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Characterization by thermal methods of carbonate surface species on methane-coupling catalysts ☆

R. Spinicci*, A. Tofanari

Dipartimento di Energetica, Università di Firenze, Via S. Marta 3, 50139 Firenze, Italy

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Abstract

The adsorptive properties of two catalysts for methane coupling, namely 2% Li_2O–Y_2O_3 and $LiYO_2$, have been studied by means of temperature-programmed desorption (TPD) in order to gain a deeper insight into the reaction mechanism and to distinguish the role of the heterogeneous surface reaction and homogeneous gas phase reaction.

Experiments concerning the temperature-programmed desorption of methane and oxygen (adsorbed either at room temperature or at 973 K) have been therefore carried out. In order to improve their characterization, TPD peaks have been also analyzed from a kinetic point of view. Afterwards, carbon dioxide desorption has also been evaluated, its presence on the catalyst surface being considered decisive in determining the prevailing reaction mechanism.

The possibility of detecting, by means of a mass analyzer, that the desorption process of methane is accompanied by its surface oxidation has been decisive in the characterization of its interactions with the catalysts surfaces.

The results seem to indicate that carbonate surface species are important for the adsorption of methane, but the formation of C_2-hydrocarbons mainly occurs in the gas phase.

Keywords: Lithium oxide; Methane coupling; Temperature-programmed desorption; Yttrium oxide

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1. Introduction

Temperature-programmed desorption (TPD) is a well known technique used for the characterization of catalysts; the knowledge of the desorption peaks, their shapes, and

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* Corresponding author.

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the temperatures at which they occur, can give important information on the interactions of gaseous adsorbate and solid catalysts. Obviously many experimental parameters can affect the meaningfulness of the results: the temperature of adsorption, the flow rate of carrier gas, the heating rate of the catalyst sample, and so on, so that care must be taken in selecting the right conditions for extracting meaningful information [1,2].

On the other hand methane coupling is an interesting reaction, which enables the selective oxidation of methane with the consequent formation of C_2-hydrocarbons. The temperatures required to achieve appreciable activity are, however, very high with the following consequences: a) the homogeneous gas phase reaction contributes greatly to the overall activity; b) the formation of carbon dioxide through the total oxidation strongly affects the catalysts selectivity [3–5].

Catalysts based on Li_2O and Y_2O_3 have interesting activity and selectivity for this reaction in the range 923–1053 K. Consequently, in order to know the role of the surface reaction in the overall process, it is interesting to clarify the features of their activity and selectivity by means of temperature-programmed desorption of reactants and products.

2. Experimental

Two catalysts have been investigated:

a) 2% Li_2O_3–Y_2O_3, prepared by impregnating $LiNO_3$ (C. Erba R.P.) on Y_2O_3 (Strem Chem. R.P.) drying to eliminate the excess solution, decomposing $LiNO_3$, and calcining Li_2O–Y_2O_3 at 873 K for 2 h;

b) $LiYO_2$, prepared by mixing $LiNO_3$ and Y_2O_3 and heating this mixture up to 1173 K, to enable a solid state reaction which leads to the formation of $LiYO_2$, as already reported in the literature [6].

Temperature-programmed desorption (TPD) has been performed in a classical apparatus, already described [7], where desorption of previously adsorbed gas is carried out by allowing the flow of the carrier gas (He; 100 ml min^{-1}) through the reference side of the hot wire detector, then through the catalyst, subjected to a linear temperature program, and finally through the sensing side of the detector. The flow subsequently passes into a UTI mass analyzer, in order to determine the nature of the desorbed substances, since desorption can occur with surface reaction.

The adsorption has been brought about, allowing a continuous flow of the chosen gas through the catalyst samples (generally 0.06–0.1 g) at room temperature or at 973 K. After the adsorption a flow of carrier gas has been allowed for the time necessary for the stabilization of the baseline of HWD detector. Then the temperature program has been started in order to perform TPD experiments.

Firstly, TPD experiments were performed on samples which were not previously pretreated and not subjected to any adsorption. The results of these experiments show that both catalysts are characterized by a complex desorption spectrum, with peaks: at low temperatures (473–673 K), due to water and carbon dioxide; at intermediate temperatures (673–773 K), due to excess surface oxygen and carbon dioxide; at higher temperatures (873–973 K), mainly due to carbon dioxide, coming from strongly bound carbonate surface species, and, also, to small amounts of excess surface oxygen.

These results allow us to define a pretreatment procedure, to be adopted in every TPD experiment in order to obtain meaningful responses. It consists in heating for a sufficient time (2 h) at a temperature of 943 K for 2% $Li_2O–Y_2O_3$ and of 973 K for $LiYO_2$ in a flow of helium plus a small percentage of oxygen (in order to avoid lattice oxygen depletion). This pretreatment procedure has been used either in activity and selectivity measurements in the temperature range 943–1033 K or in TPD experiments. The necessity of this procedure can be stressed by the experimental result that unpretreated catalysts show a very small activity (1–2% methane conversion) within the temperature limits explored in this work.

The study of the desorption peaks has been carried out by evaluating their position in the temperature scale and, above all, by determining the kinetic parameters of the related desorption processes through a well establishd procedure [8], which is based on the correlation of the peak height at different times (proportional to the desorption rate) to the corresponding partial area (proportional to the fractional surface coverage), and then it is also based on the evaluation of the related Arrhenius plot. Mass analysis allows, if necessary, an experimental deconvolution of the peaks; if different peaks of the same substance are present, a computerized deconvolution can be performed by means of empirical equations, the parameters of which are adjusted in order to simulate first-or second-order desorption, with or without readsorption.

3. Results and discussion

Previous investigations have demonstrated that the presence of carbonate surface species or of oxygen surface species is decisive in determining either activity or selectivity [9. 10]. Therefore it appeared important to clarify the adsorptive properties of the catalysts towards CO_2 and O_2.

(1) CO_2—On $Li_2O–Y_2O_3$ carbon dioxide, adsorbed either at room temperature or at 973 K, desorbs giving a main peak (due to desorption of CO_2) with $T_{peak} = 983$ K at 8 K min^{-1} (accompanied by a shoulder with $T_{peak} = 933$ K), which after the deconvolution can be described by first order kinetics in the range of the fractional surface coverage $\theta = 0.85–0.35$ with $E_a = 370.2$ kJ mol^{-1}. (Fig. 1, curve a).

On $LiYO_2$ carbon dioxide, adsorbed either at room temperature or at 973 K, desorbs giving a main peak (due to desorption of CO_2 with $T_{peak} = 998$ K at 8 K min^{-1} (accompanied by shoulders at lower and higher temperatures), which when deconvoluted can be described by first order kinetics in the range $\theta = 0.99–0.35$, with $E_a = 226.1$ kJ mol^{-1}. (Fig. 1, curve b).

It must be stressed here that the most stable surface species (which desorb at higher temperatures) have already also been found in desorption of unpretreated catalysts, not subjected to any adsorption; this correlation gives a strong indication of the ease of adsorption of CO_2 on these catalysts. On the other hand, the very low activity of unpretreated catalysts shows that surface sites exposed to reaction or to adsorption of CO_2 in TDP experiments must have some different features in respect of the surface

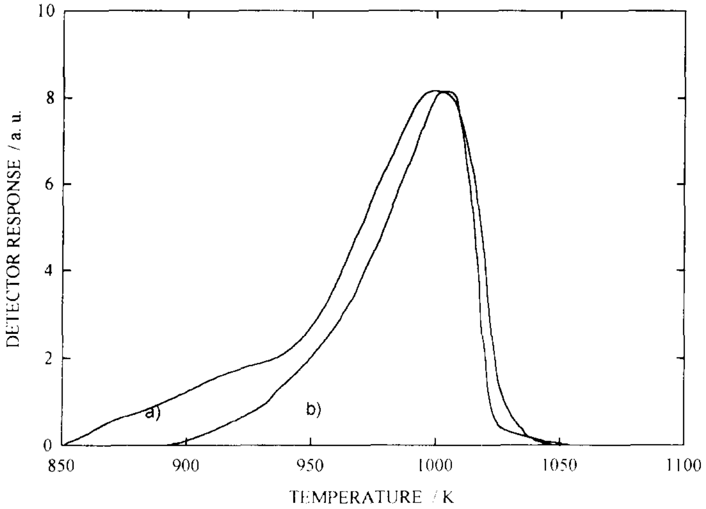

Fig. 1. The meaningful part of the TPD spectrum of CO_2 desorbed at 8 K min^{-1} with a helium flow rate of 100 ml min^{-1}. Curve a) 0.08 g of 2% Li_2O–Y_2O_3 pretreated at 670 K for 2 h in a flow of helium plus oxygen; curve b) 0.08 g of $LiYO_2$ pretreated at 700 K for 2 h in a flow of helium plus oxygen.

sites evidenced only after a prolonged exposure to air; in this case, indeed, the exposed surface sites are affected by the presence of water vapor, which can induce some differences in the properties of the carbonate species [11].

(2) O_2—If oxygen is adsorbed at room temperature, its desorption gives very low and widespread peaks at 673–773 K, but gives a well defined peak with $T_{peak} = 996$ K on Li_2O–Y_2O_3 and $T_{peak} = 1010$ K on $LiYO_2$; no appreciable desorption peaks are obtained if absorption is carried out at 973 K (Fig. 2, curves a, b). According to the literature the peaks evidenced by these experiments at lower temperatures can be attributed to less basic surface species (especially O_2^{2-}), while those shown at the higher temperatures can be attributed to the most basic oxygen ions, O^{2-}, adsorbed on the surface [12].

(3) CH_4—As far as methane is concerned, if adsorption is carried out on samples with surfaces free of oxygen species (pretreated at about 1050 K, that is at temperatures higher than those corresponding to the possible existence of these species) no desorption process is observed on both catalysts at low or high temperatures. On the contrary, if adsorption is performed on catalyst samples pretreated at their respective optimal temperatures, and therefore still containing oxygen surface species, it is possible to observe some diffeerences, in relation to the adsorption temperatures:

(a) if adsorption is performed at room temperature, we can observe a peak (due, nearly entirely, to desorption of carbon dioxide) with $T_{peak} = 988$ K on Li_2O–Y_2O_3 and $T_{peak} = 1053$ K on $LiYO_2$ at 8 K min^{-1}; in both cases the peak is described by first order kinetics, with $E_a = 328$ kJ mol^{-1} for Li_2O–Y_2O_3 and $E_a = 235.5$ kJ mol^{-1} for $LiYO_2$ (Fig. 3, curves a, b);

(b) if adsorption is performed at 973 K, only negligible peaks are detected on both catalysts unless they are carbonated after the usual pretreatment. In this case, however,

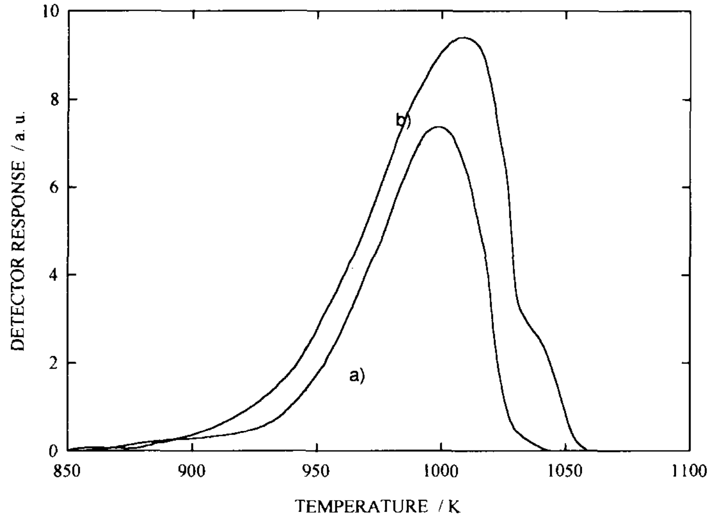

Fig. 2. The meaningful part of the TPD spectrum of O_2 desorbed at 8 K min^{-1} with a helium flow rate of 100 ml min^{-1}. Curve a) 0.08 g of 2% $Li_2O-Y_2O_3$ pretreated at 670 K for 2 h in a flow of helium plus oxygen; curve b) 0.08 g of $LiYO_2$ pretreated at 700 K for 2 h in a flow of helium plus oxygen.

the number of the peaks (corresponding to desorption with formation of CO_2), their position along temperature axis, and their kinetic features indicate the same behavior as those produced by carbon dioxide.

These experimental results seems to suggest that methane is negligibly adsorbed on the fresh surface at reaction temperatures (and not adsorbed if this surface is free of oxygen species) and that adsorbed methane reacts with the surface of these catalysts releasing carbon dioxide; evidently, the greater the strength of the bonds of oxygen ions in the catalyst, the more difficult is the possibility of adsorption of methane, and the easier the possibility of total oxidation of methane adsorbed. It can be supposed that in these conditions methane interacts, during desorption, with the lattice O^{2-} ions through the breaking of the C–H bond and the total oxidation or the dimerization of the methyl radicals formed [13].

If we consider the adsorption on the surface, still containing oxygen surface species, it must be clarified whether in such conditions the total oxidation by the most basic species, and oxidative coupling by the less basic species is possible.

The same conditions are obtained with a carbonated surface. In such a case the surface contains CO_3^{2-}, which can act as basic centers of absorption. But, unfortunately, as far as interactions of methane with the carbonated surface are concentrated, we cannot distinguish between CO_2 derived from the carbonating treatment and CO_2 derived from desorption with surface reaction of adsorbed methane.

Therefore it appeared interesting to perform temperature-programmed desorption on samples, after having stopped th coupling reaction and having frozen the catalyst sample at lower temperatures.

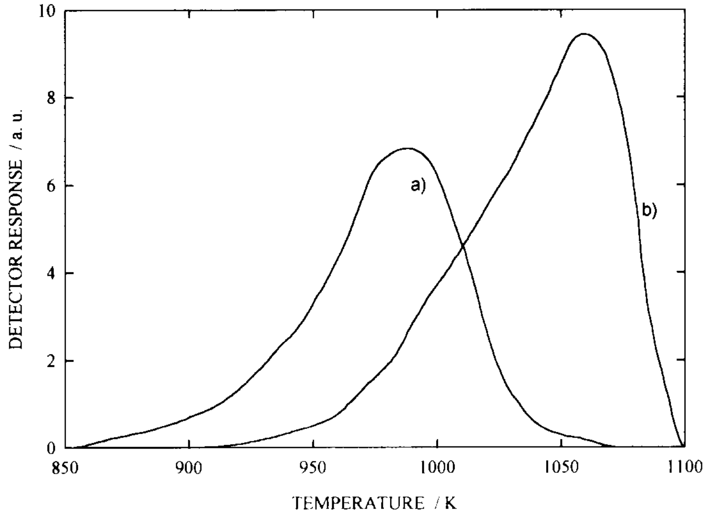

Fig. 3. The meaningful part of the TPD spectrum of CH_4 adsorbed at room temperature, and desorbed at 8 K min^{-1} with a helium flow rate of 100 ml min^{-1}. Curve a) 0.08 g of 2% Li_2O–Y_2O_3 pretreated at 670 K for 2 h in a flow of helium plus oxygen; curve b) 0.08 g of $LiYO_2$ pretreated at 700 K for 2 h in a flow of helium plus oxygen.

No appreciable peak is detected if the reaction is allowed for few minutes. Instead, if the reaction is allowed for 1/2 or 1 h, the "reaction products" give, on 2% Li_2O–Y_2O_3, a well formed peak (due to desorption of CO_2) with $T_{peak} = 991$ K at 8 K min^{-1} (accompanied by shoulders with $T_{peak} < 910$ K and $T_{peak} = 1023$ K), which, when deconvoluted, can be described by first order kinetics in the range $\theta = 0.95$–0.20, with $E_a = 332.5$ kJ mol^{-1} (Fig. 4, curve a).

The "reaction products" give, on $LiYO_2$, a well formed peak (due to desorption of CO_2) with $T_{max} = 788$°C at 8°C min^{-1} (accompanied by shoulders with $T_{max} = 670$°C and $T_{max} = 805$°C), which, when deconvoluted, can be described by first order kinetics in the range $\theta = 90 - 25\%$, with $E_{att} = 233$ kJ mol^{-1} (Fig. 4b).

It should be underlined here that desorption of CO_2 formed during adsorption or surface reaction of methane is shifted towards slightly higher temperatures in respect of desorption of adsorbed CO_2; this could mean that CO_2 molecules are more strongly fixed when derived from methane surface reaction than when derived from simple adsorption; however, the first order kinetics show that the mechanism should be the same.

These results can be compared with those obtained from the transient response experiments, where responses of reactants and products are followed at the beginning of the reaction. Through these experiments it can be shown that the response of C_2-hydrocarbons immediately reaches its steady state, while the response of CO_2 reaches its steady level only after some minutes [8]. Therefore, either transient of TPD results suggest that methane is not adsorbed or it is adsorbed in a small amount on the fresh surface; transient experiments show that the presence of gaseous oxygen in the

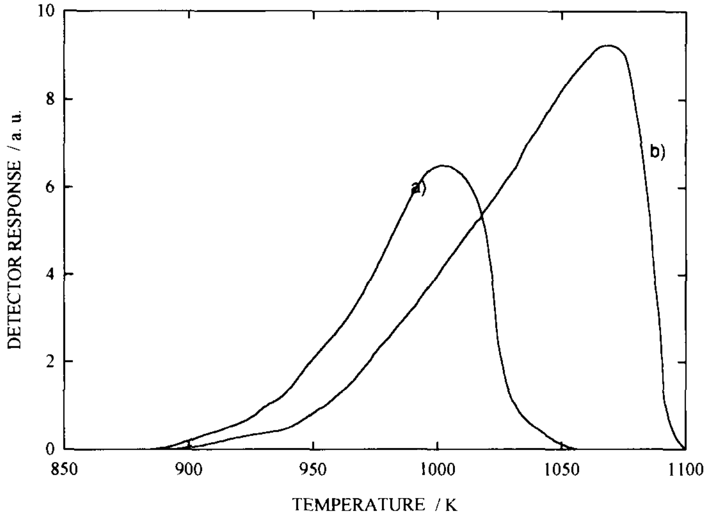

Fig. 4. The meaningful part of the TPD spectrum of coupling products remaining adsorbed after the cooling of the catalyst to room temperature, and desorbed at 8 K min^{-1} with a helium flow rate of 100 ml min^{-1}. Curve a) 0.08 g of 2% Li_2O–Y_2O_3 pretreated at 670 K for 2 h in a flow of helium plus oxygen; curve b) 0.08 g of $LiYO_2$ pretreated at 700 K for 2 h in a flow of helium plus oxygen.

reactant mixture during the reaction leads to the formation of C_2-hydrocarbons, as well as of CO_2. This last substance is slowly adsorbed and enables the stabilization of carbonate surface species, which in their turn do not favor surface selective oxidation. Certainly, adsorption of methane is made easier on catalyst surfaces containing carbonate species, but the temperature limits of the CO_2 stability, deduced from the TPD peaks, can explain a general evidence; the influence of the surface in the general progress of methane coupling progressively decreases the gas phase reaction becomes more and more important.

Another general feature clarified from the kinetic analysis of the TPD peaks concerns the evidence that desorption peaks due to Li_2O–Y_2O_3 occur at low temperatures in respect of the corresponding ones due to $LiYO_2$, but are characterized by a higher activation energy. This unusual result can be only explained by taking into account that for Li_2O–Y_2O_3 preexponential factors are considerably higher 10^{21}–10^{23} versus 10^{11}–10^{14} for $LiYO_2$.

During the description of the experimental results, preexponential factors have never been reported. This is because the procedure employed for the kinetic analysis of the peaks accumulates in this parameter some constant terms, which can, however, be affected by experimental error (for example the heating rate). Therefore, the values obtained must be considered with caution and only the strong observed difference allows us to give an explanation of the phenomenon in terms of preexponential factors. However, the results seem to support the hypothesis that active sites are not related directly to the surface areas of the catalysts (which are strictly similar) but to their intimate structure.

4. Conclusions

TPD represents a powerful method for characterizing catalysts and has allowed us to obtain important results providing information about methane coupling on 2% Li_2O–Y_2O_3 and on $LiYO_2$.

As a first result, desorption processes of unpretreated samples have suggested the best conditions of pretreatment for both catalysts. Moreover, desorption spectra of methane and of reaction products demonstrate that, when methane itself can be adsorbed on the catalysts' surfaces, its desorption is accompanied by a surface reaction which gives carbon dioxide; the experimental evidence shows that it can be mainly adsorbed on carbonated surfaces, as confirmed by the study of the catalytic activity transient conditions.

The results seem to suggest that the contribution of the surface reaction to the formation of C_2-hydrocarbons during the methane coupling reaction is very low. Indeed, one must take into account also the possibility that methane adsorption simply leads to the abstraction of an hydrogen atom and the formation of the methyl radical, which subsequently reacts in the gaseous phase. The presence of oxygen in the gaseous reactant mixture is, however, necessary for the production of C_2-hydrocarbons, because it can be involved in the formation of less basic oxygen surface species.

Another peculiarity of the experimental results reported here, which must be underlined, is surely represented by the fact that in the case of $LiYO_2$ desorption of adsorbed CO_2 occurs at slightly lower temperatures than desorption of reaction products or desorption with reaction of methane. On the contrary, this difference cannot be ascertained when examining TPD spectra from 2% Li_2O–Y_2O_3. Evidently, the surface reaction giving CO_2 is a process slightly more activated on $LiYO_2$, than its simple desorption, probably on account of the formation of a slightly different intermediate; however, the two desorption processes must be similar, if both follow first order kinetics.

The experimental results of transient method runs and of steady state activity experiments, and the awarencess of the importance of the carbon dioxide derived from total oxidation during methane coupling, suggested us to put in the background the study of the interactions of C_2-hydrocarbons. But the complete characterization of these catalysts will surely be completed by knowledge of the adsorptive properties of these substances.

References

[1] J.L. Falconer and J.A. Schartz, Catal. Rev.-Sci. Eng., 25 (1983) 141.

[2] R.J. Gorte, J. Catal., 75 (1982) 164.

[3] A.W. Czanderna, J.R. Biegen and W. Kollen, J. Colloid. Interface Sci Sci., 34 (1970) 406.

[4] Y. Amenomiya, V.I. Birss, M. Goledzinowki, J. Galuszka and A.R. Sanger, Catal. Rev.-Sci. Eng., 32 (1990) 163.

[5] G. Mirodatos, A. Holmen, R. Mariscal and G.A. Martin, Catal. Today, 6 (1990).

[6] R.K. Ungar, X. Zhang and R.M. Lambert, Appl. Catal., 42 (1988) L1.

[7] R. Spinicci, Catal. Today, 4 (1989) 311.

[8] R. Spinicci, J. Therm. Anal., 29 (1984) 1061.
[9] J.A. Roos, S.J. Korf, R.H.J. Veehof, J.G. Van Ommen and R.J.H. Ross, Appl. Catal., 52 (1989) 131.
[10] W. Dingjun, X. Mingting, S. Chunlei and J.H. Lunsford, Catal. Lett., 18 (1993) 323.
[11] A. Kooh, H. Mimoun and C.J. Cameron, Catal. Today, 4 (1989) 333.
[12] M. Yu Sinev, V. Yu Bichkov, V.N. Korchak and O.V. Krylov, Catal. Today, 5 (1992) 157.
[13] O.T. Onsager, R. Lodeng, P. Soraker, A. Anundskaas and B. Helleborg, Catal. Today, 4 (1989) 355.