the Al_2O_3 and Cr_2O_3 phases);
- (c) $\text{LaAl}_{11-x}\text{Cr}_x\text{O}_{18}$ with $0 \leq x \leq 3$ (solids formally derived from the $\beta\text{-Al}_2\text{O}_3$ type phase $\text{LaAl}_{11}\text{O}_{18}$ by progressive substitution of Al^{3+} ions by Cr^{3+} ones).

Moreover, referring to the preparation conditions for the support/catalyst system mentioned in Ref. 2, we examined a sample with chemical composition included between Al_2O_3 and LaCrO_3 ($\text{Al}_2\text{O}_3/\text{LaCrO}_3 = 3/1$) obtained by two different preparation techniques.

The possible reciprocal substitution of Al^{3+} and Cr^{3+} , in the LaCrO_3 and LaAlO_3 phases has been proved in the (a) series. The influence of this substitution on the symmetry of the perovskite lattice has been followed in the mixed crystals at room temperature. The samples of the (b) series were used to verify the solid solutions, already reported in the literature, at the experimental temperatures. The samples of the (c) series were prepared in order to follow the partial substitution of Cr^{3+} ions for Al^{3+} , in the $\beta\text{-alumina}$ type $\text{LaAl}_{11}\text{O}_{18}$ phase, and to verify the existence of other possible ternary phases in the examined zone.

Additional tests were furthermore made with a sample which composition was on the $\text{Al}_2\text{O}_3\text{--LaCrO}_3$ line, in order to study, at different temperatures, its evolution towards the equilibrium conditions, defined by the results of the tests carried out on samples of the three above series.

2 Experimental

The samples of the three series were prepared starting from mixtures of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, with glycerol added (about 10% wt) as reductant, accordingly to the method previously settled by our group.¹¹ The mixtures were first slowly heated until complete dissolution of the nitrates immediately poured in porcelain vessels preheated at 250°C . This treatment led to the formation of amorphous solids, with a large development of gas (NO_x , CO_2 , H_2O). After about 1 h at 250°C the crumbly products were carefully ground and heated in air at 600°C for 10 h. The final treatment was carried out in platinum vessels at about 1450°C for a time necessary for the thermodynamic equilibrium conditions to be achieved. This corresponds at about 24 h for the terms of the (a) and the (b) series, and about 120 h for those of the (c) series. In order to minimize the not negligible volatility of Cr_2O_3 , caused by this long thermal treatment at high temperature, the samples of the last series were pressed in pellets and wound in a thin platinum sheet.

The samples with composition $\text{Al}_2\text{O}_3/\text{LaCrO}_3 = 3/1$ were obtained according to two different synthesis routes: (1) mechanical mixture of poorly crystalline commercial $\gamma\text{-Al}_2\text{O}_3$ (EC Akzo-Chemie; B.E.T area = $210 \text{ m}^2 \text{ g}^{-1}$) and LaCrO_3 (prepared in air at 1200°C for 48 h; B.E.T. area ($\leq 1 \text{ m}^2 \text{ g}^{-1}$), whose XRD spectrograms were compared with JCPDS cards number 10-0425 and 33-0710, respectively); (2) impregnation of the above $\gamma\text{-Al}_2\text{O}_3$ with equimolar aqueous solution of La and Cr nitrates, followed by drying. Both the solids were subjected to an identical heat treatment, i.e. heating in air at progressively increasing temperatures from 900°C up to 1450°C , without any intermediate grinding, for 5 days each.

All samples were quenched in air and examined by XRD powder analysis at room temperature.

Concerning the (a) and (b) series, to verify the Vegard law we have considered the shifts of the (024) and (113) reflection d values, respectively, using as internal standards Y_2O_3 (99.99% pu.) and KCl (99.99% pu.), respectively.

3 Results and Discussion

On the basis of the XRD analysis carried out on the samples of the (a), (b) and (c) series, it has been possible to build the phases diagram shown in Fig. 1.

Concerning the (b) series $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 2$) we confirmed, at the experimental temperature, the presence of a complete field of mixed crystals, as

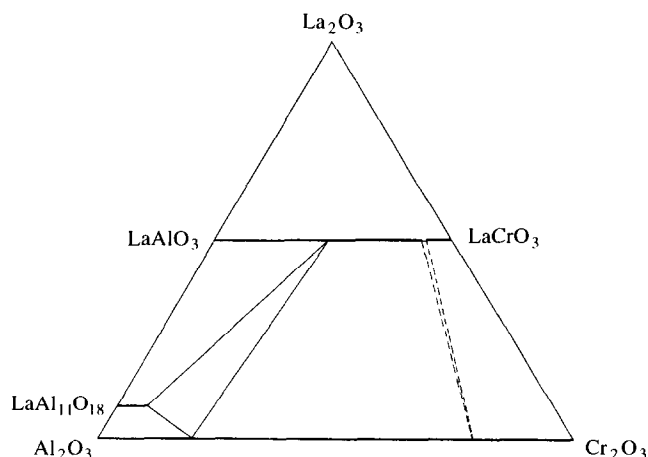


Fig. 1. The state diagram of Al_2O_3 - La_2O_3 - Cr_2O_3 in air at 1450°C .

reported in literature.⁴ It has been stated a perfect linearity between the increasing x values and the (113) reflection d values.

The analysis of the solids in the (a) series, $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 1$) allowed us to confirm the existence of an extended field of mixed crystals showing rhombohedral symmetry. This region lies from LaAlO_3 as far as the limit term $\text{LaAl}_{0.15}\text{Cr}_{0.85}\text{O}_3$. Also in this case we found a linear relationship between the x values and the d values of the (024) reflection. Beyond this composition, the XRD spectrograms show additional weak reflections, typical of a lattice with orthorhombic symmetry, like the LaCrO_3 low temperature form. Due to the peculiar limitations of the used analytical technique, it has not been possible to define the range of the rhombohedral-orthorhombic biphased zone that, even if very narrow, must necessarily appears in the state diagram between the two monophased fields.

As regards the (c) series, with formal composition $\text{LaAl}_{11-x}\text{Cr}_x\text{O}_{18}$ ($0 \leq x \leq 3$) the existence of a narrow field of mixed crystals has been verified, with substitution of Al^{3+} ions by Cr^{3+} to an x value lower than one (*vide infra*). Incidentally, it is important to point out that, starting from the amorphous precursor, the time required to obtain pure samples of $\text{LaAl}_{11}\text{O}_{18}$ and of other terms of the above solid solutions, were 5 days only, i.e. very shorter than those reported in literature (over 130 days at the same temperature starting from a mixture of the crystalline oxides).^{12,13}

The sample with formal composition $\text{LaAl}_{10}\text{CrO}_{18}$ ($x=1$) shows an XRD spectrogram already containing other small reflections, beside those typical of the β - Al_2O_3 type phase. These minor reflections arise from both traces of perovskite $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$ and mixed crystals $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ (α - Al_2O_3 -type). The room temperature X-ray patterns of the more significant samples of the (c) series are reported in

Fig. 2 in order to substantiate the equilibrium relationships, shown in the state diagram in Fig. 1.

As a matter of fact one passes from monophased solids 1 and 2 (β - Al_2O_3 type) to the triphased solid 3 (β - $\text{Al}_2\text{O}_3 + \text{LaAl}_{1-x}\text{Cr}_x\text{O}_3 + \text{Al}_{2-x}\text{Cr}_x\text{O}_3$) to the biphased solid 4, characterized by the presence of only the perovskite-type and α - Al_2O_3 -type phases. To define more accurately the limits of the triphased zone $\text{LaAl}_{11-x}\text{Cr}_x\text{O}_{18} + \text{LaAl}_{1-x}\text{Cr}_x\text{O}_3 + \text{Al}_{2-x}\text{Cr}_x\text{O}_3$, from the spectrogram of sample 3 shown in Fig. 2, we have determined, by means of the internal standard Y_2O_3 , the reflections (024) and (113) d values belonging, respectively, to the perovskite type and α - Al_2O_3 -type phases. These values were compared with the corresponding ones of the two series of mixed crystals $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$ and $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ previously described. The triphased samples are formed by mechanical mixtures of the

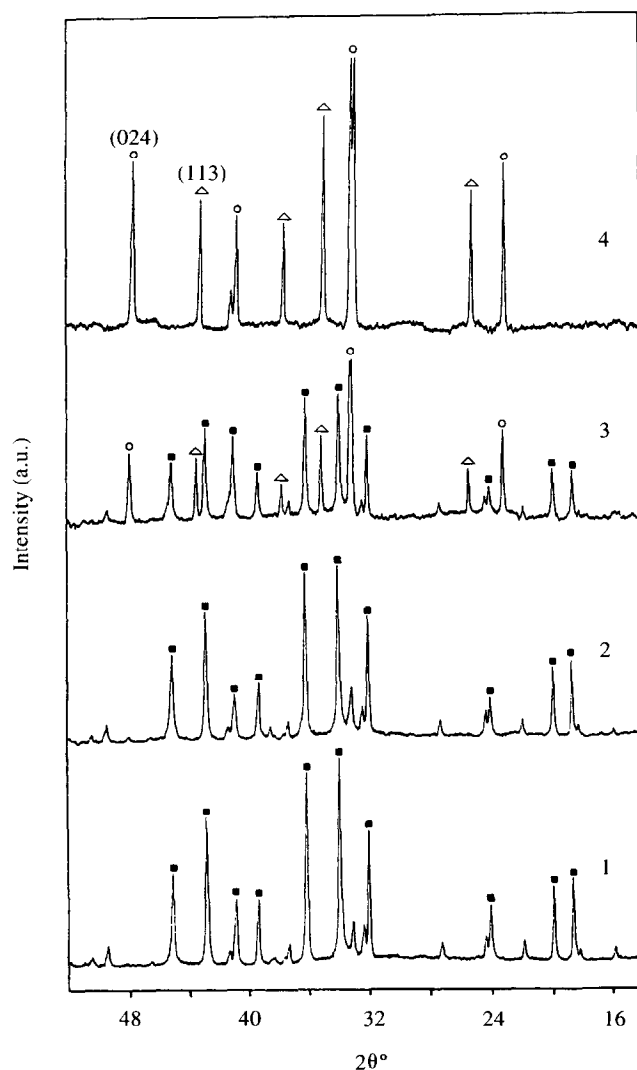


Fig. 2. Powder XR diffractograms of the (c) series $\text{LaAl}_{11-x}\text{Cr}_x\text{O}_{18}$ heated in air at 1450°C for 120 h: (1) $x=0$; (2) $x=0.75$; (3) $x=2$; (4) $x=3$. (■) indicates only the highest peaks of the β - Al_2O_3 type structure; (▲) the highest peaks of the α - Al_2O_3 structure; (○) the highest peaks of the perovskite structure with rhombohedral symmetry.

limit term of the series β - Al_2O_3 type, the perovskite term with composition $\text{LaAl}_{0.53}\text{Cr}_{0.47}\text{O}_3$ and that with corundum type structure $\text{Al}_{1.66}\text{Cr}_{0.34}\text{O}_3$. Considering the results just shown, we infer that mechanical mixtures of LaCrO_3 and Al_2O_3 , whatever prepared (LaCrO_3 supported on, or dispersed in Al_2O_3) and with any composition, result thermodynamically unstable at the experience temperature. These mixtures, according to their compositions (see the dotted line in Fig. 3) must necessarily give rise to:

- biphased solids formed by mechanical mixtures of the solid solutions $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$ and $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ (section A);
- triphased solids constituted by the limit term of the $\text{LaAl}_{11-x}\text{Cr}_x\text{O}_{18}$ phase, the perovskite term and that one with corundum type structure (section B);
- biphased solids formed by mixed crystals of α - Al_2O_3 type in equilibrium with terms of the $\text{LaAl}_{11-x}\text{Cr}_x\text{O}_{18}$ series (section C).

The evolution of the mechanical mixture $\text{Al}_2\text{O}_3/\text{LaCrO}_3 = 3/1$ [denoted by a (*) in Fig. 3] can be characterized by three consecutive stages, related to the increase of temperature, as shown in Fig. 4: 900–1000°C—there is no essential variation in the starting mixture, if one excludes a beginning of substitution of Cr^{3+} ions by Al^{3+} ones in the lattice of LaCrO_3 , with broadening of the reflections typical of this phase; 1100–1300°C—appearance of reflections typical of the α - Al_2O_3 structure and completion of the Al/Cr substitution in the perovskite type phase (already observed in the previous stage); 1450°C—beside the reflections of the two above phases, it starts to appear the set of reflections typical of β -alumina as predicted by the

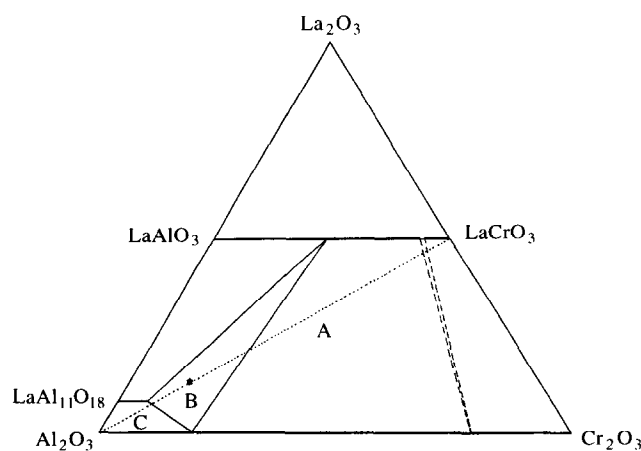


Fig. 3. Equilibrium conditions concerning solids Al_2O_3 - LaCrO_3 of different compositions, heated in air at 1450°C: the (*) point marks the composition 3:1.

equilibrium relationships that we have stated, at this temperature, in the examined system.

The evolution of the solid obtained by impregnation of γ - Al_2O_3 (as shown in Fig. 5) can also be described in three consecutive stages: 900–1000°C—the XRD patterns of the samples heated at these two temperatures are characterized by the presence of reflections typical of the perovskite phase with low crystallinity, beside the broadened ones characteristic of the γ - Al_2O_3 structure; 1100°C—the prolonged heating of the sample at this temperature (5 days) does not cause any particular variation as regards the above phases, except for the beginning of the transition from γ to α -alumina; 1200–1450°C—the main observation is the occurrence of the β - Al_2O_3 phase at 1200°C instead of 1450°C, as reported in Fig. 4. Taking into account the relative intensities of the reflections typical of the three phases (β - Al_2O_3 , α - Al_2O_3 and perovskite) in the sample heated at 1450°C, we can infer that, at this last temperature, the conditions of thermodynamic equilibrium have been attained.

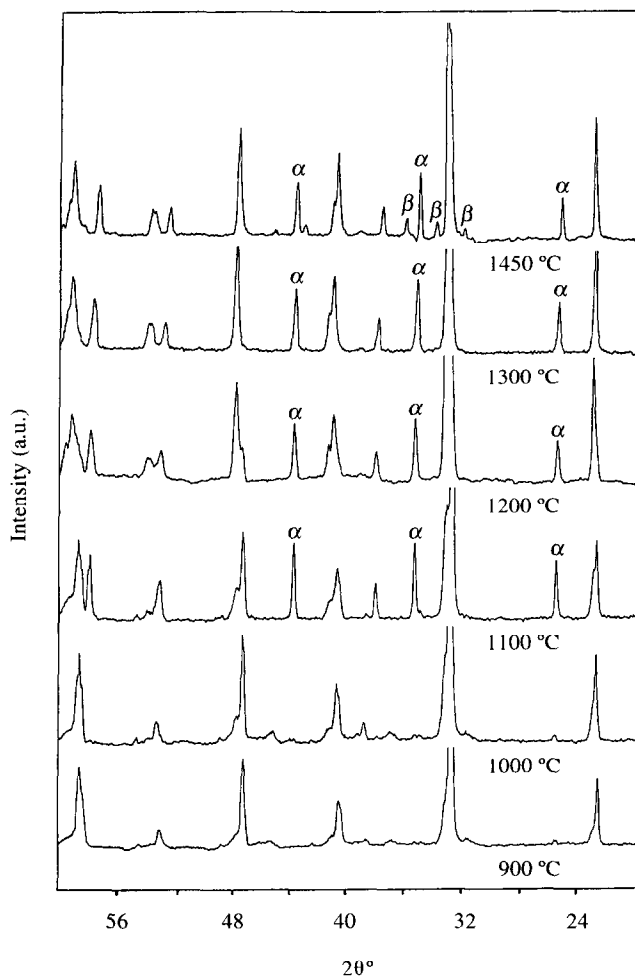


Fig. 4. Evolution of the mechanical mixture with formal composition $\text{Al}_2\text{O}_3/\text{LaCrO}_3 = 3/1$ obtained from γ - Al_2O_3 and LaCrO_3 , heated in air for 5 days at different temperatures.

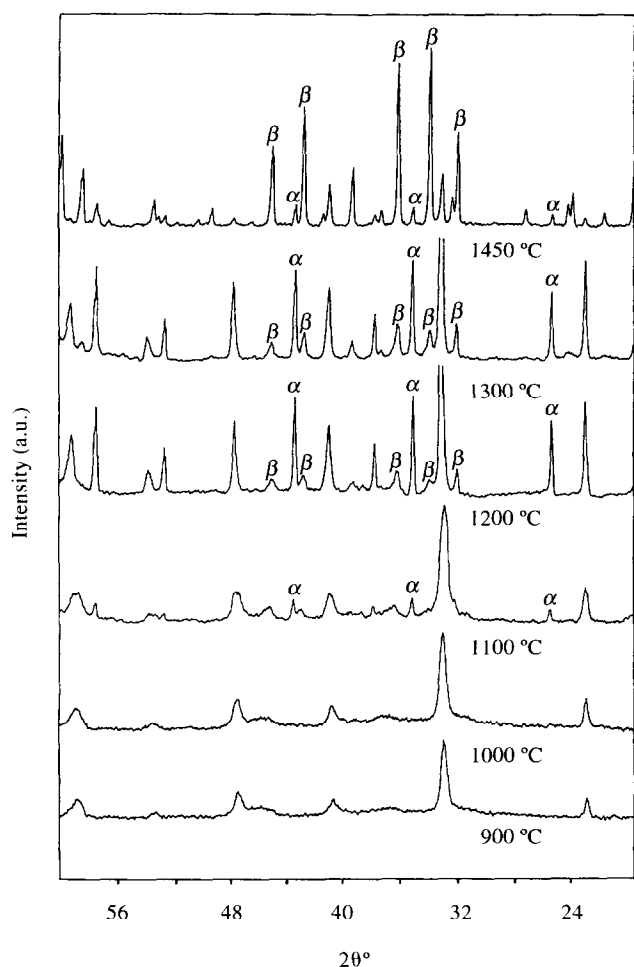


Fig. 5. Evolution of the mechanical mixture with formal composition $\text{Al}_2\text{O}_3/\text{LaCrO}_3 = 3/1$ obtained by impregnation of $\gamma\text{-Al}_2\text{O}_3$ with an aqueous equimolar solution of La and Cr nitrates, heated in air for 5 days at different temperatures.

4 Conclusions

In the zone of ternary system $\text{Al}_2\text{O}_3\text{-La}_2\text{O}_3\text{-Cr}_2\text{O}_3$ included among LaCrO_3 , LaAlO_3 , Al_2O_3 and Cr_2O_3 , the presence of a wide field of mixed crystals has been confirmed, with rhombohedral symmetry $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 0.85$), while for $x > 0.85$ the solids show XR powder diffraction spectrograms typical of the orthorhombic form of the LaCrO_3 phase. In the β -alumina type phase, it has been pointed out a very small substitution of Cr^{3+} for Al^{3+} ions, that leads to the solid solution $\text{LaAl}_{11-x}\text{Cr}_x\text{O}_{18}$ ($0 \leq x \leq 0.75$). In the binary system $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ it has been stated the existence of a complete solid solution $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 2$), with a corundum-type lattice.

Taking into account the reasons of this research and the results that we obtained, we can therefore infer that the catalytic systems formed by

mechanical mixtures of LaCrO_3 and Al_2O_3 , whatever prepared (LaCrO_3 dispersed or supported on Al_2O_3) and with any composition, result thermodynamically unstable. As a matter of fact, these mixtures must evolve, according to their composition, giving rise to:

- biphased solid formed by $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$ and $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ solid solutions;
- triphased solids formed by $\text{LaAl}_{10.25}\text{Cr}_{0.75}\text{O}_{18}$ (the limit term of the β -alumina type phase), $\text{LaAl}_{0.53}\text{Cr}_{0.47}\text{O}_3$ (the perovskitic term), and $\text{Al}_{1.66}\text{Cr}_{0.34}\text{O}_3$ (the corundum type structure);
- biphased solids formed by mixed crystals α -alumina type in equilibrium with terms of the series $\text{LaAl}_{11-x}\text{Cr}_x\text{O}_{18}$.

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