

Hexane total oxidation on LaMO_3 ($M = \text{Mn, Co, Fe}$) perovskite-type oxides

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Abstract

LaMO_3 ($M = \text{Mn, Fe, Co}$) perovskites were prepared by calcining the citrate precursors at 800°C for 5 h. $\text{PdO } 3\% / \text{Al}_2\text{O}_3$, a largely used combustion catalyst, was also studied for comparison. The catalytic behavior was examined in the hexane total oxidation. The following activity scale was found: $\text{LaFeO}_3 > \text{LaCoO}_3 > \text{LaMnO}_3 > 3\% \text{PdO}/\text{Al}_2\text{O}_3$, the three perovskites activating the C–H bond cleavage of hexane better than $\text{PdO}/\text{Al}_2\text{O}_3$. At temperature around $250\text{--}300^\circ\text{C}$ mobile surface oxygen species are involved in the oxidation process, whereas at $T > 300^\circ\text{C}$ oxygen mobile species are no more present and so, particularly for LaCoO_3 and $\text{PdO}/\text{Al}_2\text{O}_3$, the activation mechanism becomes more energetic. The activity values were compared with those obtained from the total oxidation of methane. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile organic compounds (VOCs) are considered as great contributors to the atmospheric pollution and dangerous for their effect on the human health [1,2]. VOCs are produced by both mobile and stationary sources and are present in solvents, industrial manufacturing and fuel combustion. Since the environmental legislation has already established in many countries severe regulations for the control of VOCs emissions [3], in the last years the reduction of their atmospheric concentration by means of preventive catalytic combustion has acquired great importance.

Catalysts based on noble metals (Pt, Pd) supported on alumina or silica or other oxides have been

studied and developed for the abatement of VOCs [4–6]. However, because of the high cost of noble metals, considerable efforts have been spurred in searching effective but cheaper catalysts, mainly based on mixed oxides. Due to their variable structure and chemical composition, ABO_3 perovskite-type oxides have so far attracted great interest in catalysis as model catalysts as well as real catalysts for hydrocarbon oxidation [7]. Perovskite oxides are characterised by great stability at high temperature, high mobility of oxygen, and stabilisation of unusual cation oxidation states in the structure. Both latter properties lead to oxygen non-stoichiometry that makes them suitable for the catalytic hydrocarbon oxidation.

Many metals are stable in the ABO_3 perovskite structure provided that their ionic radii fit well the sizes of the 12-coordinated A and 6-coordinated B sites, e.g. $r_A > 0.90 \text{ \AA}$ and $r_B > 0.51 \text{ \AA}$. The effect of the nature of the B cation on the physico-chemical and

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catalytic properties of lanthanum-based perovskites has been widely studied, those containing Mn, Co or Fe having been found the most active in methane combustion [7–10]. According to the kinetic model proposed for hydrocarbon activation, weakly adsorbed oxygen is involved in the reaction at low temperature whereas lattice oxygen becomes reactive at high temperature [8].

It therefore appeared of interest to correlate the structural, adsorptive and redox properties of LaMO_3 ($M = \text{Mn, Fe, Co}$) perovskites with their catalytic activity in the total oxidation of hexane, a compound largely used as solvent and whose catalytic abatement on supported noble metals has been already reported [11,12]. The activation of the C–H bond ($E_{\text{C-H}} = 380$ and 438 kJ mol^{-1} for hexane and methane, respectively) was found to be responsible for the hexane reactivity [13–16].

Note that the oxidation reactivity of the volatile organic compounds is in the following order: alcohols > aldehydes > aromatics > ketones > alkenes > alkanes [15,17]. Therefore, an alkane compound represents a good test for the activity of a certain class of catalysts, and a comparison between perovskites and supported noble metals towards hexane combustion appeared interesting.

It was also considered of interest to correlate the activity values of hexane oxidation with those of methane combustion, a reaction already studied by us on the same perovskite catalysts.

2. Experimental

LaMO_3 ($M = \text{Mn, Co and Fe}$) perovskites were prepared by citrate precursors [18]. La, Mn (or Co, or Fe) nitrates were mixed in suitable proportions to give a concentrated solution. Citric acid was then added to the metal solution to have the same amount of equivalents. The solution was evaporated at 90°C to produce viscous syrup. The final product, after grinding, was calcined at 800°C for 5 h. $\text{PdO 3\%/Al}_2\text{O}_3$ was prepared by impregnating Akzo Chem alumina in a palladium nitrate solution, evaporating the excess solution, drying and then calcining the precursor at 300°C .

Phase analysis was performed by X-ray powder diffraction using a Philips PW 1029 diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation.

BET surface areas were measured at the liquid nitrogen temperature by krypton (on the Fe perovskite) or nitrogen (on Mn and Co compounds) adsorption in a vacuum glass apparatus.

Catalytic activity experiments were carried out in a continuous flow tubular reactor 1 cm o.d., employing 0.08 g of catalyst. For hexane combustion a flow of hexane (1%) in helium mixed with oxygen (10%) in helium (ratio oxygen:hexane = 28.5:1) was used. For methane oxidation a flow of pure methane mixed with pure oxygen (ratio oxygen:methane = 6:1) was used, balancing by means of helium. Even if the oxygen/hexane ratio is lower than that usually employed in VOCs catalytic combustion, it appeared useful to use the same oxygen excess (3/1) in both reactions. The flow of gases, purified and dehydrated with suitable filters, was regulated by means of MKS electronic mass flow controllers.

The oxidation of hexane was investigated in the range $170\text{--}325^\circ\text{C}$, whereas that of methane in the range $240\text{--}400^\circ\text{C}$. An in situ pre-treatment in a flow of 10% oxygen in helium at 400°C , and a cooling down to the reaction temperature in the same flow, were performed for both reactions. After checking that at the highest temperatures not very significant deactivation phenomena occurred in long times, the reaction was carried out by increasing stepwise the temperature and analysing the reaction mixture in steady state conditions at every pre-determined temperature. The reaction mixture was analysed by means of a Perkin-Elmer Autosystem gas chromatograph, equipped with Mol-Plot capillary columns.

In TPD runs, oxygen adsorption was realised in a tubular reactor, on sample amounts of 0.06–0.08 g, after the same oxidative pre-treatment used in the catalytic experiments. Samples were then cooled down to RT and kept at such temperature for 3 h. Desorption was then performed in a flow of He as carrier gas, at a heating rate of $4\text{--}16^\circ\text{C min}^{-1}$. In the same apparatus TPR runs were carried out (after a previous in situ cleaning pre-treatment with pure He at 400°C) by means of a continuous flow of 10% H_2 diluted in helium from room temperature up to 700°C , at a heating rate of 8°C min^{-1} . Gaseous flows, dried and purified with suitable filters and with a liquid nitrogen trap, were regulated by Brooks electronic mass flow controllers, and the peaks were detected by means of a HWD detector.

3. Results and discussion

The three LaMO_3 catalysts are single phase perovskite oxides (Fig. 1), with primitive rhombohedral cell, $R\bar{3}m$ space group, for LaMnO_3 and LaCoO_3 , and orthorhombic, $Pnma$ space group, for LaFeO_3 . Specific surface area values are 22 , 15 and $3 \text{ m}^2 \text{ g}^{-1}$ for LaMnO_3 , LaCoO_3 and LaFeO_3 , respectively, and $159 \text{ m}^2 \text{ g}^{-1}$ for $\text{PdO}/\text{Al}_2\text{O}_3$. Particle size values are 300 , 270 and 580 \AA for LaMnO_3 , LaCoO_3 and LaFeO_3 , respectively. Note that LaFeO_3 already forms at very low temperature (350°C), while LaMnO_3 and LaCoO_3 are still amorphous. The lowest surface area found for LaFeO_3 is due to the very high sintering suffered by this compound at 800°C .

Redox titration showed that there is a substantial fraction (35%) of Mn^{4+} in LaMnO_3 [9], a very small fraction (1.3%) of Fe^{4+} in LaFeO_3 [10], whereas no Co^{4+} was detected in LaCoO_3 [9]. Since the close-packed perovskite structure cannot host interstitial oxygen atoms to compensate the higher charge of Mn^{4+} or Fe^{4+} , cation vacancies on both the 12-coordinated and octahedral metal sites of the perovskite structure are present in LaMnO_3 and LaFeO_3 .

The catalytic activity in the total oxidation of hexane is shown in Fig. 2 for the three perovskites and for

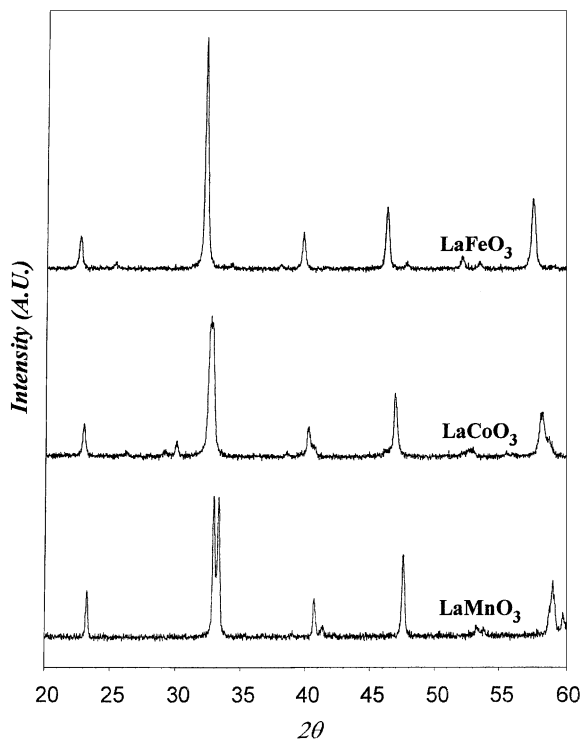


Fig. 1. X-ray patterns of LaMnO_3 , LaCoO_3 and LaFeO_3 perovskites.

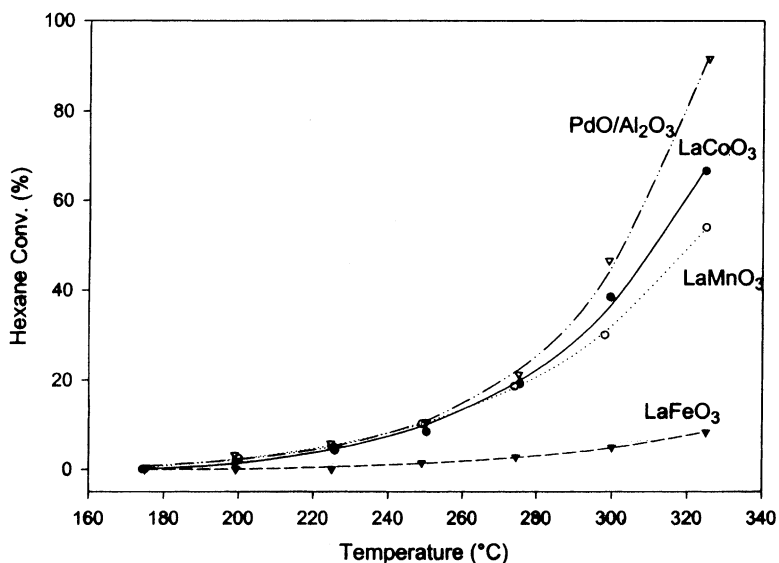


Fig. 2. Hexane conversion vs. temperature (samples amount 0.08 g , space velocity 61000 h^{-1}).

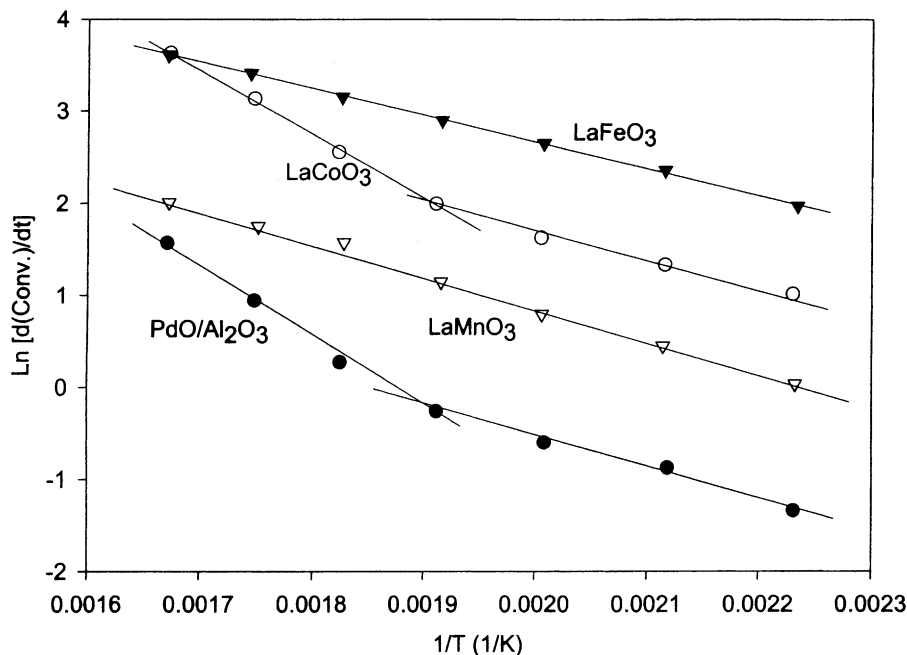


Fig. 3. Arrhenius plot of $\ln d(\text{Conv.})/dt$ vs. $1/T$ for hexane total oxidation.

PdO/Al₂O₃. The selectivity towards CO₂ was 100% and no intermediates were detected.

LaFeO₃ shows a much lower activity than both LaCoO₃ and LaMnO₃. This result could be interpreted in terms of the lower surface area exhibited by LaFeO₃. Moreover, up to about 280°C, PdO/Al₂O₃ has an activity similar to that of the LaCoO₃ and LaMnO₃ perovskites in spite of its higher surface area. Only at $T > 280^\circ\text{C}$ the catalytic activity of PdO/Al₂O₃ becomes higher than LaCoO₃ and LaMnO₃.

In the attempt of gaining a deeper insight in the reaction mechanism it appeared interesting to examine the dependence of the reaction progress in function of the temperature. Fig. 3 reports the natural logarithm of derivatives (in respect of contact time) of hexane conversion (normalised with respect to the surface area) versus $1/T$.

All the catalysts are characterised by a similar temperature dependence up to about 280°C, that is by an apparent activation energy of 24 kJ mol⁻¹. Above this temperature, the hexane oxidation over PdO/Al₂O₃ and LaCoO₃ shows different temperature dependence,

characterised by a greater value of the apparent activation energy (63 kJ mol⁻¹).

As already pointed out, methane combustion runs were carried out in order to compare the capability of the examined catalysts in activating the C–H bond of different hydrocarbons. Fig. 4 shows that, in methane combustion, PdO/Al₂O₃ is much more active than the perovskite materials. The activity ratio for the hexane and methane reactions is about 2.5 for PdO/Al₂O₃, and 10–15 for the three perovskites. Therefore, the perovskites are better catalysts for activating the C–H bond of hexane, than PdO/Al₂O₃.

TPD profiles, shown in Fig. 5, reveal a large oxygen peak at high temperature (600°C) on LaMnO₃ (corresponding to a desorption of 8.1×10^{-6} mol O₂ m⁻²) and a baseline deflection for the other two catalysts. At lower temperature a broadened peak (corresponding to 1.5×10^{-7} mol O₂ m⁻² for LaMnO₃) and centred at about 200°C for LaMnO₃ and at 250–300°C for the other two perovskites is observed.

The TPD spectra demonstrate that, at low temperature, there is oxygen adsorbed on the surface of the catalysts. The broadened shape of this peak may

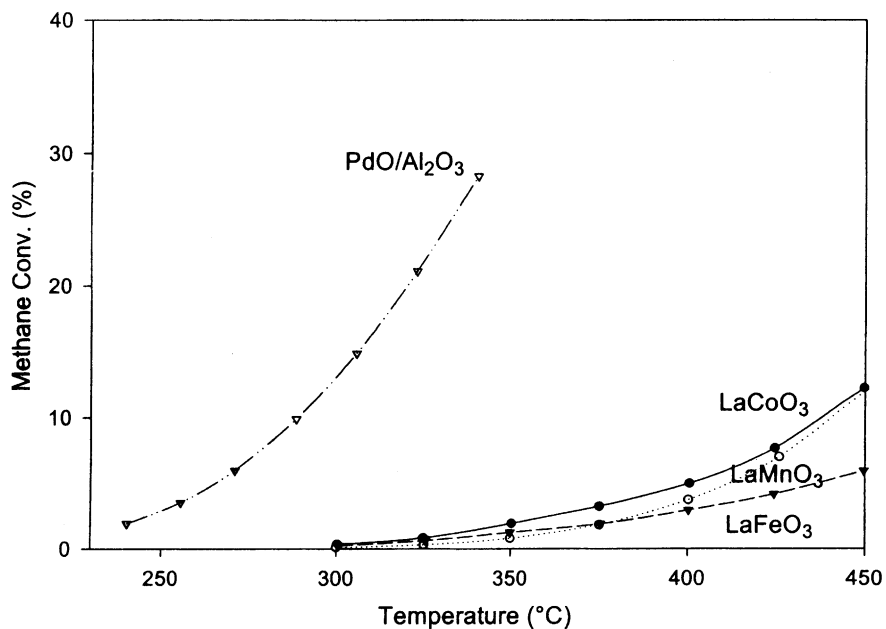


Fig. 4. Methane conversion vs. temperature (sample amount 0.08 g, space velocity 58000 h⁻¹).

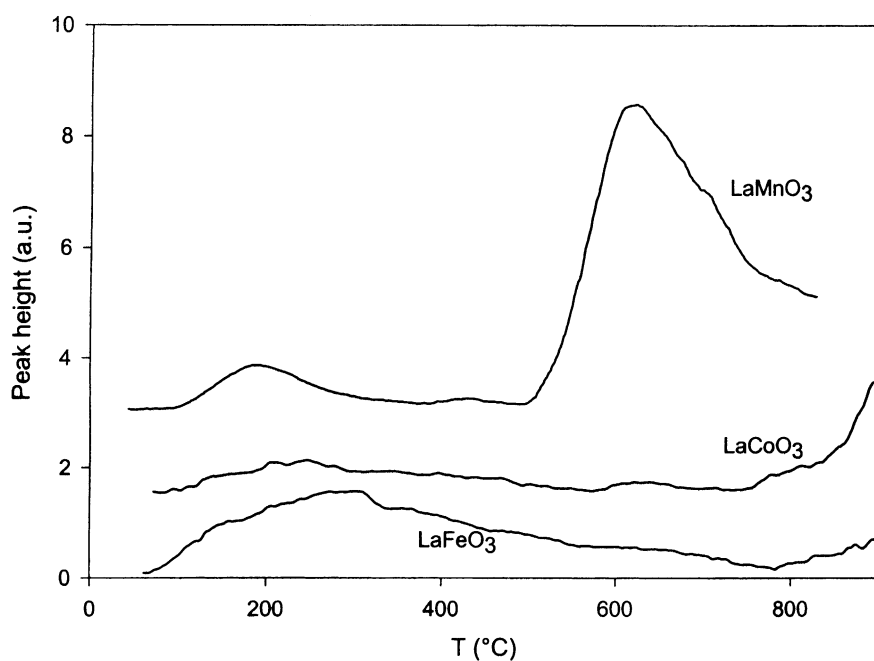


Fig. 5. TPD spectra obtained on the three perovskites with adsorbed oxygen. Sample amount 0.06 g; heating rate 8°C min⁻¹; carrier flow rate 30 ml min⁻¹.

suggest that desorption occurs with re-adsorption and then with an adsorption–desorption equilibrium between gaseous and surface oxygen.

The desorption peak, detected at higher temperature, should be referred to tightly bound oxygen species, that is to lattice oxygen whose evolution corresponds to the reduction of the transition metal.

Hexane, whose C–H bond cleavage requires less energy than methane, could follow a less energetic mechanism on the active sites, where mobile oxygen species are involved. At high temperature the above-mentioned mobile species are no more anchored to the catalyst surface, and oxygen vacancies are likely to be present. In these conditions, the activation of the C–H bond may be characterised by a more energetic mechanism on a greater number of available sites, especially for the LaCoO₃ perovskite (and also for PdO/Al₂O₃), which does not contain transition metal ions with oxidation state higher than 3+.

The TPR experiments (patterns not reported) revealed that the reduction process becomes appreciable in all the perovskites after 300–400°C.

The extraction of surface oxygen species becomes thus relevant, in reduction conditions (TPR), at about 300–400°C, while, in desorption conditions (TPD), it becomes appreciable only at higher temperature.

4. Conclusions

The activity scale for the hexane oxidation is as follows: LaFeO₃ > LaCoO₃ > LaMnO₃ > PdO/Al₂O₃.

Perovskites activate the C–H bond cleavage better than PdO/Al₂O₃, with a low energy mechanism probably involving mobile surface oxygen at temperature below 250–300°C.

At temperature higher than 300°C, oxygen mobile species are no more present and so, particularly for LaCoO₃ and PdO/Al₂O₃, the activation mechanism becomes more energetic.

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