Methane activation over $La_{2x}Y_{2-2x}O_3$ $(0 \leqslant x \leqslant 1)$ catalysts

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The influence of the structure on the catalytic methane activation coupling activity has been shown for $La_{2x}Y_{2-2x}O_3$ $(0 \leqslant x \leqslant 1)$ compounds. A perovskite structure leads to total oxidation (CO, CO_2) whereas a bixbyite structure results in C_2 hydrocarbon formation. This change in selectivity is interpreted in terms of the difference in oxygen environment of lanthanum in the two stuctures.

Keywords: Methane activation; perovskite; bixbyite; La-Y compounds

1. Introduction

Rare earth oxides (samarium, lanthanum) generally doped by lithium oxide are among the most active and selective catalytic systems for methane oxidative coupling [1]. Korf et al. [2,3] clearly established that the cubic structure Sm_2O_3 was stabilized at the expense of the monoclinic structure by addition of lithium oxide. Furthermore, they have shown a clear enhancement of the catalytic properties for the cubic form Sm_2O_3. Peil et al. [4-6] emphasized the role of lattice oxygen in the reaction on MgO and Li/MgO and explained the difference of reactivity of monoclinic and cubic Sm_2O_3 by the change of lattice oxygen mobility and exchange ability for different crystal structures. The variation of the activity depending on the exposed crystal face of MgO has been studied by Hargreave et al. [7]. All these works clearly show that a link must exist between structure and reactivity in methane activation. With pure La_2O_3, this relation cannot be confirmed since no phase transition exists like with Sm_2O_3. However the combination of La_2O_3 (hexagonal) and Y_2O_3 (bixbyite structure) leads to a mixed phase: $La_{2x}Y_{2-2x}O_3$ whose defined structure depends on the calcination temperature of the precursor [8]: e.g. bixbyite form at low temperature ($T <$ 700 ° C), perovskite form at high temperature ($T >$ 1000 ° C). The aim of this work was to provide a new example of the activity to structure relation in methane activation.

2. Experimental

a) PREPARATION

1) Fresh lanthanum and yttrium oxides were prepared as standards as follows: the rare earth (RE) hydroxide was precipitated from a 200 ml aqueous solution of 20 g of RE $(NO_3)_3$, $6H_2O$ (Aldrich 99.9% purity) by adding at 33% ammonia solution up to a pH of 9. The obtained gel or suspension was washed with pure water, dried for 15 h at 110 ° C and annealed at 800 ° C in flowing argon in order to avoid carbonate formation.

2) The $La_{2x}Y_{2-2x}O_3$ solid solutions ($x = 0.8$ or 0.5) were obtained by the same liquid phase preparation and drying. The heat treatment however depended on the desired crystal structure (pseudo cubic bixbyite type $500 < T <$ 680 ° C; perovskite type $T >$ 1000 ° C).

b) CATALYTIC TESTS [9]

The activity and selectivity of the various samples were determined in a fixed bed quartz reactor (6.6 mm I.D.) under the following conditions: Inlet temperature: 600–750 ° C; feed gas partial pressures: 0.133 atm CH_4, 0.0665 atm O_2 and 0.8 atm He; gas flow: 4.5 $lh^{-1}g^{-1}$ cat (STP); catalyst weight 0.67 g; CH_4/O_2 ratio = 2.

The CH_4, O_2 and He flows were controlled by an electronic mass flow metering system. The gases were mixed before introduction into the quartz reactor. A preheating zone exists in the quartz reactor and the temperature is measured by a thermocouple placed inside the catalytic bed. Blank experiments were performed to make sure of the complete inactivity of the quartz reactor itself.

c) ANALYSIS METHOD

1) A Siemens D 500 device was used in X-ray diffraction analyses.

2) Chromatographic conditions.

The reactant and products were analyzed by a G.C. (TCD) on Carbosphere and Porapak Q column packings. The main reaction products were CO, CO_2,

Table 1
Obtained solid phases versus temperature and duration of heat treatment

Compounds	Heat treatment temperature (°C)	duration (hr)	Crystal type
$0.8La_2O_3$, $0.2Y_2O_3$	500	2	pseudo cubic bixbyite
	550	2	pseudo cubic bixbyite
	600	2	pseudo cubic + hexagonal La_2O_3
	$\geqslant 800$	2	pseudo cubic + hexagonal La_2O_3
$0.5La_2O_3$, $0.5Y_2O_3$	500	2	uncrystallized
	680	2	bixbyite cubic phase
	$\geqslant 1000$	2	perovskite $LaYO_3$
La_2O_3	500	2	uncrystallized
	800	2	hexagonal La_2O_3

C_2H_4, C_2H_6 and H_2O. C_3 and C_4 hydrocarbons were produced in trace amounts and have not been measured.

3. Results and discussion

a) X-RAY CHARACTERISATION

For each compound the annealing temperature of the dried gel plays an important role. On table 1 the obtained solid crystal phases are related to the heat treatment temperature.

1) 0.8 La_2O_3-0.2Y_2O_3 mixture

On fig. 1a broad peaks are observed in the XR diffraction pattern. They can be attributed to a pseudo cubic phase whose stability area is located between 500 and 600 °C. At higher temperatures this pseudo cubic phase is unstable. Segregation into hexagonal La_2O_3 and a Y_2O_3 enriched pseudo cubic phase occurs as follows:

$$0.8\ La_2O_3\text{-}0.2Y_2O_3 \xrightarrow{T > 600\,^\circ C} xLa_2O_3 + (1-x)La_{\frac{1.6-2x}{1-x}}Y_{\frac{0.4}{1-x}}O_3$$

Computed interreticular distances show a decrease of the c/a ratio along with a Y_2O_3 enrichment of the mixed phase: $c/a = 1.013$ at 600 °C, $c/a = 1.002$ at 900 °C. Whatever the crystallographic results may be, the stabilizing properties of Y_2O_3 on cubic La_2O_3 compounds is evidenced. At temperatures higher than 600 °C however, the segregation phenomenon is irreversible and the mixed phase is converted into hexagonal La_2O_3 and perovskite $LaYO_3$ structures at 900 °C.

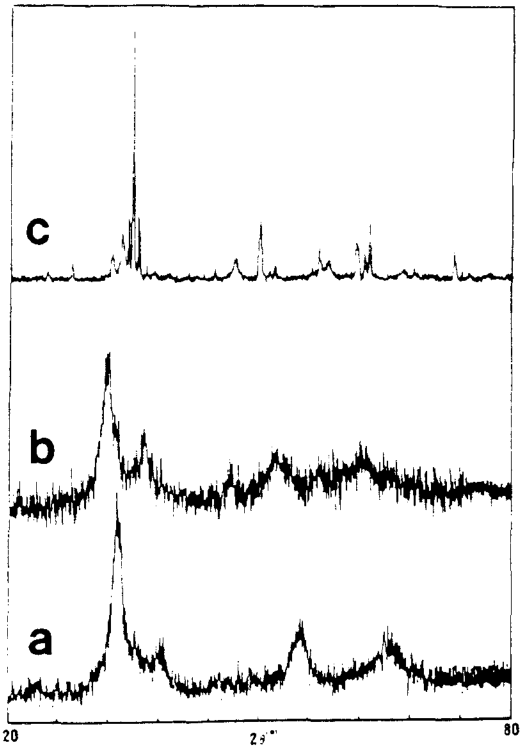

Fig. 1. X-ray patterns of samples: a) $0.8La_2O_3$, $0.2Y_2O_3$; b) $0.5La_2O_3$, $0.5Y_2O_3$; c) $LaYO_3$.

2) $0.5La_2O_3$-$0.5Y_2O_3$ mixture

The dried gel must be annealed up to 680 ° C before the apparence of a cubic phase corresponding to a bixbyite type structure, whose lattice parameter is $a = 10.900 + 0.005$ Å (fig. 1b). This cubic bixbyite phase is converted to a La_2O_3 perovskite after heat treatment at 1000 ° C (fig. 1c).

b) CERAMIC CHARACTERIZATION AND OBSERVATIONS

SEM observations (fig. 2) show a large particle aggregation for yttria-lanthana powders, but small unshaped particles are observed for pure lanthana (0.2 μm). The results are in good agreement with the BET surface area measurements (table 2).

For the $0.8La_2O_3$-$0.2Y_2O_3$ solid solution, a bixbyite structure where lanthanum cations substitute for yttrium cations, appears. This phenomenon can take place since all cation crystal sites are equivalent. However the La-O invariant length (2.596 Å) is rather big compared to the Y-O invariant length (2.385 Å). Thus upon particle growth with increased annealing temperatures, the equivalent cationic site becomes too small for lanthanum but too large for yttrium. This limits the stability of the solid solution.

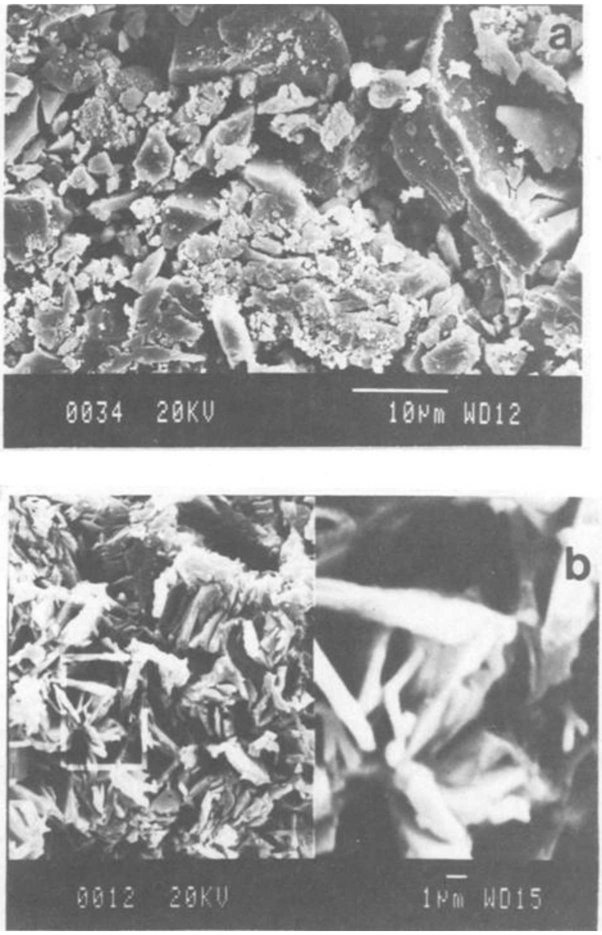

Fig. 2. Scanning electron micrographs of samples: a) $0.5La_2O_3$, $0.5Y_2O_3$; b) $0.8La_2O_3$, $0.2Y_2O_3$.

The conventional Vegard law cannot be followed at each temperature and for all solid solution composition. This leads to a segregation into hexagonal La_2O_3 and the most stable solid ($0.5La_2O_3$-$0.5Y_2O_3$).

Table 2
BET surface area of the prepared samples

Catalyst	Temperature of treatment (°C)	Surface area (BET) (m^2/g)
La_2O_3	800	22.0
$0.8La_2O_3$, $0.2Y_2O_3$	600	14.0
$0.5La_2O_3$, $0.5Y_2O_3$	680	23.6
$LaYO_3$	1000	6.3
Y_2O_3	750	6.8

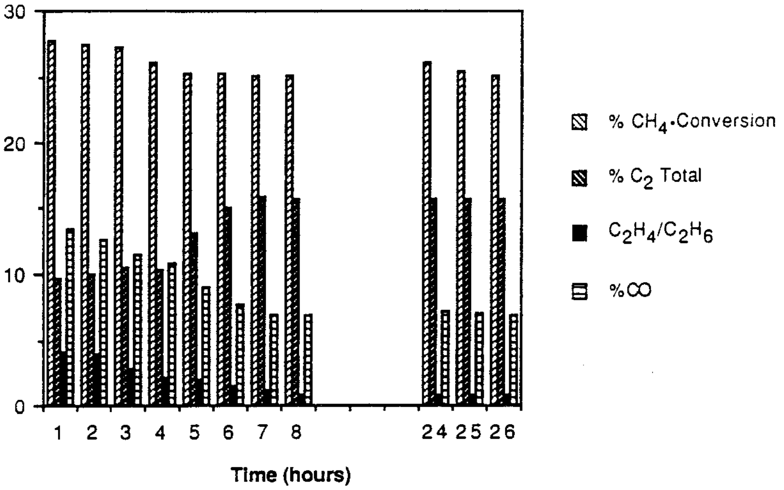

Fig. 3. Evolution of activity and selectivity over $La_{2x}Y_{2-2x}O_3$ ($x = 0.8$) catalyst versus reaction time.

For the $0.5La_2O_3$-$0.5Y_2O_3$ mixture, a well defined solid solution of bixbyite type structure is obtained. When the annealing temperature is increased, the compound progressively evolves into an entirely different crystal structure, e.g. the $LaYO_3$ perovskite structure. In this new structure, La is situated in a 12-fold and Y in a 6-fold oxygen environment. This change results in a particle sintering (decrease of BET area) as shown in table 2.

c) CATALYTIC PROPERTIES AND DISCUSSION

The catalytic performances versus time of the $La_{1.6}Y_{0.4}O_3$ catalysts at 700 °C are shown on fig. 3. The methane conversion decreases from 28 to 25% during the first eight hours on stream. The catalyst is then left under helium overnight. The initial activity is restored in these conditions and diminishes again with time on stream. The total C_2 selectivity starts at 9.5% and is stabilized at about 15%. The $C_2/C_2^{=}$ ratio decreases with time on stream (4 to 1) as well as the percentage of CO (14 to 8%). It must be noted that neither the selectivity nor the $C_2/C_2^{=}$ ratio are affected by the helium treatment. In the described reaction conditions, the surface area decreases from 14 to 9 m^2/g after 26 hours on stream and the XRD pattern clearly evidences the segregation of hexagonal La_2O_3.

As indicated for the $La_{1.6}Y_{0.4}O_3$, the evolution of selectivity and conversion for definite bixbyite structure $LaYO_3$ almost does not change with time on stream. An increase of less than 5% for C_2 selectivity between two and eight hours reactivity was observed.

The catalytic properties in methane oxidative coupling are summarized on table 3 as well as the solid solutions after 8 hours on stream.

Table 3
Activity and selectivity of pure La and Y oxide, $La_{2x}Y_{2-2x}O_3$ mixed oxides and $LaYO_3$ after 8 hours on stream

Catalyst	Conversion		Selectivity						BET area (m^2/g)	
	CH_4	O_2	C_2H_4	C_2H_6	ΣC_2	CO	CO_2	$C_2/C_2^=$	before experiment	after experiment
La_2O_3	26.9	99.5	12.3	11.2	23.5	15.3	61.2	0.9	22.0	14.0
$LaYO_3$ (bix)[1]	28.6	98.6	8.0	6.3	14.3	10.0	75.7	0.8	23.6	11.2
$LaYO_3$ (per)[2]	26.9	98.7	ϵ	0.4	0.4	14.7	84.8	–	6.3	4.9
$La_{1.6}Y_{0.4}O_3$	25.4	99.0	7.2	8.5	15.7	7.0	77.3	1.2	14.0	9.0
Y_2O_3	24.8	99.2	5.7	12.3	18.0	6.6	75.3	2.1	6.8	3.9

[1] calcinated at 700 ° C;

[2] calcinated at 1000 ° C, ratio $CH_4/O_2 = 2$.

Table 4
Activity and selectivity of $LaYO_3$ (bixbyite) and $LaYO_3$ (perovskite) after 8 hours on stream

Catalyst	conversion				selectivity			
	CH_4	O_2	C_2H_4	C_2H_6	ΣC_2	CO	CO_2	$C_2/C_2^=$
$LaYO_3$ (bix)	24.8	99.7	8.4	7.8	16.2	7.56	76.1	0.8
$LaYO_3$ (per)	22.9	100	ϵ	0.5	0.5	12.6	86.9	–

(at 700 °C, $CH_4/O_2 = 5$)

No noticeable activity difference is observed (table 3) between hexagonal La_2O_3, cubic solid solution or Y_2O_3 bixbyite. However, a clear difference in selectivity between two different crystal phases of the same composition must be emphasized. The $LaYO_3$ perovskite leads rather to an oxidation in CO and CO_2 than to the oxidative coupling of methane into C_2 hydrocarbon. The enhancement of the CH_4/O_2 ratio from 2 to 5 does change significantly neither methane conversion nor C_2 selectivity (table 4).

When the temperature increases from 600 to 750 °C, for the bixbyite form, the percentage of CO_2 decreases from 84.9 to 75.4%, selectivity of CO decreases from 12.4 to 9.9%, whereas C_2 selectivity increases from 2.6 to 14.7%. For the perovskite form, the same temperature increase only favours slightly CO_2 formation (82.5 to 84.5%) at the expense of CO and does not substantially change the C_2 selectivity.

Differences in selectivity for $LaYO_3$ (bixbyite) and $LaYO_3$ (perovskite) are not believed to be related to a difference of specific surface area. A first explanation could be found in comparing the basicity of the different structures since numerous works indicate that the addition of an alkali favours the C_2 selectivity at the expense of the total oxidation [1,10]. It is noteworthy that the XRD spectra are the same before and after the reaction both for $LaYO_3$ (bixbyite) and $LaYO_3$ (perovskite).

In order to compare the relative basicity of bixbyite and perovskite, two factors must be taken into account: The achieved temperature of the products (the acidity of a system increases with the annealing temperature) and the coordination number (the system with the highest coordination being the most basic one). These two factors have an inverse influence and any interpretation becomes consequently unreliable. A second explanation relating the oxidating power with the lability of the lattice oxygens can be suggested. In a previous work [11], a high C_2 yield was proposed to be related to a low element-oxygen binding energy for systems with the same environment ($A_2B_2O_7$ pyrochlore, environment 7). The element-oxygen binding energy can be obtained from Henry's method [12] taking the partial charge of each element in the compound and the mean oxygen-element distance determined from the invariant tables [13,14]. The relations between structure and reactivity for the $La_{2x}Y_{2-2x}O_3$ compounds are shown in table 5.

Table 5
Relationships between structure and catalytic tests for $La_{2x}Y_{2-2x}O_3$ compounds

Catalyst	Oxygen environment	Conversion CH_4 (%)	C_2 yield (%)	Coulombian energy (c^2/A)	
				La-O	Y-O
La_2O_3	7	26.9	11.2	0.1376	–
$LaYO_3$ (bix)	6	28.6	6.3	0.1374	0.1474
$LaYO_3$ (per)	12	26.9	0.4	0.1371	0.1474
Y_2O_3	6	24.8	12.3	–	0.1475

The variation of the La-O and Y-O bonding energy is weak when passing from a bixbyite to a perovskite structure. This seems to be in disagreement with a previously enounced rule. However this last rule was verified for system having the same oxygen environment, which is not true for the bixbyite and perovskite structures.

The main difference between bixbyite and perovskite structures is the number of oxygens surrounding the cationic site: 6 for lanthanum and yttrium in the bixbyite structure, and 12 for lanthanum but 6 for yttrium in the perovskite structure. Since the binding energies are equivalent, if it is admitted that the cationic sites on which methane adsorbs are the active sites, the oxidation rate will depend on the number of the oxygen neighbours for one part and the relative distance between oxygens and cations. Indeed it can be supposed that the oxygens which are nearest to the cationic site will be the most active. For the perovskite the most stable face is the (111) face followed by the other low index planes. In the (111) faces the lanthanum is surrounded by 6 oxygens compared to a minimum of 4 for the other low index planes. For the bixbyite, this environment is 4 and drops to 3 or 2 for the other index planes. This reactivity difference is a new example of the important role played by the crystal structure in the methane oxidative coupling.

This could, in our opinion, explain partly why the oxidation power of $LaYO_3$ perovskite is greater than that of the $LaYO_3$ bixbyite.

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