Effect of CO_2 and melt decarbonation on the dimerization of methane in molten Li_2CO_3–Na_2CO_3–K_2CO_3 supported by $LiAlO_2$ or Li_2TiO_3 at 750–850°C

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The oxidative dimerization of methane was investigated at 750–850°C in Li_2CO_3–Na_2CO_3–K_2CO_3 immobilized within $LiAlO_2$ or Li_2TiO_3 supports. Catalytic performance was enhanced with moderate melt decarbonation (i.e. with molten phase/$LiAlO_2$ at 850°C: CH_4 conversion of 25% and C_2 yield of 12.5%), then dramatically fell with the precipitation of sodium and lithium oxide. The effect of the partial pressure of CO_2 was analyzed. As in the case of binary carbonate eutectics, catalytic activity of the ternary melt was correlated with the presence of peroxide species. This activity was more important when using $LiAlO_2$ support.

Keywords: oxidative coupling of methane; methane dimerization; C_2 hydrocarbons yield; C_2 hydrocarbons selectivity; CH_4 conversion; supported molten carbonate catalyst; lithium aluminate; lithium titanate; lithium–sodium–potassium eutectic

1. Introduction

The role of molten carbonates in the catalytic transformation of methane has been outlined in the literature [1–8]. In particular, the behaviour of binary molten carbonates ($M_2CO_{3\,\text{liquid}} \rightleftharpoons CO_{2\,\text{gas}} + M_2O_{\text{solid}}$: M = Li, Na or K) towards the oxidative coupling of this molecule into C_2 hydrocarbons has been reported in previous studies [6–8]. The immobilization of these melts within a solid support, γ-

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$LiAlO_2$, enhanced the gas–liquid contact and allowed to reach higher methane conversion and C_2 yields (about 10% in Li_2CO_3–K_2CO_3 melt at 800°C). The catalytic performance, mainly attributed to the molten phase, was correlated with the presence of peroxide species, stabilized in oxobasic media (very low partial pressures of CO_2), according to the oxoacidity notion presented previously [6–9] and electrochemical experiments [10]. Nevertheless, in oxobasic media, obtained by melt decarbonation at high temperature, the activity of the supported catalyst progressively fell after extended use. This degradation was attributed to a microstructural change of the sample and to the formation of solid alkali oxide.

The aim of this paper was to investigate at different temperatures the activity of the ternary eutectic Li_2CO_3–Na_2CO_3–K_2CO_3, of which thermodynamic and electrochemical properties, described elsewhere[#1] [10], are close to those of Li_2CO_3–K_2CO_3 and Li_2CO_3–Na_2CO_3 [8]. Two solid supports have been used: γ-$LiAlO_2$ and, in particular, Li_2TiO_3, of which the activity as a catalyst of methane conversion has been described in the literature [11–14]. The effect of the oxoacidity, related to the partial pressure of CO_2, $P(CO_2)$, above the melt or to its decarbonation (formation of M_2O), was investigated. Special attention was paid to the recuperation of the catalyst, by imposing a CO_2 atmosphere, after a strong decarbonation due to extended use. Catalysts were analyzed by scanning electron microscopy and X-ray probe microanalysis before and after use.

2. Experimental

Lithium, sodium and potassium carbonates (Li-Na-K) mixed in a proportion of 43.5-31.5-25.0 mol% were Merck reagents of analytical grade (>98%). Synthesis and characterization of γ-$LiAlO_2$ pellets were described elsewhere [7]. Synthesis of lithium-titania support was realized according to a procedure described in the literature [12]. X-ray diffraction showed that the major compound was Li_2TiO_3 with impurities of $Li_{1.33}Ti_{1.66}O_4$. Immobilization of the molten phase within the solid supports was realized as previously described [7,8]. Catalytic reactor, gas chromatograph and quantification of the products were described in a previous paper[#2] [7]. The reactant gas was always a mixture of 136.8 Torr CH_4, 45.6 Torr O_2, 577.6 Torr He.

SEM characterization of samples before and after catalytic reaction

Scanning electron microscopy associated to X-ray probe microanalysis (Jeol T330A) was used to analyze the morphology of samples.

[#1] The extent of the acidity range, related to the decomposition of the ternary eutectic, is characterized by the autodissociation equilibrium constant: $pK_d^* = -\log K_d^* = a(M_2O)P(CO_2)$, where a is the activity and P the partial pressure. According to thermodynamic data: pK_d^* of Li-Na-K are 4.34, 3.91 and 3.61 at 700, 750 and 800°C respectively. A neutral medium is obtained with $P(CO_2) = K_d^{*1/2}$, i.e. at 750°C: $P(CO_2) = 1.1 \times 10^{-2}$ atm.

[#2] It must be noted that the relative error on C_2 yield is about 2–5%.

SEM micrographs of pure $LiAlO_2$ and Li-Na-K/$LiAlO_2$ before and after catalytic reaction are similar to those obtained with binary carbonate eutectics, as described elsewhere [7,8]. Before catalysis, both the support and the supported carbonate showed a similar structure of regular particles from 0.1 to 0.5 μm. The molten phase forms a thin layer of about 200 μm at the surface of the support. After catalytic reaction particles of supported molten phase coalesced into aggregates from 2 to 10 μm and numerous whiskers formed by sodium or potassium oxide were observed by X-ray probe microanalysis.

Fig. 1 shows a SEM micrograph and X-ray probe microanalysis of pure Li_2TiO_3. The general structure of this sample with a dendritic aspect was not regular: particles of 10–50 μm, often coalesced, were observed. The proportion of oxygen with respect to titanium O/Ti was the same, whatever the analyzed area. The structure of the immobilized molten phase before the catalytic reaction is shown in fig. 2. The morphology is, in general, similar to that of pure lithium titanate, but the surface is smoother and a higher proportion of O/Ti reveals the presence of molten carbonate. Irregular heaps of molten phase, in which carbon and important amounts of sodium and potassium were detected by X-ray probe microanalysis (fig. 2b), are observed in fig. 2a. A microstructural change was detected after extended catalytic use (about 50 h at 750–850°C) under the reactant gas and helium, as it can be seen in fig. 3 in the case of Li-Na-K/Li_2TiO_3: 10.58 wt%. Particles coalesced very strongly showing a smooth surface with white inclusions (fig. 3a). X-ray probe microanalysis shows (fig. 3b) that carbon disappeared from the general structure and that the white products contained higher amounts of oxygen and sodium. It results that the molten carbonate eutectic was totally transformed into sodium oxide by melt decarbonation during the catalytic reaction at high temperature. It is worthy to mention that lithium oxide is thermodynamically more stable than sodium oxide. This means that Li_2O was probably also present in the white products, but its detection is not possible by X-ray probe microanalysis.

3. Results and discussion

The catalytic behaviour of pure lithium aluminate or lithium titanate pellets and of the supported Li-Na-K eutectic is reported at different temperatures in table 1[#3].

3.1. CATALYTIC ACTIVITY OF $LiAlO_2$ AND Li_2TiO_3 SUPPORTS

It can be observed that the catalytic activity of both solid supports without mol-

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[#3] The same gas conditions were established before each analysis, in order to make the different assays comparable. The catalyst was conditioned under $P(CO_2) = 1$ atm during 40 min (avoiding an important melt decarbonation in the case of the supported catalysts) and then under the reactant gas mixture during 20 min (provoking a moderate decarbonation in the case of the supported catalysts).

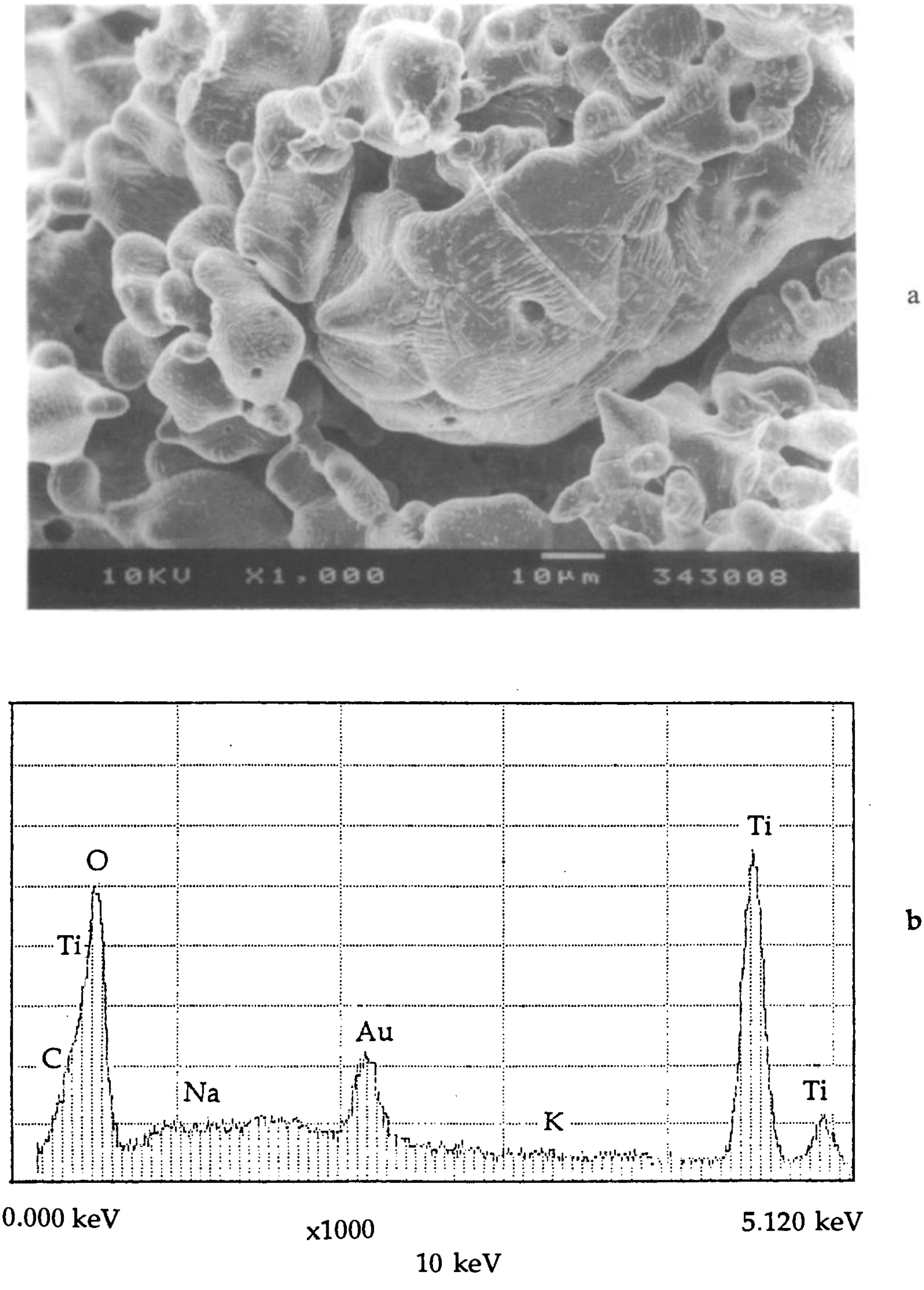

Fig. 1. Pure Li_2TiO_3 pellet: (a) SEM micrograph. (b) X-ray probe microanalysis.

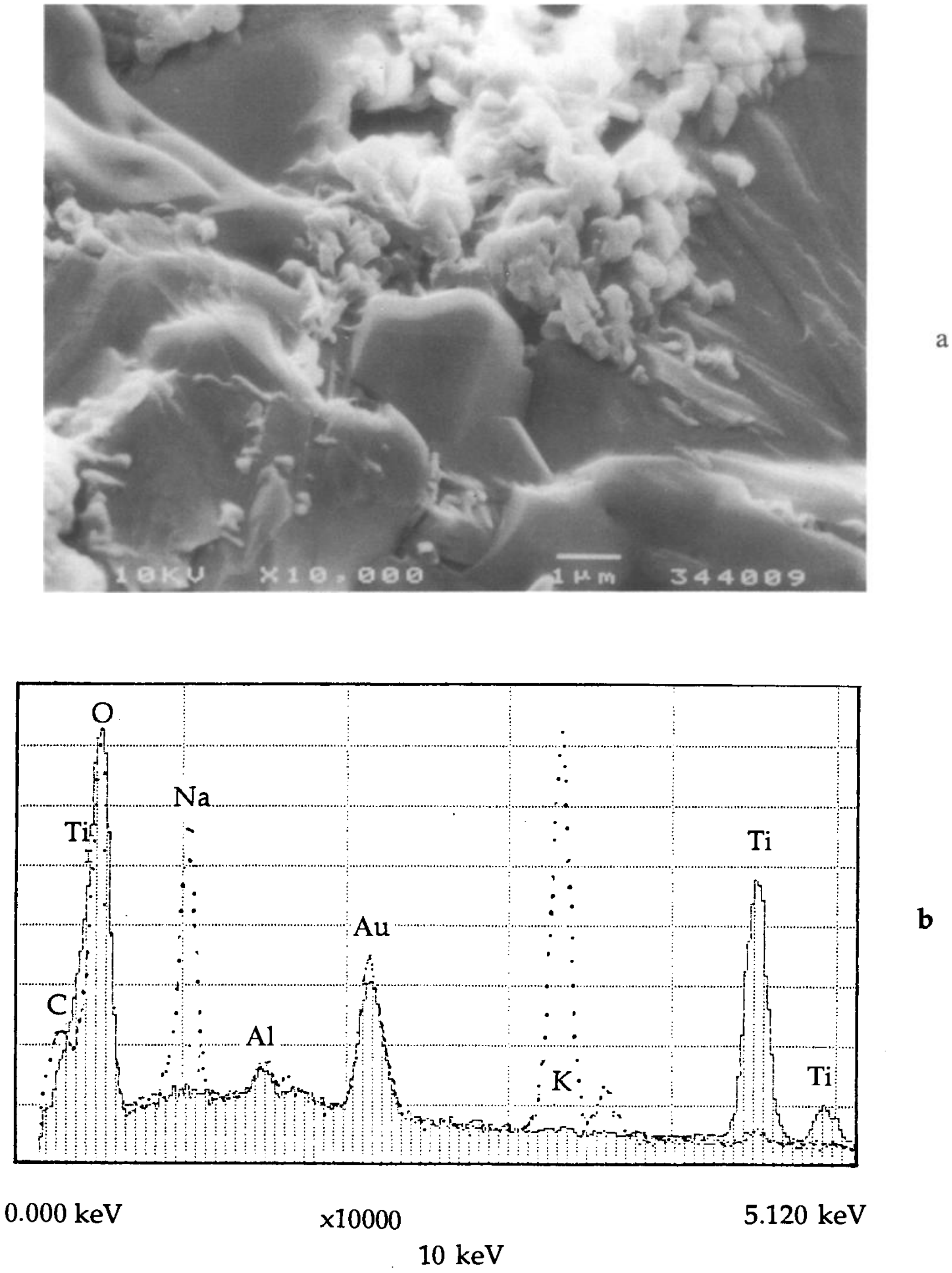

Fig. 2. Li_2CO_3–Na_2CO_3–K_2CO_3 / Li_2TiO_3: 7.82 wt%, before catalytic reaction: (a) SEM micrograph. (b) General and white heaps X-ray probe microanalysis.

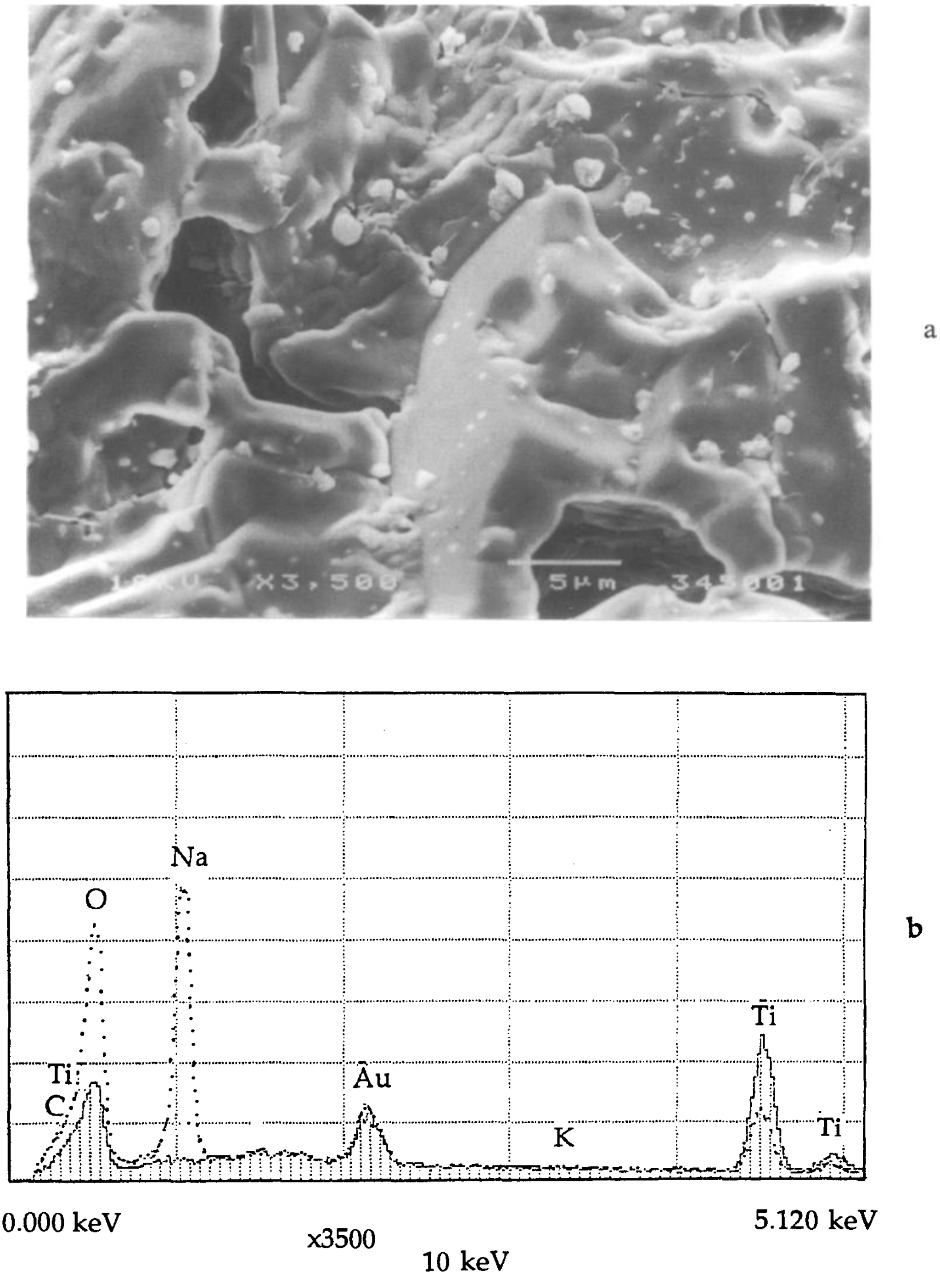

Fig. 3. Li_2CO_3–Na_2CO_3–K_2CO_3/Li_2TiO_3: 10.58 wt%, after catalytic reaction: 50 h at 750–850°C: (a) SEM micrograph. (b) General and white particles X-ray probe microanalysis.

Table 1
Influence of the temperature on the oxidative dimerization of methane in contact with the supported Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic and with pure $LiAlO_2$ and Li_2TiO_3 supports. Li-Na-K content/ $LiAlO_2$: 7.52 wt% and Li-Na-K content/Li_2TiO_3:7.87 wt% (total amount of catalyst 0.3 g). Reactant gas: 136.8 Torr[a] CH_4, 45.6 Torr O_2, 577.6 Torr He, total flow rate of 61.4 ml/min. Analysis at different temperatures was realized under the same experimental conditions: before each assay the catalyst was kept during 40 min under $P(CO_2) = 1$ atm and the under the reactant gas mixture during 20 min. Results with pure $LiAlO_2$ and Li_2TiO_3 pellets (0.3 g) are given in italics

Support	T (°C)	O_2 conv. (%)	CH_4 conv. (%)	C_2 select. (%)	C_2 yield (%)
Li-Na-K/$LiAlO_2$	750	44.9	14.0	48.3	6.8
		39.0	*9.8*	*30.5*	*3.0*
	800	58.7	20.6	51.2	10.4
		53.7	*15.1*	*40.5*	*6.1*
	850	83.4	24.5	50.5	12.4
		70.1	*19.7*	*46.5*	*9.1*
Li_2TiO_3/$LiAlO_2$	750	8.2	4.0	57.3	2.3
		6.8	*2.2*	*47.5*	*1.0*
	800	31.9	10.8	55.6	6.0
		14.0	*4.5*	*51.5*	*2.3*
	850	60.2	18.5	50.8	9.4
		26.5	*8.5*	*52.6*	*4.5*

[a] 1 Torr = 133.3 Pa ($N m^{-2}$).

ten phase cannot be neglected. It increases with the temperature, reaching C_2 yields of 9.1 and 4.5% at 850°C for $LiAlO_2$ and Li_2TiO_3 respectively. The performance of $LiAlO_2$ is significantly more important than that of Li_2TiO_3. This can be attributed either to the morphology of the prepared samples – $LiAlO_2$ structure is more divided (particles of 0.1–0.5 μm) than that of Li_2TiO_3 (particles of 10–50 μm) and should allow a better gas–liquid contact – or to the acidic or basic properties of these solids. In effect, it has been shown that the activity and selectivity of oxide catalysts towards the oxidative dimerization of methane is correlated to their basicity [15,16]. According to Ding et al. [15], surface basicity of the catalyst and the presence of reduced oxygen species are necessary for methane oxidative dimerization. Lahousse et al. [17] have studied the acidic properties of alumina Al_2O_3 and rutile TiO_2, precursors of the supports used in this work. They have shown that TiO_2, an n-type semi conductor, has more acid sites and less basic sites than Al_2O_3. This is in agreement with our experimental results.

3.2. EFFECT OF THE ADDITION OF Li-Na-K

Fig. 4 shows a comparison between C_2 yields obtained with the solid supports and with the supported ternary eutectic at 800°C. In the case of lithium-titanate support, the presence of Li-Na-K increased methane conversion from 4.5 to 10.8%

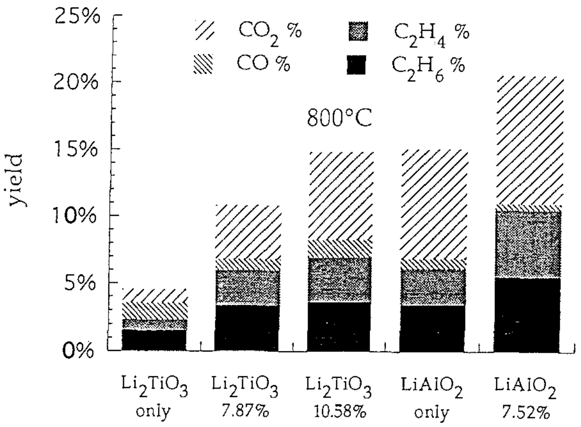

Fig. 4. Comparison of the catalytic performance of the solid supports, Li_2TiO_3, $LiAlO_2$ without molten phase and of supported Li_2CO_3–Na_2CO_3–K_2CO_3/Li_2TiO_3 (7.87 and 10.58 wt%), Li_2CO_3–Na_2CO_3–K_2CO_3/$LiAlO_2$ (7.52 wt%) at 800°C.

(7.87 wt% eutectic content) and 14.5% (10.58 wt% eutectic content). C_2 yield climbed from 2.3 to 6.0 and 7.0% respectively. It results that the oxidation of methane and its dimerization are enhanced by the presence of the molten phase. It must be precised that the activity of the catalyst is mostly promoted by the molten carbonate eutectic, because this phase recovers the solid support and partially masks its activity. The catalytic performance is enhanced with the proportion of the carbonate eutectic supported by Li_2TiO_3. In the case of the lithium-aluminate support the situation is more complex. Methane conversion increased moderately from 15.1 to 20.6%, but C_2 selectivity also increased from 40.5 to 51.2% showing the positive effect of carbonate on the dimerization process. C_2 yield increased significantly with temperature whatever the selected support. This is in agreement with the hypothesis of the involvement of peroxide species in the catalytic mechanism. In effect, according to thermodynamics and electrochemical measurements [8–10], the amount of peroxide species increases with temperature, enhancing the molten phase catalytic performance.

3.3. CATALYTIC ACTIVITY OF SUPPORTED Li-Na-K AT DIFFERENT ACIDITY LEVELS

The effect of the acidity of the melt on the performance of the catalysts is described in figs. 5 and 6. Acidic media were obtained by passing through the supported molten phase a partial pressure of carbon dioxide and basic media by decarbonation of the melt under the reactant gas (without addition of CO_2).

The evolution of a moderately decarbonated Li-Na-K/Li_2TiO_3 catalyst (3 h under the reactant gas) towards acidic media (a few hours under $P(CO_2) = 0.02$ atm or $P(CO_2) = 0.11$ atm) is indicated on the left-hand side of fig. 5. C_2

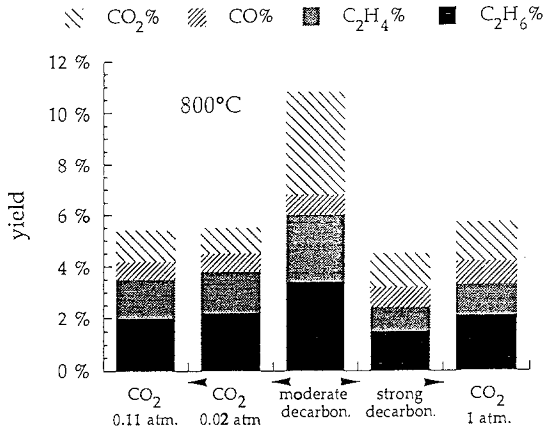

Fig. 5. Effect of CO_2 and melt decarbonation on the catalytic performance of Li_2CO_3–Na_2CO_3–K_2CO_3/Li_2TiO_3 (7.87 wt%) at 800°C.

yield decreased with the acidity from 6.1 to 3.8 and 3.5% respectively. The negative effect of CO_2 on the oxidative dimerization of methane [7,8] and, in particular, on the formation of methyl radicals has been outlined by different authors [18,19]. The effect of a strong decarbonation (30 h under He) of the melt can be observed on the right side of the figure. This evolution results from a more difficult gas–liquid contact due to: – a total decarbonation of the melt, provoking the formation of solid particles of Na_2O (fig. 3) and probably Li_2O, and – a strong coalescence of particles after extended use of the catalyst (fig. 3a). This detrimental effect could also be due to the disappearance in the molten phase of active alkali species, forming $[M^+O^-]$ centers, with O^-, dissociated form of O_2^{2-} at high temperature [20], or other

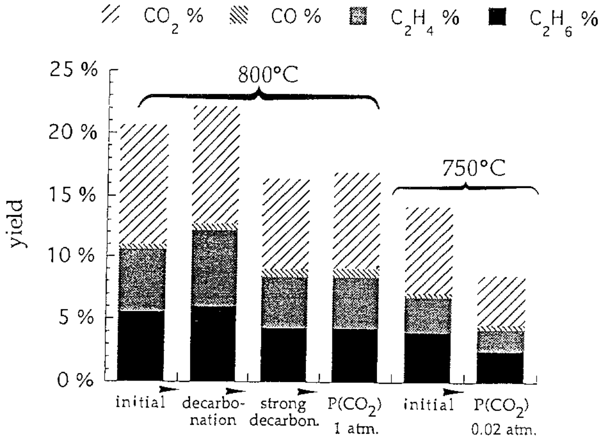

Fig. 6. Effect of CO_2 and melt decarbonation on the catalytic performance of Li_2CO_3–Na_2CO_3–K_2CO_3/$LiAlO_2$ (7.52 wt%) at 750 and 800°C.

alkali-peroxycarbonate species [#4]. The catalyst partially recovered its activity after 15 h under $P(CO_2) = 1$ atm.

Fig. 6 shows the behaviour of Li-Na-K/$LiAlO_2$. A moderate decarbonation of the initial supported melt (with a neutral acidity level), at 800°C during 15 h under the reactant gas, enhanced the catalytic activity. C_2 yield decreased with a strong decarbonation (60 h under the same conditions) yielding solid alkali oxides. This process appears irreversible, because the catalytic activity was not recovered at all after keeping the catalyst a few hours under $P(CO_2) = 1$ atm. The negative effect of CO_2 is shown at 750°C in fig. 6.

These results confirm that the catalytic dimerization of methane is correlated with the basicity of the melt obtained by a moderate decarbonation of the melt. Nevertheless, highly basic media must be avoided, because the molten phase is totally decarbonated, which has a negative effect on the oxidation reaction. Acidic media must also be discarded, because they do not allow the formation of peroxide species. The fixation of a very low partial pressure of CO_2 (around 10^{-3} atm at 750°C: this value must be lower than that representing the neutral medium 1.1×10^{-2} atm) stabilizing the acidity level and avoiding the solidification of the melt is the best way of increasing the catalyst lifetime. The effect of the partial pressure of CO_2 formed by the catalytic reaction should also be taken into account. Nevertheless, the amount of CO_2 varies according to each assay and is continuously carried away by the reactant gas.

The amount of C_2 species vs. temperature is reported in fig. 7 for supported carbonates and other Li-containing melts [7,8]. C_2 formation is more efficient in Li-

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[#4] Formation of CO_4^{2-} has been suggested [21], but no experimental evidence has been given.

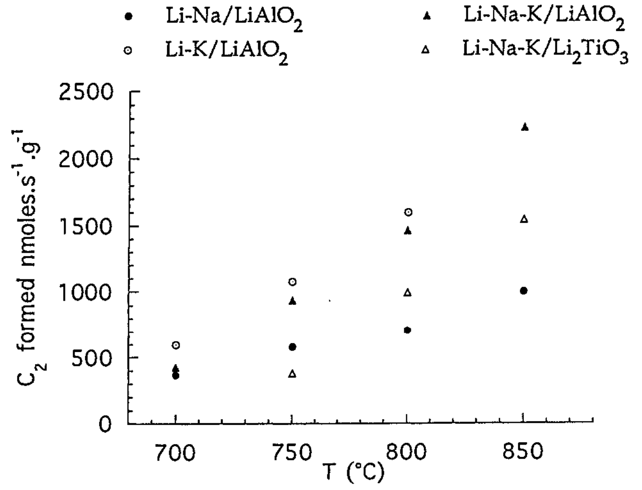

Fig. 7. Comparison of C_2 amounts formed per second and per gram of catalyst in supported binary and ternary molten carbonate eutectics at different temperatures.

Na-K/$LiAlO_2$ and Li-K/$LiAlO_2$ than in Li-Na/$LiAlO_2$. This result can be related to the higher stability of O_2^{2-} species in these melts [10]. Although the activity of Li-Na-K/Li_2TiO_3 appears lower, it could be significantly improved by optimizing the preparation technique, with a more adapted morphology (smaller grain size) and the best proportion of Li in this compound [12].

4. Conclusion

The analysis of the catalytic behaviour of Li_2CO_3–Na_2CO_3–K_2CO_3 supported by $LiAlO_2$ or Li_2TiO_3 shows that the catalytic performance of these catalysts, mostly due to the molten phase, is enhanced at high temperatures and low acidity levels. The involvement of peroxide species in the oxidative mechanism has been confirmed. The control of very low CO_2 partial pressure above the supported melt, in order to avoid melt solidification, is an important parameter. Li_2TiO_3 support seems promising but further investigation on the preparation technique and the proportion of Li and Ti is required. No important advance could be reached in this field without new technological solutions: (a) reducing the dead volume in the reactor and, thereby, avoiding a further oxidation of C_2 products into CO_2, and (b) designing a more appropriate reactor, i.e. a column similar to that used in chromatographic techniques with the catalyst recovering the internal surface.

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