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Effect of strontium doping on catalytic behaviour of lanthanum oxide on oxidative coupling of methane

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The doping of lanthanum oxide with strontium maintains the good selectivity of the oxidative methane coupling for the catalysts prepared or calcined at high temperature (>800°C) by preserving the platelet shape of oxide particles.

Keywords: OCM; lanthanum oxide; strontium doping; morphology

1. Introduction

Among the numerous catalysts cited in the literature [1–4] for the reaction of oxidative coupling of methane (OCM), those based on rare-earth oxides are among the most promising as they simultaneously present good selectivity to C_{2+} products, high activity, good stability at reaction conditions and a relatively low cost. These properties have incited the study of lanthanum oxide based catalysts in the reaction of OCM.

It appears from the literature that the strontium-doped lanthanum oxide is one of the best known OCM catalysts [5] which presents better catalytic performance than the pure oxide.

The aim of this paper is to clarify the possible role of strontium doping on the catalytic behaviour of the OCM reaction.

2. Experimental

Two series (pure La_2O_3 and Sr/La_2O_3) of three samples each have been prepared by controlled thermal decomposition of very pure lanthanum nitrate (supplied by Rhône-Poulenc) or of a mixture of strontium (Aldrich Chemicals) and lanthanum nitrates to obtain a molar ratio Sr/La = 1/6. Three procedures of preparation have been used:

(1) Lanthanum nitrate or a mixture of strontium and lanthanum nitrate were heated from ambient temperature to 650°C at a rate of 20°C/min. The final temperature was then maintained for 2 h. These samples were called La_2O_3-650 and Sr/La_2O_3-650.

(2) The same procedure was used, but the final temperature was 800°C and was maintained for 16 h. These samples were called La_2O_3-800 and Sr/La_2O_3-800.

(3) A further calcination of La_2O_3-800 and Sr/La_2O_3-800 at 950°C in air or oxygen for 2 h led to La_2O_3-950 and Sr/La_2O_3-950.

We have checked by XRD that La_2O_3 samples are crystallized in hexagonal form. The XRD patterns of Sr/La_2O_3 samples can be assigned to a solid solution of strontium in hexagonal La_2O_3. The SrO phase was never detected by XRD.

EDS experiments have been performed on a LINK AN 10000 system connected to the electron microscope JEOL JEM 100 CX II. The strontium content appears to be constant within the platelet-shaped particles observed.

In order to be meaningful and comparable, the catalytic properties have to be determined under rigorously identical conditions of temperature and reactant conversion [6]. The catalytic measurements have been performed at steady state in the cofeed mode at atmospheric pressure with a methane to oxygen ratio of 4, diluted by helium ($CH_4/O_2/He = 8/2/90$ mol%). The reactor was a simple tube of sintered alumina with an internal diameter of 3 mm, the catalyst being held between two quartz-wool plugs. The total flow rate was varied between 25 and 150 ml/min for a catalyst weight in the range 3 to 20 mg. The results are expressed relative to the consumption of methane.

The following procedure was used. The selectivities at different reaction temperatures and at various methane conversions were obtained by varying the flow rate and/or the catalyst weight. We have previously ascertained that the catalytic reaction was not influenced by mass transfer limitations and occurred under strictly isothermal conditions. The variation of the C_{2+} selectivity for a given conversion of methane as a function of the reaction temperature was then determined by the intercepts of the isothermal selectivity-conversion curves with a vertical line located at the selected conversion.

3. Results and discussion

The isoconversion curves are shown in figs. 1a and 1b for a methane conversion of 10%, which corresponds to an oxygen consumption in the range 30–50%, depending on the selectivities. A maximum of selectivity in coupling products is observed between 850 and 900°C, independent of the catalyst. Such

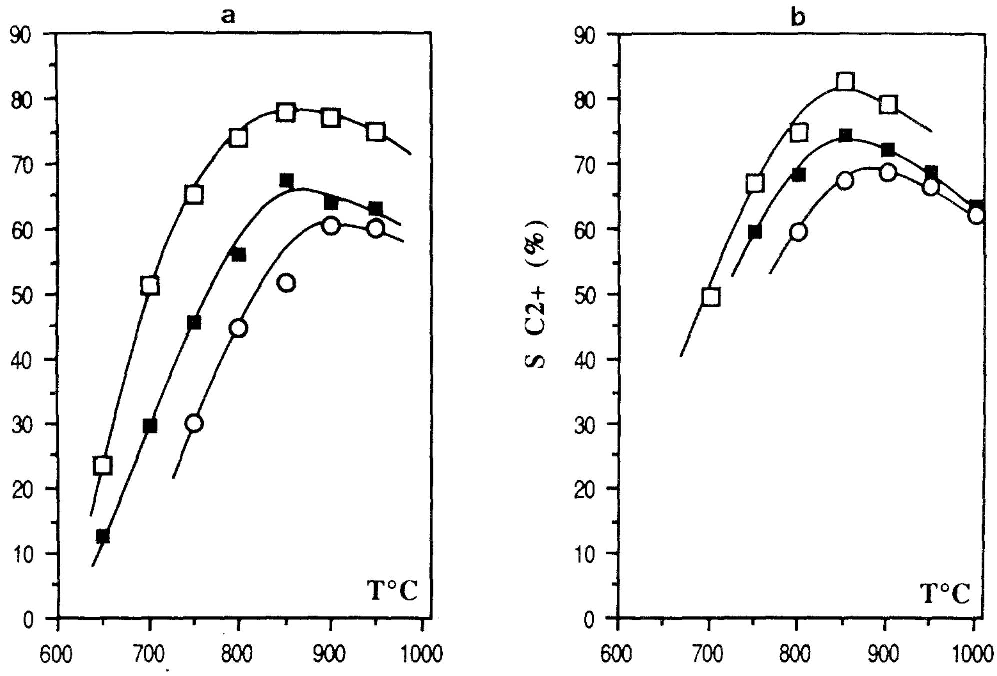

Fig. 1. C_{2+} selectivity measured at isoconversion of methane (10%) as a function of temperature. (a) Pure La_2O_3 (□ La_2O_3-650, ■ La_2O_3-800, ○ La_2O_3-950); (b) Sr/La_2O_3 (□ Sr/La_2O_3-650, ■ Sr/La_2O_3-800, ○ Sr/La_2O_3-950).

high temperatures for the optimal C_{2+} selectivity have been previously reported by Cameron et al. [7] for pure La_2O_3. The ranking of the catalysts according to the C_{2+} selectivity is identical for the two series: the C_{2+} selectivity decreases by increasing the final calcination temperature. The comparison between pure and strontium-doped lanthanum oxides points out the beneficial effect of strontium doping on C_{2+} selectivity. Two observations are noteworthy:

(i) the catalytic performances of La_2O_3-650 and Sr/La_2O_3-650 are similar, and

(ii) all the Sr/La_2O_3 samples are better than La_2O_3-800.

This latter observation means that the control of the preparation conditions is less important for the strontium-doped catalysts than for the pure lanthanum oxide.

As already mentioned, the shape of the catalyst particles can modify the selectivities in the OCM reaction [8–11]. We have previously pointed out that the better selectivity of La_2O_3-650 was correlated to the thin platelet morphology of the oxide particles, which exhibit mainly the (001) face of the hexagonal La_2O_3 structure [9,10]. As shown in fig. 2, the platelets of oxide are assembled into tridimensional particles in two different manners, which depend on the preparation conditions. The La_2O_3-650 samples exhibit particles made by ran-

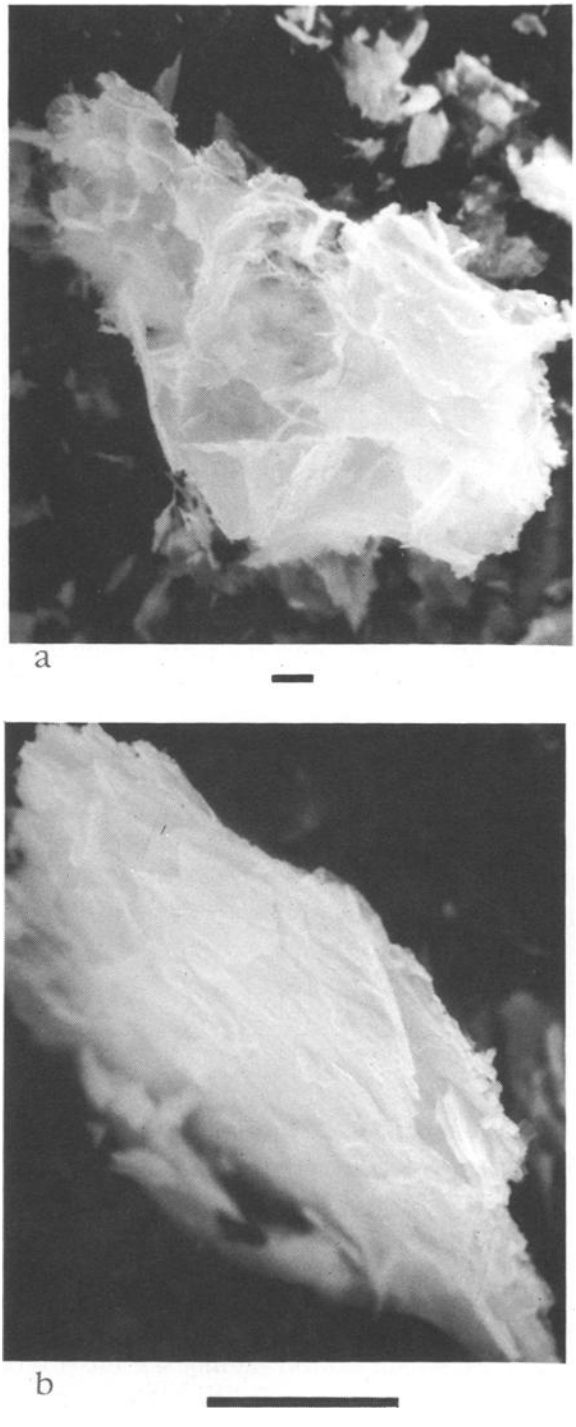

Fig. 2. Scanning electron micrographs of undoped La_2O_3 after reaction at 750°C (the scale bars represent 20 μm). (a) La_2O_3-650 and (b) La_2O_3-800.

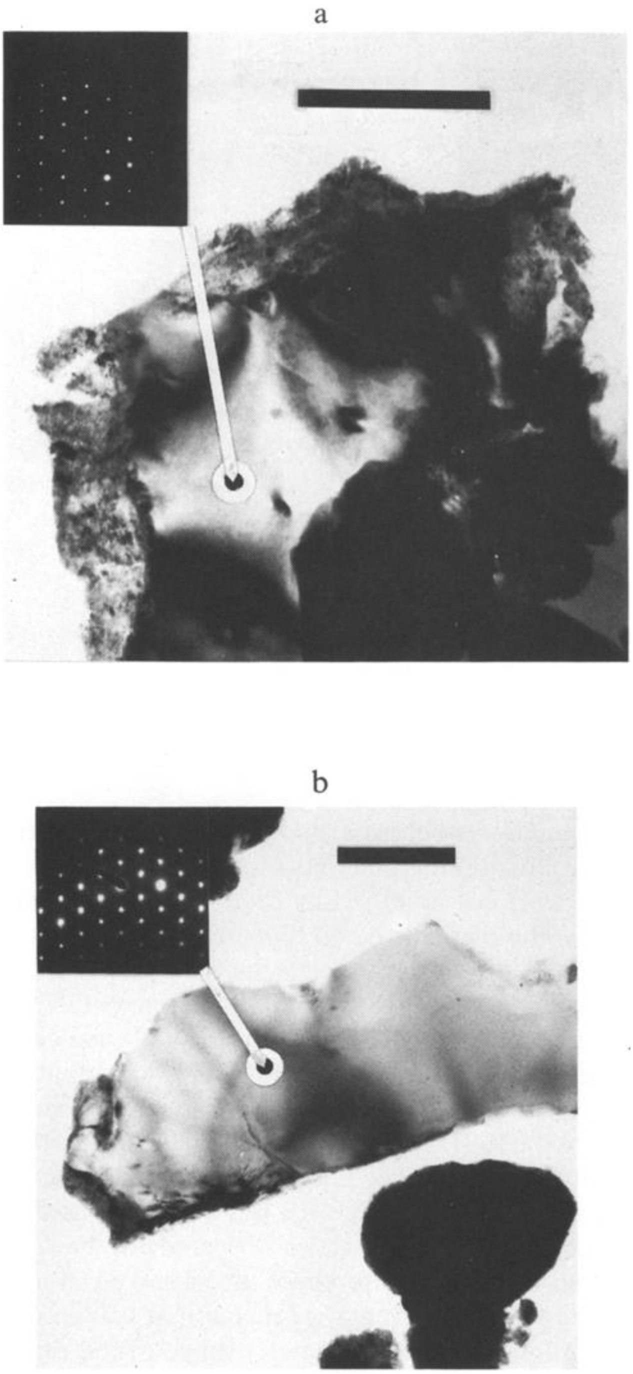

Fig. 3. Transmission electron micrographs and microdiffraction patterns of Sr/La_2O_3 catalysts (the scale bars represent 0.2 μm). (a) Sr/La_2O_3-650, (b) Sr/La_2O_3-800 and (c) Sr/La_2O_3-950.

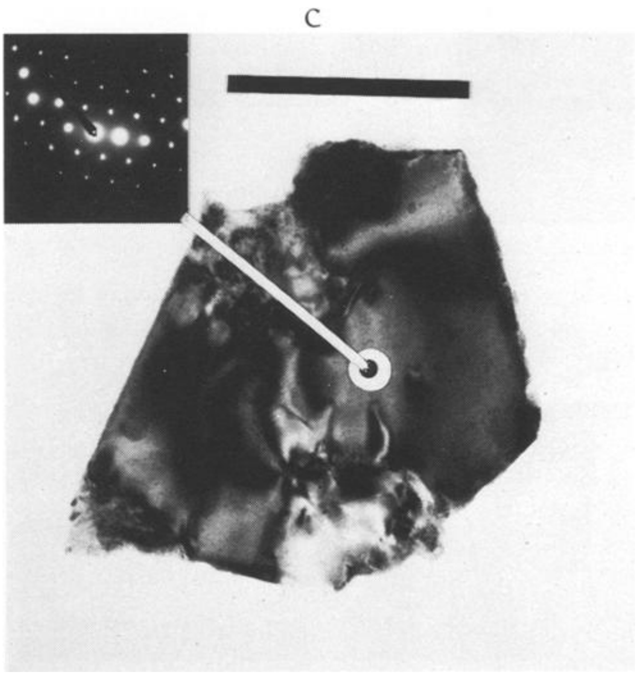

Fig. 3. (continued).

domly assembled platelets whereas La_2O_3-800 and La_2O_3-950 show compact particles formed by piling up the platelets on their largest face. The morphology of La_2O_3-650 samples is not modified by catalytic reaction until 800°C, but for higher temperatures, the platelets begin to sinter into compact particles and the C_{2+} selectivity tends to draw near the selectivity of La_2O_3-800 and -950.

The BET surface area, before the reaction, decreases (3.7, 1.4 and 1.1 m^2/g for La_2O_3-650, -800 and -950 respectively) with the C_{2+} selectivity.

Transmission electron micrographs and microdiffraction patterns of Sr/La_2O_3 samples (fig. 3) show the presence of platelet-shaped, monocrystalline particles, which exhibit mainly the (001) face of the hexagonal La_2O_3 structure, as already mentioned for La_2O_3-650 [9,10]. The scanning electron migrographs of Sr/La_2O_3 after catalysis (fig. 4), are consistent with the TEM observations. The catalyst particles are practically identical to those observed for La_2O_3-650. Unlike the pure oxide series, no important differences are observed in aspect or morphology for the Sr/La_2O_3 samples, even after reaction at 950°C. These observations highlight the correlation between the platelet shape of the catalyst particles and the high selectivity in coupling products [9–10,12], and strongly suggest that the main role of strontium doping could be to preserve the favorable platelet shape of the oxide particles during high temperature treatment or catalytic reaction.

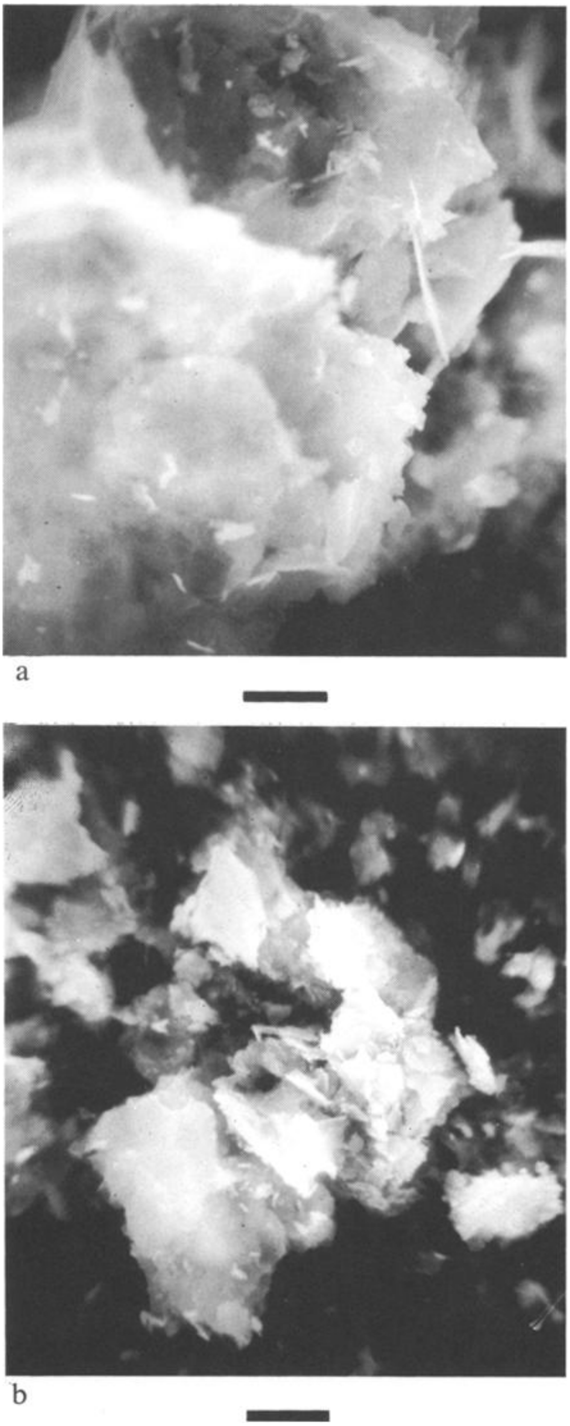

Fig. 4. Scanning electron micrographs of Sr/La_2O_3 catalysts after reaction at 950°C (the scale bars represent 40 μm). (a) Sr/La_2O_3-650, (b) Sr/La_2O_3-800 and (c) Sr/La_2O_3-950.

Fig. 4. (continued).

This latter effect is probably connected to the hydration resistance observed for Sr/La_2O_3 solid solutions [4,13,14], which could limit the formation of surface or bulk hydroxide, thus avoiding the sintering of oxide particles during the high temperature reaction or calcination. This assertion is consistent with the slight variation of BET surface area observed before the catalytic reaction for the Sr/La_2O_3 series (3.5, 2.8 and 2.1 m^2/g for Sr/La_2O_3-650, -800 and -950 respectively), and with the preservation of platelet morphology after catalysis at high temperature.

4. Conclusion

It appears that the role of strontium doping of lanthanum oxide is to maintain in the course of high reaction temperature the high C_{2+} selectivity also obtained for the undoped oxide prepared by a low decomposition temperature of the precursor. The better catalytic performances of these catalysts have been attributed to the platelet shape of oxide particles. From this standpoint, the main role of strontium, introduced in La_2O_3 as solid solution, could be textural, retarding the sintering of these highly selective oxide particles. The high temperature (850–900°C) required for the optimum of C_{2+} selectivity requires the use of a thermally stable catalyst, and this requirement excludes the pure lanthanum oxide La_2O_3-650, for which the favorable platelet morphology is destroyed by high temperature reaction or calcination. For eventual industrial use, the lanthanum oxide doped by strontium appears to be favored because it is able to work a long time at high temperature without decrease of C_{2+} selectivity.

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