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Isotopic tracing experiments in syngas production from methane on Ru/Al_2O_3 and Ru/SiO_2

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Abstract

The catalytic production of syngas from methane was investigated over alumina- and silica-supported ruthenium catalysts. It is shown that the support is involved in reactions with reactants and products somewhat modifying the catalytic behaviour. From isotopic tracing experiments it is concluded that the syngas production reaction follows the same indirect pathway over the two catalysts, i.e. the sequence of total oxidation of methane, followed by reforming of the unconverted methane with carbon dioxide and steam to syngas. Recent literature is analysed in the light of our results. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Synthesis gas; Ru/alumina; Ru/silica; Isotopic tracers

1. Introduction

Nowadays, natural gas, in which CH_4 is the principal component, is mainly consumed for heating or power generation purposes, but in the next century many chemical products will be produced from this raw material. For this reason, in the last few years many studies have been dedicated to develop catalytic processes for methane activation and in particular for its transformation into synthesis gas ($CO+H_2$) [1]. Conversion of CH_4 to CO and H_2 (syngas) is of great practical importance because syngas is an important feedstock. Industrially, syngas is traditionally produced by steam reforming of natural gas [2]. In recent years, partial oxidation [3] and CO_2 reforming [4] of methane have been largely studied because of their potential to reduce the cost of syngas, for their application in solar energy storage and/or for CO_2 utilization technologies. From a mechanistic standpoint, the partial oxidation of CH_4 has been evidenced to proceed via a two-step reaction pathway, i.e. first, deep oxidation of a part of the CH_4 to CO_2 and steam and second, reforming of the remaining CH_4 with CO_2 and steam to syngas [5]. However, partial oxidation of CH_4 to CO and H_2 in a single step has also been suggested [6–9]. Partial oxidation is an exothermic reaction while reforming processes are strongly endothermic. Moreover, the reaction temperature for partial oxidation has been reported to be lower than that for reforming reactions, but various authors have claimed that the real temperature of catalytic bed is higher than that of reactor wall [10,11] due to the initial complete combustion of CH_4. Nowadays, for non-noble metals (Ni, Fe, Co) a two-step mechanism is generally accepted, while for noble metals the question remains open to investigation.

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Reaction between CH_4 and oxygen at high temperatures can give principally CO_2, H_2O, CO and H_2. The composition of the product gas depends on the temperature, pressure, initial gas composition, and also on kinetic factors. Among these gases different reactions can occur:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \text{(total oxidation)} \tag{1}$$

$$CH_4 + O_2 \rightarrow CO + 2H_2O \tag{2}$$

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \tag{3}$$

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \text{(partial oxidation)} \tag{4}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \text{(steam reforming)} \tag{5}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \text{(dry reforming)} \tag{6}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(water gas shift)} \tag{7}$$

Also direct decomposition reactions of CH_4 or CO should be considered particularly from the point of view of carbon deposition:

$$2CO \leftrightarrow C + CO_2 \quad \text{(Boudouard reaction)} \tag{8}$$

$$CH_4 \leftrightarrow C + 2H_2 \tag{9}$$

Thermodynamic calculations allow obtaining the gas composition in equilibrium conditions as a function of the temperature, pressure and reactant mixture [12]. However, in the presence of catalytic solids, and under non-diffusion controlled conditions, the reactions will be directed by the interactions of reactants and products with the catalyst surface. This catalytic control of activity and selectivity will be more apparent at lower reaction temperatures, where primary adsorbed species are more stable. Many metals (Ni, Co, Fe and platinum group metals) catalyse the above described CH_4 reactions. Ruthenium catalysts are among the more active and selective to produce syngas either by dry and steam reforming reactions [13] or by partial oxidation [4]. The oxidation state of this metal changes depending on the reaction conditions [14] and compared with other metals a reduced carbon deposition has been observed on it [15]. On the other hand, the catalytic support can exert a great influence on the type of carbonaceous species formed by CH_4 interaction with the metallic particles dispersed on its surface [16]. Turning again to the reaction mechanism, it has recently been reported that, by the adequate choice of the support (Ru/TiO_2), a single step partial oxidation of CH_4 can occur [11,14].

A good understanding of the role of the support and the reaction pathway is a key point for a scientific design of a better catalyst. In order to address these questions, we have studied the reaction of CH_4 and $^{18}O_2$ over alumina- and silica-supported ruthenium catalysts. We have also performed a series of complementary oxygen exchange reactions.

2. Experimental

2.1. Catalysts

Catalysts were prepared by the incipient wetness technique using aqueous solutions of ruthenium chloride to introduce a nominal metallic loading of 1 wt.%. Al_2O_3 from Condea (175 m^2/g) and SiO_2 from Degussa (180 m^2/g) were used as catalyst supports. After impregnation, the catalysts were dried overnight at room temperature and calcined in air at 773 K for 3 h. Prior to each experiment, the catalysts (50 mg) were reduced in situ under H_2 at 673 K for 2 h and outgassed at 723 K for 1 h. Quantitative composition of catalysts was determined by atomic absorption. Ruthenium surface areas were obtained from hydrogen chemisorption using a Micromeritics 2700 Pulse Chemisorb and assuming an adsorption stoichiometry of a hydrogen per surface ruthenium atom. Hydrogen adsorption was carried out at 373 K because of its characteristic kinetically activated chemisorption on ruthenium crystallites [17].

2.2. Apparatus and procedure

The reaction of CH_4 and $^{18}O_2$, as well as the complementary oxygen exchange reactions between: (a) $C^{18}O_2$ and the bare supports, (b) ($C^{18}O_2$+$^{16}O_2$) and the bare supports, and (c) ($C^{18}O_2$+$^{16}O_2$) and the alumina and silica-supported Ru catalysts, were carried out in a fixed bed quartz microreactor (4 mm i.d.) coupled to a vacuum volumetric apparatus (100 cm^3 total volume). Some experiments were also performed using a reaction mixture of CH_4+$C^{18}O_2$+$^{16}O_2$. The gas reactant mixture (pure $C^{18}O_2$, $C^{18}O_2$+$^{16}O_2$ or CH_4+$^{18}O_2$ with molar ratios 2:1, and CH_4+ $C^{18}O_2$+$^{16}O_2$ with a molar ratio of 2:1:0.5) was circulated through the catalyst bed (about 50 mg) by a mechanical pump (170 $cm^3\ s^{-1}$) in a closed system.

The total absolute pressure in the system was kept close to 15 Torr and the reaction temperature around 723 K, this latter was monitored by a thermocouple placed at the external reactor wall near the catalyst bed. This moderate reaction temperature was chosen in order to avoid a rapid consumption of reactants and to maximize the conditions more favorable to the partial oxidation reaction. Gas analysis was performed by a Balzers QMG-421-C Quadrupole Mass Spectrometer connected via a leak valve to the reactor. By admitting a negligible part of the gaseous phase into the mass spectrometer and operating in the multiple ion monitoring mode it was possible to follow up to 10 m/z values simultaneously. A complete analysis was collected each 20 s on an interfaced computer. Results were corrected considering the secondary mass-to-charge ratios of various products. Isotopic purity of oxygen labeled compounds (supplied by Isotec, USA) is higher than 98.9 and 96.3 O^{18} atom% for $^{18}O_2$ and $C^{18}O_2$, respectively.

3. Results and discussion

The chemical analysis of the catalysts gives metal loadings of 0.64 and 0.72 wt.% for Ru/Al_2O_3 and Ru/SiO_2, respectively. The ruthenium dispersion calculated from the hydrogen chemisorption data at 373 K is 51% for Ru/Al_2O_3 and 13% for Ru/SiO_2.

Fig. 1 shows the variations of isotopic distribution at 723 K, after contacting $C^{18}O_2$ with Al_2O_3 (Fig. 1(A)) support and after circulating a mixture of $C^{18}O_2+^{16}O_2$ over Al_2O_3 (Fig. 1(B)) and SiO_2 (Fig. 1(C)) supports, as a function of the time. Clearly, dioxygen ($^{16}O_2$) is not dissociated on the supports, as revealed by the absence of oxygen exchange between $C^{18}O_2$ and $^{16}O_2$. On the contrary, carbon dioxide suffers an extensive oxygen exchange reaction with both supports. This oxygen exchange reaction is not affected by the presence of $^{16}O_2$ in the gas phase (Fig. 1(B) and 1(C)). Comparison of the two supports shows that the oxygen exchange with $C^{18}O_2$ follows a different mechanism over Al_2O_3 and SiO_2. In the former, the oxygen exchange reaction is more rapid and the main reaction product is $C^{16}O_2$. However, the oxygen exchange reaction of $C^{18}O_2$ with SiO_2 yields only $C^{16}O^{18}O$ as product. The behaviour observed for Al_2O_3 can be related with the formation of surface carbonates (polydentate species) upon carbon dioxide adsorption. These polydentate carbonates can suffer a near total exchange of oxygen atoms when they desorb from the surface [18]. The partial exchange of oxygen atoms between the $C^{18}O_2$ molecules and the SiO_2 surface can be interpreted as due to the formation of well defined bidentate CO_2 species, for which only the exchange of one oxygen atom is expected [19]. From the point of view of the carbon dioxide reforming of methane, these differences of surface reactivity can justify the general choice of basic oxide materials (MgO, La_2O_3,...) as support for catalysts [4] or as catalyst additives [20]. It has been suggested that the

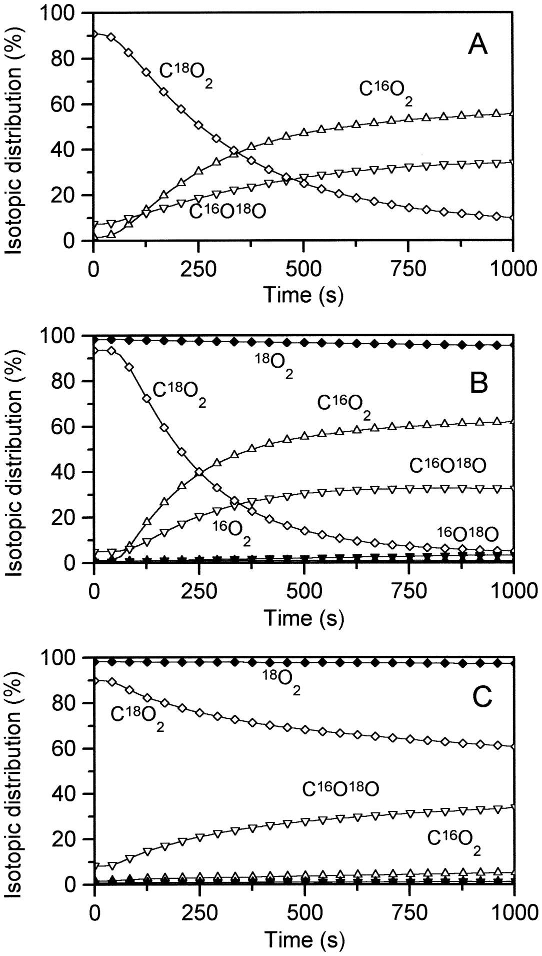

Fig. 1. Isotopic distribution of labelled oxygen species when $C^{18}O_2$ interacts with (A) Al_2O_3 and when $C\ ^{18}O_2+^{16}O_2$ interacts with: (B) Al_2O_3 and (C) SiO_2. (◇) $C^{18}O_2$, (△) $C^{16}O_2$, (▽) $C^{16}O^{18}O$, (◆) $^{18}O_2$, (▲) $^{16}O_2$ and (▼)$^{16}O\ ^{18}O$.

specific interaction of CO_2 with the basic component constitutes a source of carbonate intermediates near the metallic active sites of the catalyst, assisting in the achievement of a higher catalyst activity or a better selectivity or a diminished deactivation by carbon deposition during the dry reforming reaction [20]. Furthermore, these carbonates on the basic oxide components of the catalyst can react quickly with the surface carbonaceous species, originated by dehydrogenation of CH_4, to form CO following a pathway similar to that proposed by Baerns and coworkers for the partial oxidation of CH_4 [21].

The evolution of the isotopic distributions when a mixture $C^{18}O_2+^{16}O_2$ reacts over the supported ruthenium catalysts at 723 K is presented in Fig. 2. Dioxygen is activated on the ruthenium particles and is able to exchange oxygen atoms with $C^{18}O_2$, as revealed by the presence of ^{18}O labeled dioxygen in the gas phase. Apparently this exchange reaction between ^{16}O atoms and $C^{18}O_x$ labeled molecules is more intense on the Ru/SiO_2 catalyst. However, the relative concentration of ^{18}O labeled carbon dioxide molecules is higher for the Ru/SiO_2 sample than for the Ru/Al_2O_3 one, as consequence of the more extensive oxygen exchange of $C^{18}O_2$ with the Al_2O_3 support. These results also indicate that over the metallic surface oxygen atoms and carbon dioxide species coexist, either directly adsorbed from the gas phase and/or migrated from the support. Unfortunately our experiments are not conclusive enough to distinguish between these possibilities.

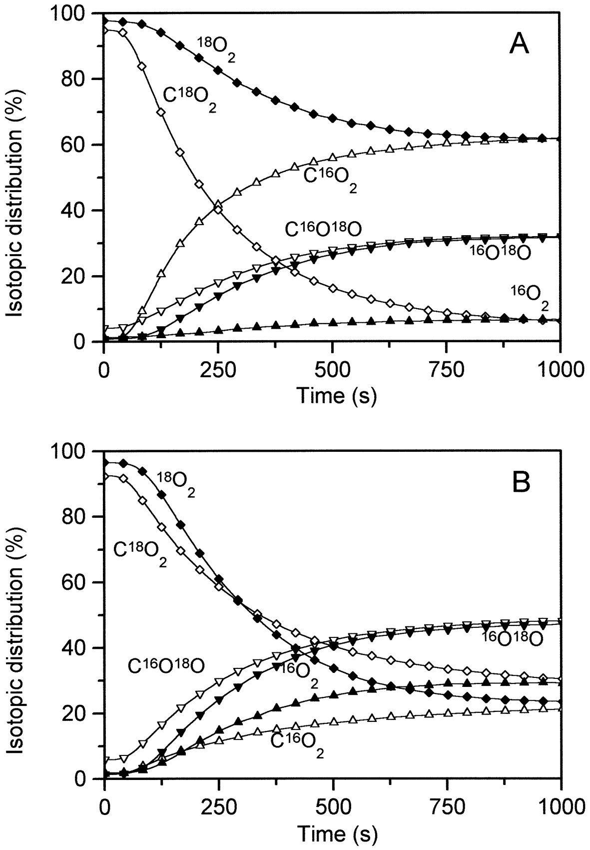

Fig. 2. Isotopic distribution of labelled oxygen species when a mixture $^{18}O_2+^{16}O_2$ interacts with the ruthenium catalysts: (A) Ru/Al_2O_3 and (B) Ru/SiO_2. (◇) $C^{18}O_2$, (△) $C^{16}O_2$, (▽) $C^{16}O^{18}O$, (◆) $^{18}O_2$, (▲) $^{16}O_2$ and (▼) $^{16}O^{18}O$.

When the mixture $CH_4+^{18}O_2$ is circulated through the supported ruthenium catalysts at 723 K a long delay period is appreciated (250 s under our experimental conditions) before H_2 and CO are detected (Fig. 3). During this period a significant difference between Ru/SiO_2 and Ru/Al_2O_3 can be observed, i.e. the temporal generation of a small amount of H_2 for the Ru/Al_2O_3. A tentative explanation for this H_2 production could be the direct decomposition of CH_4 molecules, which yields an H_2 release before methane reforming or oxidation reactions start. Such a phenomenon is more outstanding in the case of the alumina-supported ruthenium catalyst than in the silica-supported one, probably due to an enhanced ease of CH_x species migration on alumina surface and/or to the higher metallic dispersion of the Ru/Al_2O_3. This hydrogen disappears probably by reaction with oxygen to give H_2O. It is also apparent from Fig. 3 that carbon dioxide is produced before the generation of H_2 and CO starts. The isotopic composition of CO_2 is controlled by the oxygen exchange reaction with the support being $C^{16}O_2$ the main product for Ru/Al_2O_3 while $C^{16}O^{18}O$ was the main product for Ru/SiO_2. But these evolutions can be better observed in a normalized representation of the different consumed or generated gases vs. the time in the $CH_4+^{18}O_2$ reaction as shown in Fig. 4 for the Ru/SiO_2 catalyst. It is clear that oxygen, either reactant $^{18}O_2$ or exchanged oxygens ($^{18}O^{16}O$ and $^{16}O_2$), disappears while C^xO_2 is formed and before CO and H_2 production rises. Simultaneously with the initial formation of $C^{18}O_2$ and its subsequent oxygen

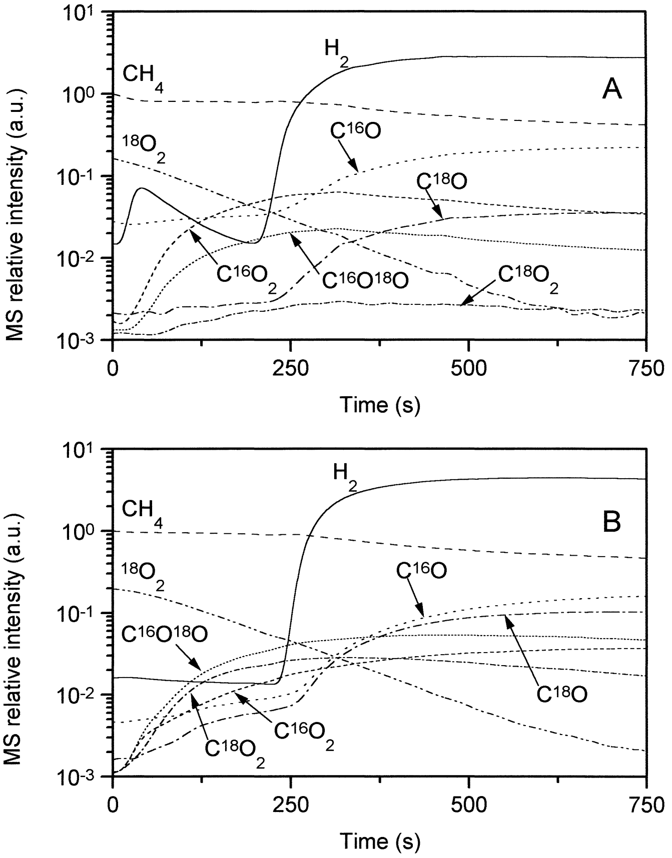

Fig. 3. Evolution of the gas phase composition when a mixture CH_4+18O_2 is circulated through the ruthenium catalysts at 723. (A) Ru/Al_2O_3 and (B) Ru/SiO_2.

exchange reactions, the production of water ($H_2^{16}O$ and $H_2^{18}O$) is also observed. Finally the $C^{18}O$, $C^{16}O$ and H_2 productions begin when carbon dioxide and water are already being consumed. It can be concluded that partial oxidation of methane to syngas on our catalysts proceeds via a two-step reaction mechanism, where the formation of carbon monoxide and hydrogen is the result of secondary reactions between unreacted methane and the carbon dioxide or water formed during the initial combustion of methane.

In the above discussion no assumptions concerning the oxidation state of the Ru surface was made. We could think that an initial oxidation of the Ru surface would probably delay the formation of H_2 and CO. However, there is lack of information about the oxidation states of the metal during the reaction. Although some authors indicate that noble metals became oxidized under dry reforming conditions being more active these oxidized states reduced the metal. Thus, no speculations about the transformation of the Ru surfaces in our experiments should be done.

The same conclusion about the two-step reaction mechanism for the methane partial oxidation was inferred performing experiments where a mixture of $CH_4+C^{18}O_2+{}^{16}O_2$ was circulated over the supported ruthenium catalysts at 723 K. Apart from the extensive oxygen isotopic exchange reaction, the formation of $C^{x}O_2$ precedes the generation of $C^{x}O$. Similar studies on Ni/Al_2O_3 and Pt/Al_2O_3 samples also indicate the two-step (indirect) mechanism.

The indirect mechanism for partial oxidation of methane is at present generally accepted [22]. Only few groups have found evidence about a direct one step partial oxidation reaction. First, Choudhary et al.

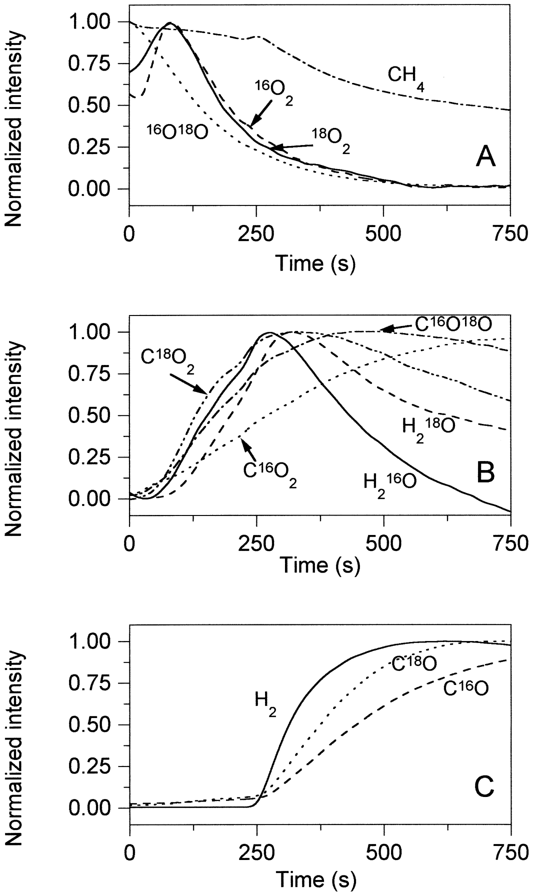

Fig. 4. Normalized representation of the gas phase composition when a mixture CH_4+$^{18}O_2$ is circulated through the Ru/SiO_2 catalyst at 723 K. (A) Reactants: (-×-) CH_4, (××××) $^{18}O_2$, (3–4) $^{16}O_2$ and (– – –) $^{16}O^{18}O$; (B) Intermediate products: (– – –) $H_2{}^{18}O$, (3–4) $H_2{}^{16}O$, (-××-) $C^{18}O_2$, (-×-) $C^{16}O^{18}O$ and (××××) $C^{16}O_2$; (C) Final products: (—) H_2, (· · · ·) $C^{18}O$ and (—) $C^{16}O$.

[6,7] found high yields and selectivities to syngas at relatively low temperatures (close to that used in the present study) and high gas hourly space velocity. Under these experimental conditions partial oxidation takes place, but the catalysts are not active for dry or steam reforming. However, the presence of hot spots in the catalytic bed as consequence of the exothermicity of the combustion reaction [10] makes possible to account the Choudhary's observations like a two-step mechanism [12]. Also, Schmidt and coworkers [8,9] indicate that CO and H_2 are primary products of the partial oxidation over monolith-supported metal catalysts. These results can be explained because in this case gas phase reactions (non-catalytic) may play a decisive role in the control of activity and selectivity [22]. More recently Qin et al. for Rh/MgO [23] and Verykios et al. for Ru/TiO_2 [14] based on transient experiments using isotope-labelled molecules found evidence about a direct formation of synthesis gas by partial oxidation of methane. But, we have shown in the present work that isotopic exchange reactions with the support, which are very fast even at the moderate temperatures here used, can make a conclusive interpretation of their results difficult. Furthermore, they assume that reforming reactions do not take place at lower temperatures (<800 K) even if thermodynamic equilibrium indicates that reactions are possible with moderate conversions.

Table 1 presents the results of catalytic performance of our alumina- and silica-supported ruthenium catalysts for the dry reforming reactions at 723 K. We can observe that the selectivity increases with increasing conversions. Also, the catalytic selectivity is somewhat affected by the support. The interaction

Table 1
Catalytic results for carbon dioxide reforming of methane over the supported ruthenium catalysts[a]

Catalyst	Reaction temperature (K)	CH_4 conversion (%)	CO_2 conversion (%)	Selectivity	
				CO (%)	H_2 (%)
Ru/Al_2O_3	700	2.2	2.8	51	62
	730	4.1	4.6	64	61
	760	6.4	8.1	76	76
Ru/SiO_2	665	3.2	2.7	61	26
	705	5.0	4.9	77	41
	750	8.2	9.5	83	55

[a] Reaction mixture 10 cm^3/min CH_4, 10 cm^3/min CO_2, 80 cm^3/min He. Amount of catalyst 25 mg.

of the support with reactants and products can be a key factor to explain differences in catalytic behaviour and in mechanistic interpretations. Thus, the concentration of carbonate species over some types of supports or the reactivity of surface hydroxyls groups [16], which can be regenerated by reaction with H_2O molecules, are phenomena whose occurrence makes it possible both to understand differences in catalytic properties of different samples and to rationalize the proposed reaction mechanisms.

In conclusion the evidences given in this work indicate that over supported noble metals the partial oxidation of methane to syngas proceeds via a two-step mechanism (combustion+reforming).

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