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STRUCTURE SENSITIVITY OF THE CATALYTIC OXIDATIVE COUPLING OF METHANE ON LANTHANUM OXIDE

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The oxidative coupling of methane (OCM) has been found to be structure sensitive on La_2O_3 catalysts exhibiting different crystallite morphologies. Thin plates obtained by thermal decomposition of lanthanum nitrate at 650 ° C are more selective on OCM reaction performed at 750 ° C than the particles obtained by decomposition of the nitrate at 800 ° C. It is assumed that the oxycarbonate observed is formed from the methane deep oxidation on the catalyst surface. This compound appears to act as an intermediate in the production of CO_2 and is thus important in the resulting selectivity.

The structure sensitivity of the catalytic mild oxidation of alcohols and olefinic hydrocarbons is now well established [1–6] and forms a basic concept for the understanding of the different catalytic behavior generally observed for different preparations of the same catalyst. A catalytic reaction is called structure sensitive if the activities and/or the selectivities for the formation of the products depend on the structure of the catalytic site [4,5]. This effect is most effectively observed for catalyst particles with different morphologies obtained by modifying the nature and the extent of the exposed crystallographic planes.

In order to test whether the reaction of oxidative coupling of methane (OCM) is structure sensitive on lanthanum oxide catalysts, two samples were prepared by thermal decomposition of lanthanum nitrate ($La(NO_3)_3.5H_2O$) in air at 650 ° C for 2 h and at 800 ° C for 16 h hereafter referred to as La_2O_3-LT and La_2O_3-HT, respectively. The X-Ray Diffraction (XRD) patterns of both oxides are consistent with the formation of pure hexagonal La_2O_3 [7]. The BET specific surface areas of La_2O_3-LT and -HT, measured by N_2 adsorption before catalysis, are measured to be 2.1 and 6.0 $m^2.g^{-1}$ respectively.

The morphologies of the two samples observed by electron microscopy before catalysis exhibit strong differences. It appears clearly that the La_2O_3-LT sample is mainly constituted of thin plates (fig. 1) whereas La_2O_3-HT is rather formed of tridimensional and smaller particles (fig. 2).

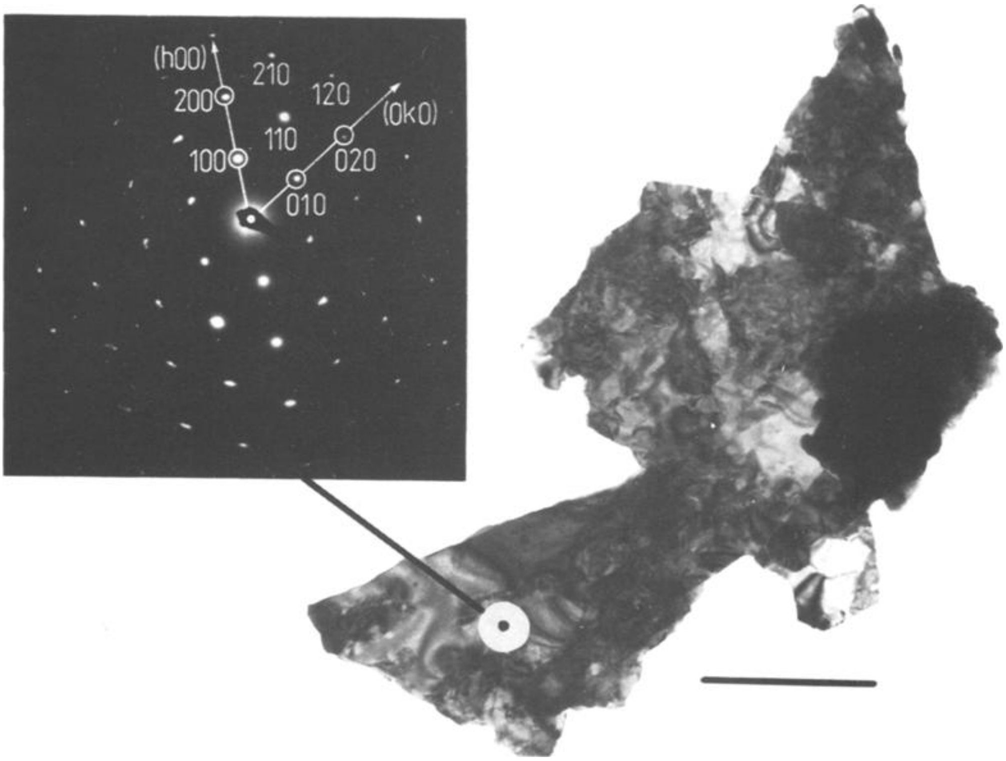

Fig. 1. Electron micrograph (TEM) of La_2O_3-LT (×16800) and microdiffraction pattern. Black bar represents 0.5 μm.

The microdiffraction patterns of the two samples are consistent with the hexagonal structure and show that the tin plates of La_2O_3-LT are almost monocrystalline and expose mainly (001) faces (fig. 1).

The catalytic studies were conducted at atmospheric pressure in an isothermal plug-flow type microreactor of 2 mm of inner diameter, made of sintered alumina. It was first verified that the empty reactor is almost inert in our catalytic conditions with a total conversion of less than 0.2% at 750 ° C. The steady-state was reached after about 3 h of reaction. During this period, for both samples, total activity increases by about 40–45%, but selectivities do not change significantly. The carbon balance is always within experimental error. The reaction conditions and catalytic results measured at steady-state are summarized in table 1. These values are constant for at least 7 hours. The results show a higher total intrinsic activity and C_2^+ selectivity for the La_2O_3-LT sample.

The *in-situ* infrared characterization of the catalysts has shown that lanthanum oxycarbonate ($La_2O_2CO_3$) can be formed during the OCM reaction at a temperature below 700 ° C. On the other hand, Cameron et al. [8] have pointed out the great importance of carbonate or oxycarbonate precursors for a good catalyst; it

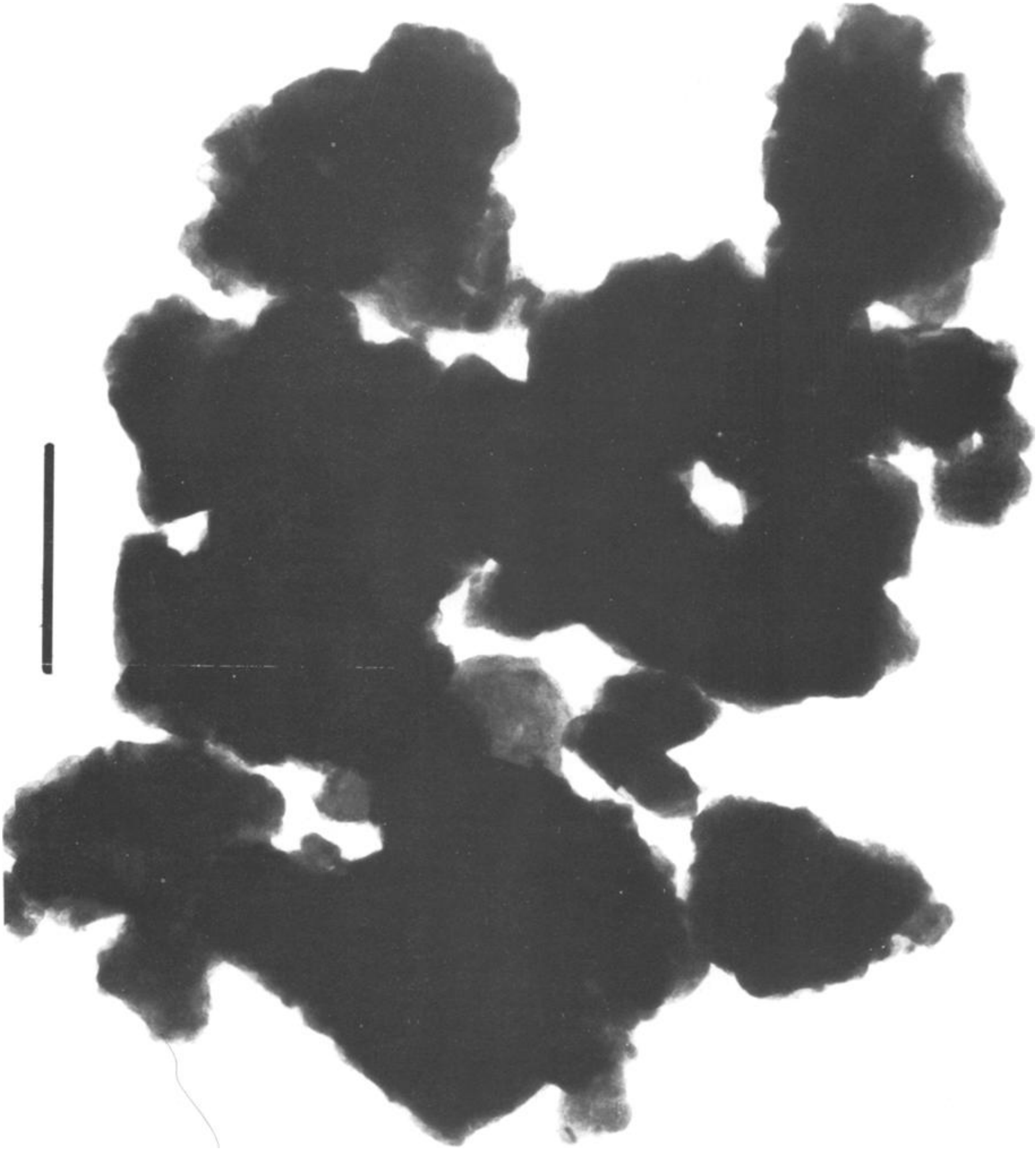

Table 1
Influence of the preparation temperature of La_2O_3 on the catalytic properties in the OCM reaction
Catalytic conditions [a]: $T = 750\,°C$; $CH_4/O_2/He = 8/2/90$ (mol%)
Total flow rate = 50 ml/min

	m (g)	%CH_4 conv.	%O_2 conv.	selectivity (%)					total act. (mol/h/m^2)
				C_2H_6	C_2H_4	CO_2	CO	ΣC_2	
La_2O_3-LT	0.005	12.2	27	47.4	16.6	14.8	17.8	67.4	0.124
La_2O_3-HT	0.005	9.5	35	37.4	11.8	25.5	24.0	51.5	0.034

[a] the total conversion of the empty reactor, using those conditions is always < 0.2%.

was then important to study the formation and stability of lanthanum oxycarbonate. Two types of oxycarbonate can be detected; a monoclinic form called type 1a and a hexagonal form called type 2 [9,10]. The formation and the thermal stability of those oxycarbonates were studied by thermogravimetry (TG), by using a gaseous mixture of 5 mol% CO_2 in air with a heating rate of 2 °C/min. The results are presented in fig. 3.

While the formation of oxycarbonate begins for both samples at about 540 °C, the decomposition by contrast occurs at different temperatures. The oxycarbonate from La_2O_3-HT appears thermally less stable than that from La_2O_3-LT.

Prior to the XRD analysis, the samples were carbonated as described above for the TG experiments but at a temperature of carbonatation chosen to be below the oxycarbonate decomposition temperature and then rapidly cooled to room temperature in the CO_2/air mixture. The selected temperatures were 750 and 860 °C for the LT sample and 780 °C for the HT sample (fig. 3). For all the samples, a mixture of oxycarbonates of types 1a and 2 [7] was identified, but for the samples

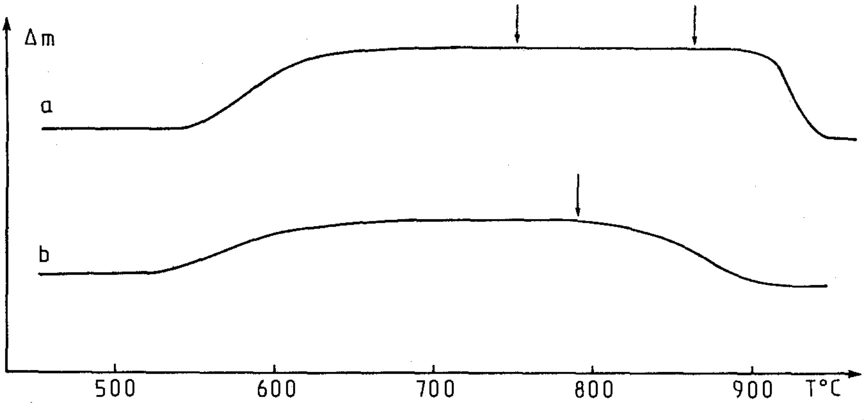

Fig. 3. Thermogravimetric analysis of lanthanum oxides (5 mol% CO_2 in air-heating rate 2 °C/min) a) La_2O_3-LT b) La_2O_3-HT. Arrows indicate the sampling temperature for X-ray diffraction analysis.

originating from La_2O_3-LT the type 1a is present only in small amounts. It has been already pointed out that type 1a is thermally less stable than type 2 [9]. This fact might be consistent with the behaviour observed in TG experiments where the oxycarbonate, mainly of type 2 formed from La_2O_3-LT oxide is decomposed at a higher temperature than those (mixture of type 1a and 2) from La_2O_3-HT. The formation of type 2 seems to be highly favoured by the thin plates shape of the La_2O_3-LT sample. These results suggest that the oxycarbonate formation is structure sensitive leading preferentially to the more stable oxycarbonate on the La_2O_3-LT. This effect can be directly connected to the catalytic behavior observed for the two La_2O_3's assuming that the oxycarbonate is formed from the methane deep oxidation on the catalyst surface.

From this point of view, once the oxycarbonate is transiently formed during the catalytic reaction, the CO_2 could mainly originate from its decomposition so that the higher the stability of oxycarbonate the lower the selectivity is CO_2. The structure sensitivity effect could then be due to a decrease in the rate of decomposition of the oxycarbonate (formally the desorption step of CO_2), which appears to act as an intermediate for CO_2 formation.

On the other hand, the more important reactivity of La_2O_3-LT suggests that a structure sensitive effect also exists for the rate limiting step of the OCM reaction. If, according to recent isotopic kinetic experiments with the CH_4/CD_4 mixture [11–14] the rate limiting step of the reaction is the methyl radicals formation, it means that the (001) faces, mainly exposed by the La_2O_3-LT catalyst, are more active and selective for the methyl radicals formation than the other exposed faces present in the La_2O_3-HT sample.

Lunsford et al. [15] have mentioned that the OCM reaction on Li-doped MgO catalysts does not directly depend on the catalyst morphology, whereas Hargreaves et al. [16] have found a strong influence of the shape of pure MgO catalyst particles. The experimental observations reported here seem to indicate that the mechanism on Li doped and pure oxide such as MgO and La_2O_3 is different. One may speculate as to why this is the case. A possible answer is that the oxide surface is "smoothed" by Li_2CO_3 which forms a liquid film under the experimental conditions used for the OCM reaction. This is not the case for $La_2O_2CO_3$ and pure MgO where the OCM reaction is structure sensitive. This in turn would suggest that the different coordination of the oxygen species present on the surface of MgO [17,18] is an important factor in the H abstraction from CH_4, i.e., the formation of methyl radicals.

In conclusion, the structure sensitivity of the OCM reaction observed on La_2O_3 catalysts strongly suggests that CO_2 is at least, produced on the surface, evidencing the heterogeneous catalytic character of the reaction and points out the very important role of the thermal stability of the carbonates formed on the catalyst surface as a consequence of the OCM reaction. The rate of CO_2 formation seems to be determined by the decomposition rate of the carbonate species and is likely to affect the final selectivity.

Acknowledgments

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