Oxidative coupling of methane over alkali-promoted Ti–La oxide catalysts. Effect of bulk and surface properties on catalytic performance

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The reactivity of lanthanum titanate catalysts is investigated in the oxidative coupling of methane (OCM) under lean-oxygen conditions. The catalyst performances are influenced by the catalyst preparation method and by the amounts of the alkali dopant. A transient method was also used to study the mobility of lattice oxygen species under OCM reaction conditions. It is found that (i) in the absence of gas phase oxygen the sample does not possess lattice oxygen species which participate in the reaction; (ii) the alkali doping does not appreciably modify the mobility of lattice oxygen; and (iii) the role of the alkali promoter in the reaction is that of modifying the surface acid/base and oxidizing properties.

Keywords: methane coupling; lanthanum titanate catalysts; OCM

1. Introduction

The oxidative coupling of methane (OCM) has attracted great attention in recent years as a possible alternative route for the direct production of ethylene and ethane [1–4]. The reaction is carried out at high temperatures (700–850°C) in the presence of a catalyst, which seems to be responsible for the formation of methyl radicals from methane.

A number of catalysts have been reported in the literature as suitable for the OCM reaction. Among them, rare-earth oxides and alkali-promoted rare-earth oxides show promising catalytic properties [5–10]. In particular, lanthanum oxide shows significant activity in the catalytic production of gas-phase methyl radicals from methane [10] and is used as a major costituent in several OCM catalysts [11].

In previous studies on the OCM reaction we have reported that ternary systems containing titanium, lanthanum and sodium effectively catalyze the oxidative coupling of methane [12,13]. However, the catalytic properties of these materials have not been fully addressed so far. The present investigation has been undertaken to provide new insight in the behaviour of TiLaNa samples in the OCM reaction. For this purpose, unpromoted and Na-doped titanium lanthanum oxide catalysts were prepared, characterized and tested under OCM conditions. The Ti/La atomic ratio was fixed to 1/1 or to 1/2 and the content of the alkali dopant was varied up to a maximum of 8% w/w. The samples were prepared by different procedures to investigate the effect of the preparation method on the final properties of the materials. Catalyst characterization included XRD, surface area measurements, investigation of the surface acid/base properties by the isopropyl alcohol decomposition method [14] and transient experiments with CH_4/O_2 mixtures to establish the role of lattice oxygen as compared to that of adsorbed oxygen species formed during reaction conditions.

2. Experimental

2.1. Catalyst preparation and characterization

Samples with Ti/La atomic ratios 1/1 and 1/2 were prepared by two different procedures: the slurry method and the citric acid complexation method.

In the former case, TiO_2 anatase was mixed into a water solution of lanthanum nitrate (all reagents were 99.9% purity Fluka products). The slurry so obtained was concentrated by evaporation under stirring at about 80°C and finally dried at 110°C. The dried sample was calcined in air at 800°C for 4 h.

In the citric acid complexation method, titanium isopropoxide (Carlo Erba reagent) was complexated with a hot citric acid solution under stirring until complete dissolution was obtained, and then mixed with lanthanum acetate dissolved in a citric acid solution. One equivalent of citric acid per equivalent of metal was used. The resulting solution was concentrated and desiccated under vacuum and then calcined at 800°C for 6 h under a flow of $N_2 + O_2$. The oxygen concentration was slowly increased with temperature from 5% v/v up to 21% v/v to avoid uncontrolled oxidation reactions of the organic precursor of the catalyst.

The calcined samples were compacted into discs by compression from which granules (20–40 mesh) were

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obtained by grinding. The catalysts were then impregnated with different amounts of Na by the incipient wetness technique starting from either a sodium nitrate solution (samples prepared via the slurry method) or a sodium carbonate solution (citric acid complexation method).

In the following the Ti/La oxide catalysts prepared according to the slurry and the citric acid complexation method will be reported as TiLa(s) and TiLa(c), respectively.

2.2. *Surface area and bulk phase composition*

Surface area measurements were obtained with the BET method with nitrogen at 77 K using a Carlo Erba Sorptomatic 1900 series instrument. XRD analyses were performed using a Ni filtered Cu Kα radiation on a Philips PW 1050/70 instrument.

2.3. *Steady-state and transient activity experiment*

Unpromoted and Na-doped Ti/La oxide catalysts were tested in the oxidative coupling of methane under steady-state conditions by co-feeding methane and air ($T = 750°\mathrm{C}$, $P = 1$ atm, CH_4/O_2 molar ratio = 5). Catalytic activity runs were performed in a quartz fixed-bed reactor (inside diameter 9 mm and heated length 40 mm) fitted with a capillary exit tube (i.d. 2 mm). Reaction temperature was measured by means of a 0.5 mm quartz shielded K-type thermocouple directly immersed in the catalyst bed.

Reaction products were analyzed every 20–30 min by conventional on-line gas-chromatography by using a 5 Å molecular sieves column and a Porapak QS column with thermal conductivity detector (TCD) for analysis of oxygen, nitrogen, methane, hydrogen, CO, CO_2 and water; and a Poraplot Q capillary column with a flame ionization detector (FID) for detailed analysis of hydrocarbons. Gas compositions were calculated using N_2 as internal standard. The carbon mass balances, estimated as (moles of CH_4 reacted)/(moles of C in the products), were always within ±2%.

Before each activity measurement, the catalysts were activated in situ in flowing air at 800°C for 1 h. Catalytic activity runs were carried out for 6–8 h; no catalyst deactivation was observed with time on stream.

On/off switching of the reactants was performed in the same apparatus used for catalytic activity measurements, but with a reactor of smaller diameter (i.d. = 7 mm) and with smaller amounts of catalysts (200 mg). In this case, the reactants were fed to the reactor through dedicated lines with facilities for switching, and particular care was taken to eliminate all possible dead volumes before and after the catalyst bed. Blank experiments performed under the same experimental conditions but with quartz granules in the reactor indicated that no reaction occurred in the absence of the catalyst.

To determine the responses to abrupt switches of the reactants, the catalyst was oxidized in air at 800°C for 1 h and then kept at 750°C under a flow of He and oxygen (or methane) until steady state conditions were reached. Then part of the He flow was switched to methane (or oxygen) and after approximately 90 s the flow of methane (or oxygen) was switched back to He. The overall concentration of methane and oxygen in He was kept lower than 5% v/v to minimize temperature changes in the catalysts bed in correspondence to the switch.

The variations in the concentration of reaction products with time was monitored by means of an UTI 100C quadrupole mass detector (QMD) coupled with an IBM AT PC for data acquisition and processing. Mass to charge ratios of 16, 18, 26, 28, 30, 32 and 44 were selected to monitor the concentrations of methane, water, ethylene, CO, ethane, oxygen and CO_2, respectively. The fragmentation patterns for some of these components overlap considerably, and therefore a system of linear algebraic equations had to be solved to obtain the time/concentration profiles of the different species. Furthermore, on-line GC analysis of the reaction products was still possible.

Methane (99.5%), nitrogen (99.99%), oxygen (99.9%) and helium (99.999%) were obtained from SAPIO and used without any further purification.

2.4. *Acid–base properties*

The catalyst acid–base properties have been investigated according to the isopropyl alcohol (IPA) decomposition method [14,15]. Accordingly, the formation of propylene is a measure for the surface acidity, whereas the formation of acetone is related to the presence of surface basic sites. Isopropyl alcohol decomposition experiments were carried out at 300°C with a feed consisting of IPA (0.8% v/v) in air by using the same apparatus used for the OCM catalytic activity runs (see above). The reaction was performed under oxidative conditions as proposed in refs. [14,15]. Before the IPA decomposition experiments, the catalysts were calcined in situ in flowing air at 600°C for 2 h. Catalytic runs were carried out for 6–8 h and the reaction products were analyzed by on-line GC every 20–30 min. No catalyst deactivation was observed with time on stream, and the carbon mass balances were always within ±2%.

3. Results and discussion

3.1. *Surface areas and bulk phase composition*

Table 1 reports the values of the specific surface areas and the major crystalline phases detected by XRD analysis for the unpromoted Ti/La oxide catalysts after calcination at 800°C in air (fresh samples). The variations

Table 1
Surface areas and crystalline phases detected by XRD analysis in the Ti/La oxide samples. The arrows indicate the modification of the corresponding XRD lines upon addition of the alkali dopant [a]

Catalyst	Surface areas (m^2/g)	Crystalline phases detected by XRD			
Ti_1La_1(s)	5	TiO_2	$Ti_1La_2O_5$		$La_{0.66}TiO_{2.993}$
Na-doped Ti_1La_1(s)	↓	↓	↓		↑
Ti_1La_1(c)	18			$Ti_2La_2O_7$	
Na-doped Ti_1La_1(c)	↓			↔	
Ti_1La_2(s)	4	TiO_2	$Ti_1La_2O_5$		$La_{0.66}TiO_{2.993}$
Na-doped Ti_1La_2(s)	↓	↔	↓		↑
Ti_1La_2(c)	5		$Ti_1La_2O_5$		
Na-doped Ti_1La_2(c)	↓		↔		

[a] (s) Preparation via the slurry method; (c) preparation via complexation with citric acid; ↑ increase of the characteristic XRD lines; ↓ decrease of the specific surface area or of the characteristic XRD lines; ↔ no significant variation in the XRD lines.

observed in the specific surface areas and in the XRD pattern upon alkali doping are also schematically reported.

The Ti_1La_1 and Ti_1La_2 oxide samples prepared by the slurry method present low specific surface areas (5 and 4 m^2/g, respectively) and show a complex phase composition: XRD lines corresponding to TiO_2, $La_2Ti_1O_5$ and $La_{0.66}TiO_{2.993}$ phases were detected. On the other hand, both the Ti_1La_1 and Ti_1La_2 oxide catalysts prepared by complexation with citric acid appear to be monophasic and accordingly only the $La_2Ti_2O_7$ and $La_2Ti_1O_5$ phases have been detected, respectively. The values of the specific surface areas measured for these samples were 18 and 5 m^2/g, respectively. The data reported in table 1 clearly indicate that the preparation method has strong effects on the morphology and phase composition of the catalysts, and show also that the citric acid complexation method leads to the formation of monophasic samples.

The arrows in table 1 schematize the variations in the specific surface areas and in the phase composition of the samples upon alkali doping. Significant changes occur in the samples prepared with the slurry method, and in particular it is noted that the addition of the alkali promoter favors in both cases the formation of the $La_{0.66}TiO_{2.993}$ phase. By contrast, no significant variations are evident in the XRD spectra of the catalysts prepared via complexation with citric acid.

A significant loss of surface area is evident for all the samples upon alkali doping: in the case of the Ti_1La_1 oxide catalysts prepared by complexation with citric acid the specific surface area is progressively reduced down to 8 m^2/g when the alkali dopant is increased up to 3.5% w/w (as Na_2O), whereas for the other samples values as low as 1 m^2/g have been measured after doping with similar amounts of the alkali promoter.

XRD and specific surface area measurements were also performed over the catalysts discharged from the reactor. In the case of the samples prepared with the citric acid complexation method neither significant variation in the characteristic XRD lines nor loss of surface area have been observed. On the other hand, for the samples prepared by the "slurry" method, a slight increase in the characteristic XRD lines of the $La_{0.66}TiO_{2.993}$ phase has been observed.

3.2. Catalytic activity runs

Figs. 1A–1D report the performances of unpromoted and Na-doped Ti/La oxide catalysts in the oxidative coupling of methane at 750°C. For all the samples major reaction products were carbon oxides (CO_2 and CO) and C_2 hydrocarbons (ethylene and ethane). Minor amounts of C_3 and C_4 hydrocarbons were also detected, along with trace amounts of hydrogen.

All samples show significant activity in the reaction (almost complete oxygen conversion is achieved for all the catalysts), but the selectivities to the different products may change significantly according to the catalysts preparation method and the alkali loadings.

In the case of the unpromoted Ti_1La_2 samples only minor differences were observed in the selectivity to the various reaction products between the catalyst prepared with the citric acid complexation method and that prepared according to the slurry method (figs. 1C and 1D), thus indicating that in this case the preparation procedure does not influence the catalyst performances to a great extent. A different picture is apparent in the samples with Ti/La atomic ratio 1/1 (figs. 1A and 1B): indeed, whereas the catalyst prepared with the citric acid complexation method leads to complete selectivity to CO_x, the sample prepared according to the slurry method shows appreciable selectivity to C_{2+} species. Results clearly indicate that in this case the different preparation method and the catalysts bulk composition strongly affect the catalyst performances in the OCM reaction.

Upon addition of the alkali promoter, significant variations in the catalytic performance were observed for both the Ti_1La_1 and Ti_1La_2 catalysts. In the case of the Ti_1La_1(s) samples the selectivity to C_{2+} products slightly increases upon alkali addition, and eventually reaches a maximum in correspondence of 1% Na_2O. On the other hand, a dramatic enhancement of the catalytic perfor-

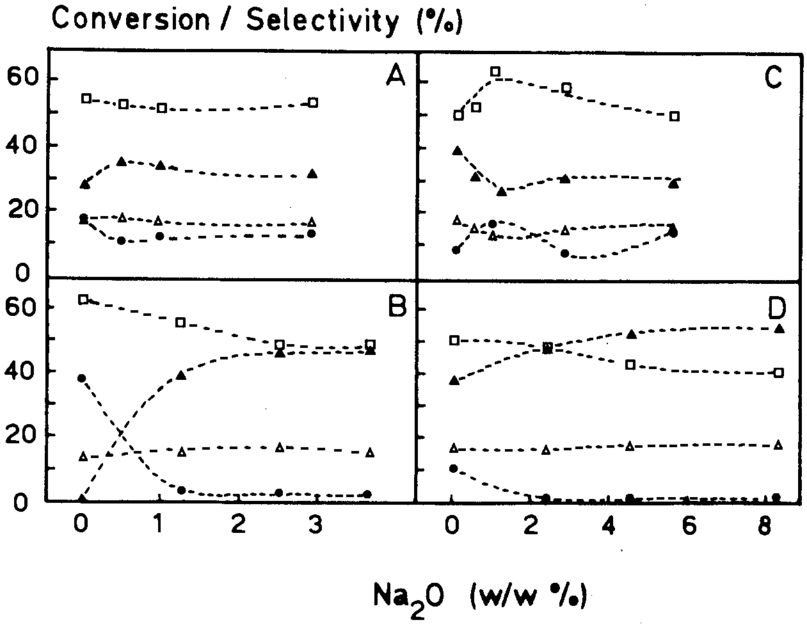

Fig. 1. Results of catalytic activity runs performed over Na-promoted lanthanum titanate catalysts. $T = 750°C$, $P = 1$ bar, GHSV = 2500 h^{-1}, $CH_4/O_2 = 5$. (A) Ti_1La_1 prepared with the slurry method; (B) Ti_1La_1 prepared by complexation with citric acid; (C) Ti_1La_2 prepared with the slurry method; (D) Ti_1La_2 prepared by complexation with citric acid. (△) CH_4 conversion; (●) selectivity to CO; (□) selectivity to CO_2; (▲) selectivity to C_2.

mances is evident for the sample prepared with the citric acid complexation method. Indeed the selectivity to C_{2+} products increases from 0 to 50% upon addition of 4% w/w Na_2O. A corresponding decrease in the selectivity to CO_x (prevalently CO) is also observed (fig. 1B).

The alkali promoter also significantly affects the catalytic behaviour of the catalysts with Ti/La atomic ratio = 1/2. An increase in the selectivity to C_{2+} products has been observed for the sample prepared via the citric acid complexation method (fig. 1D), whereas the sample prepared with the slurry method shows a complex behaviour. As a matter of fact, the selectivity to C_{2+} products at first decreases upon addition of the alkali dopant and then increases with further alkali increase. This fact can be related to different and possibly opposite effects induced by the presence of the alkali promoter, which is responsible for changes in the acid/base properties of the surface and modifications in the bulk phase composition as well (see table 1).

3.3. Surface acid/base properties

In order to investigate the role of the surface acid/base properties on the OCM reaction and the variations induced by the alkali promoter, unpromoted and sodium-promoted samples were tested in the decomposition of isopropyl alcohol. It has been reported that formation of propylene and acetone in this reaction related to the presence of acid and basic sites, respectively [14,15].

Only the catalysts prepared according to the citric acid complexation method were used in these experiments, being simple phases also upon alkali addition.

Results obtained by decomposition of isopropyl alcohol over unpromoted and Na-doped Ti_1La_1(c) and Ti_1La_2(c) oxide catalysts are reported in figs. 2 and 3, respectively. For purpose of comparison, the figures also report the selectivity to C_{2+} products obtained over the same catalysts in the OCM reaction, already reported in fig. 1.

In the case of the unpromoted Ti_1La_1 oxide catalyst, fig. 2 shows that the main reaction product is propylene, with selectivity near 55%. Acetone is also produced to a significant extent together with minor amounts of CO_2, possibly originated by acetone oxidation. Upon alkali

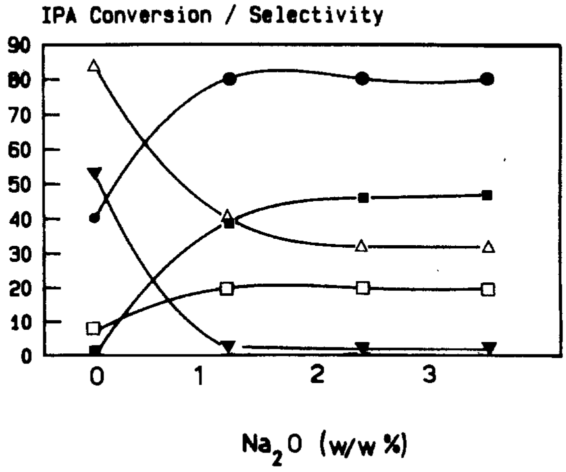

Fig. 2. Results of isopropyl alcohol (IPA) decomposition in air at 300°C over the Na-promoted Ti_1La_1 catalyst prepared by complexation with citric acid. Feed: 60 cm^3/min air+0.74% v/v IPA, catalyst weight 800 mg, $P = 1$ bar. (△) IPA conversion; (●) selectivity to acetone; (▼) selectivity to propylene; (□) selectivity to CO_2; (■) selectivity to C_2 in the oxidative coupling.

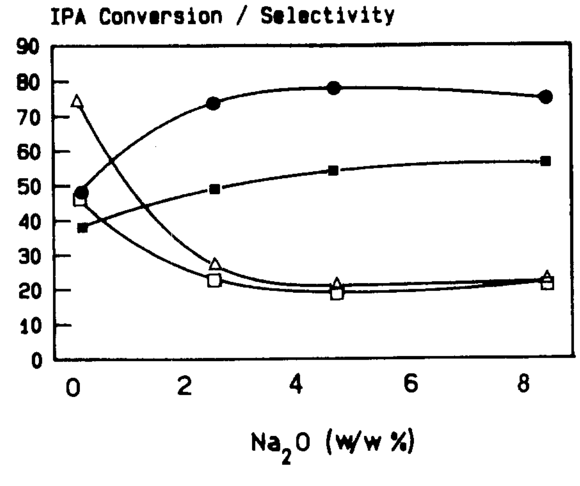

Fig. 3. Results of isopropyl alcohol (IPA) decomposition over the Na-promoted Ti_1La_2 catalyst prepared by complexation with citric acid. Symbols and operating conditions as in fig. 2.

addition, the selectivity to propylene becomes negligible, whereas the formation of acetone is significantly enhanced. A slight increase in the selectivity to CO_2 is also apparent.

These results clearly indicate that surface acid sites are present over the unpromoted Ti_1La_1 oxide catalyst, which are almost completely suppressed by alkali addition. This is reflected in the decrease of propylene formation upon alkali doping. It is worth noting that (i) no formation of C_{2+} species was observed in the OCM reaction over the umpromoted Ti_1La_1 oxide catalyst, and (ii) fig. 2 shows that the variation in the selectivity to C_{2+} products in the OCM upon alkali addition closely resembles that of acetone during IPA decomposition. This eventually indicates that the presence of surface acid sites leads to the formation of deep oxidation products in the OCM reaction and that basicity plays a crucial role in obtaining high C_{2+} selectivity in the OCM reaction.

It has been reported in the scientific literature that the selectivity of the catalysts in the OCM reaction is dependent on both catalyst acidity and basicity. In particular, it has been proposed that methane activation occurs via heterolytic C–H bond rupture of the CH_4 molecule over an acid–base couple, resulting in CH_3^- and H^+ ions [10,16,17]. In the presence of O_2, an electron transfer from the CH_3^- carbanion to O_2 takes place [18] leading to the formation of an O_2^- and a methyl radical which is released in the gas phase. Accordingly, both the carbanions and the radical species are expected to be strongly adsorbed over strong acid sites, leading to the formation of combustion products via reaction with adsorbed oxygen species. Hence, acid sites might play a role in the activation of methane, but they should be of very moderate strength to avoid formation of combustion products. Similar conclusions have also been reported by Becker et al. [19].

Results concerning isopropyl alcohol decomposition experiments over the Ti_1La_2 oxide samples are reported in fig. 3. The most abundant products over both unpromoted and Na-doped catalysts are acetone and CO_2, which possibly originates from a subsequent oxidation of acetone. In this case only traces of propylene are detected, which, however, because of their limited amounts have not been reported in the figure. The results indicate that in this case even the unpromoted catalyst does not possess strong surface acid sites able to catalyse the alcohol dehydratation reaction. In line with previous results, the catalyst exhibits significant C_{2+} selectivity in the OCM reaction. By increasing the alkali loading, significant variation in the selectivity to acetone and CO_2 was observed, and a decrease in the selectivity to CO_2 is particularly evident. This may indicate that the alkali dopant lowers the catalyst surface oxidative properties. As in the case of the Ti_1La_1 oxide samples, the selectivity to C_{2+} products in the OCM closely resembles the selectivity to acetone during IPA decomposition. Accordingly, one can speculate that the same surface sites that are involved in the deep oxidation of acetone to CO_2 are also responsible for the formation of CO_x in the OCM.

3.4. On/off switching of reactants

In order to investigate the role of adsorbed and lattice oxygen in the OCM reaction, a series of transient experiments was performed over pure and Na-doped Ti–La oxide catalysts (Ti/La=1) in which oxygen (or methane) were fed stepwise to the reactor.

Fig. 4 shows the transient responses of the various reaction products following the switch $He + CH_4 \rightarrow He + CH_4 + O_2$ over the unpromoted Ti_1La_1(c) oxide catalyst. The duration of the switch was ≈ 90 s.

From fig. 4 it appears that in correspondence to the oxygen switch an abrupt decrease in the concentration of methane is apparent, with the contemporary formation of CO_2, CO and minor amounts of ethylene and ethane whose formation was not observed in the absence of oxygen. The low amounts of ethylene and ethane, detected in the gases leaving the reactor, compare well with results obtained over the same catalyst under steady-state conditions. When the O_2 pulse was stopped, the rate of production of all the reaction products was suddenly reduced to zero, thus clearly indicating that in the absence of gas-phase oxygen the $La_2Ti_2O_7$ catalyst is inactive towards the CH_4 molecule. Accordingly, it is suggested that the sample does not possess bulk amounts of lattice oxygen that participate in the activation of methane and that a physisorbed or other surface oxygen species generated in the presence of gas-phase oxygen are responsible for CH_4 activation, as reported in the case of La_2O_3 [6].

Fig. 5 reports the results obtained upon O_2 switch in $He + CH_4$ over the alkali-promoted Ti_1La_1 oxide samples. For the sake of clarity, only the concentration profiles of ethane and CO_2 have been reported. We note

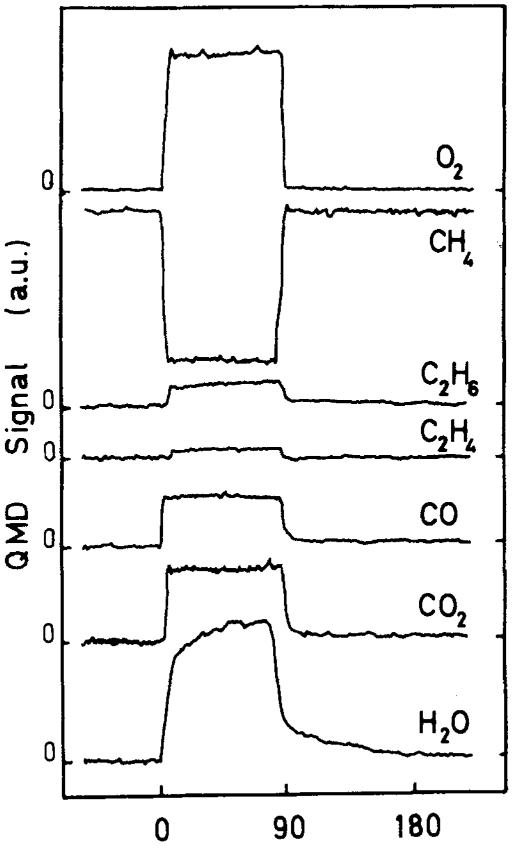

Fig. 4. Transient response to step addition of oxygen in methane + He over the Ti_1La_1 oxide catalyst prepared by complexation with citric acid. $T = 750°C$, $P = 1$ bar. The traces have been displaced vertically for clarity.

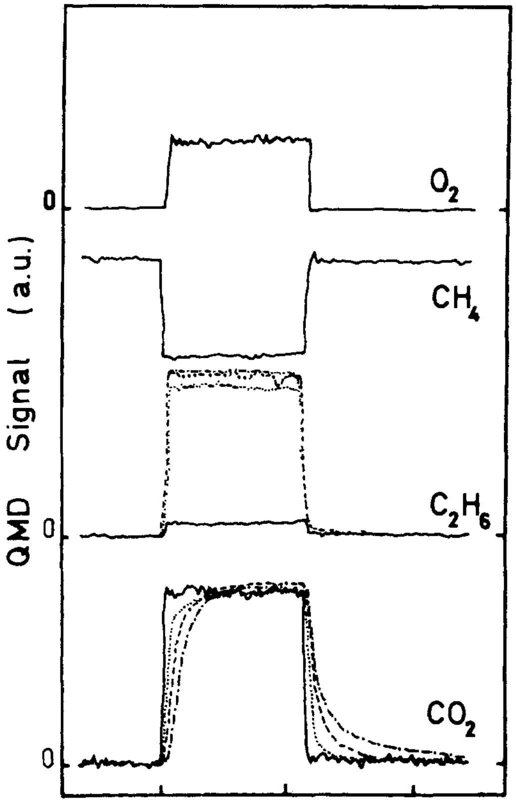

Fig. 5. Transient response to step addition of methane in He over the Ti_1La_1 catalyst prepared by complexation with citric acid. (—) 0% Na_2O; (...) 1.2% Na_2O; (---) 2.3% Na_2O; (— · — · —) 3.5% Na_2O. $T = 750°C$, $P = 1$ bar. The traces have been displaced vertically for clarity.

however that the production of ethylene is comparable to that of ethane while CO is present only in very low amounts.

Under flow of He + CH_4 only methane was detected at the reactor outlet. As in the case of the unpromoted sample, the formation of the reaction products occurs over all the catalysts immediately after oxygen introduction, and stops completely in the absence of gas-phase oxygen. Hence, the results seem to indicate that the presence of the alkali promoter does not apparently modify the mobility of catalyst lattice oxygen. In particular, as shown in fig. 5, the transient response in the formation of ethane (and of ethylene) is not significantly modified by increasing the alkali loading from 1.2 to 3.5% w/w Na_2O. Similar experiments have also been performed by Wolf et al. [9] over Li-promoted lanthanum titanate catalysts. The authors report that the addition of the lithium dopant increases the mobility of lattice oxygen, due to the formation of new lithium-containing phases. In this respect the sodium promotion apparently acts in a different way, since neither Na-containing phases have been detected by XRD analysis nor an increase of oxygen mobility has been observed, at least with our alkali loadings. We note, however, that similar results were obtained with different ternary TiLaNa catalysts in which the formation of Na-containing phases was detected by XRD spectroscopy [12].

Fig. 5 also shows that the transient step response of CO_2 upon the O_2 switch is significantly modified by passing from the unpromoted sample to the Na-doped catalysts. Indeed, upon increasing the alkali promoter the CO_2 gas-phase concentration increases more slowly with time and a pronounced tail is evident when O_2 is switched off. The broadening of the CO_2 transient response which is observed on increasing the alkali loading may be ascribed to the carbonation of the surface upon reaction which accordingly involves the alkali promoter, in line with XPS results obtained over similar catalysts [20]. Indeed, the slower rise in the CO_2 gas-phase concentration upon oxygen introduction over the alkalinized samples may be rationalized by assuming that the catalyst surface acts as a CO_2 acceptor which is progressively enriched with carbonate and hydroxyl–carbonate surface species. At the end of the oxygen switch, the reaction stops and the gas-phase CO_2 partial pressure is reduced. This leads to the decomposition of the carbonate and hydroxyl–carbonate surface species, as shown by the release of CO_2 in the gas phase. Evidences for the formation of surface sodium carbonate species upon reaction over ternary Ti/La/Na oxide catalysts has also been collected by XPS analysis performed over the discharged catalysts [13,20]. Results likely indicate that upon reaction sodium is present as a mixture of carbonate, hydroxyl–carbonate and oxide species. A similar conclusion has been reported by Lunsford et al. [5] for sodium-promoted lanthanide oxide catalysts.

Inspection of fig. 5 also shows that the transient response of ethane (and also of ethylene, not reported in the figure) is not affected by the build-up of sodium carbonate on the surface. This may indicate that sodium is not directly involved in the reaction, since its transformation into a carbonate form during the O_2 switch does not produce any significant change in C_{2+} selectivity. These data apparently contrast with our previous results obtained over TiLaNa catalysts prepared according to the slurry method and with higher sodium content (up to 35% w/w) which indicate that surface carbonation has a reverse effect on the selectivity to C_{2+} products [12]. Along similar lines, Lunsford et al. [5] reported that formation of sodium carbonate species has an adverse effect both on the generation of $CH_3\cdot$ radicals and on the conversion of methane. These contradictions may arise from the different characteristics of the samples; however our present results seem to indicate that the improvement in the catalytic performance which is observed upon alkali addition is related to the modifications of the acid/base and/or oxidizing sites of the surface.

4. Conclusions

The following conclusions can be derived from our investigation on sodium-promoted lanthanum titanate catalysts:

(1) The preparation method influences the bulk phase composition and catalytic performances of Ti/La oxide catalysts; in particular monophasic $La_2Ti_2O_7$ and $La_2Ti_2O_5$ samples can be obtained by using the citric acid complexation method.

(2) The monophasic lanthanum titanate catalysts differ widely in their catalytic and acid–base properties. The $La_2Ti_2O_7$ sample shows strong acid sites (as determined by isopropyl alcohol conversion) and behaves as a total methane oxidation catalyst, whereas the $La_2Ti_1O_5$ phase has negligible acidity and exhibits significant selectivity in the oxidative coupling of methane. Thus the presence of surface acid sites is undesirable and may be responsible for the low selectivity to C_2 products.

(3) The alkali promoter effectively decreases the surface acidity of the Ti_1La_1 catalyst and improves the catalytic performance.

(4) In absence of gas-phase oxygen the $La_2Ti_2O_7$ sample does not possess lattice oxygen species which can react with gas-phase methane; the presence of the Na promoter does not affect the reactivity of catalyst lattice oxygen.

(5) Under reaction conditions carbonation of the alkali promoter is likely to occur; formation of sodium carbonate or hydroxyl/carbonate species does not apparently modify the selectivity to C_2 species. Therefore it appears that over the investigated catalysts the alkali promoters block the acid and/or deep oxidation sites of the surface.

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