# Bifunctional pathways in the carbon dioxide reforming of methane over MgO-promoted Ru/C catalysts

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The addition of MgO to a ruthenium catalyst dispersed on an inert activated carbon is found to improve the catalyst selectivity and stability in the dry reforming of methane to syngas. Steady-state and isotopic transient kinetic experiments carried out in a TAP reactor have revealed a cooperative interaction between the metal and the basic oxide in the $CO_2/CH_4$ reaction via a bifunctional mechanism. This specific effect is proposed to explain the discovered promoting effect.

**Keywords:** dry reforming of methane, temporal analysis of products (TAP), isotopic transient kinetic experiments, bifunctional mechanism, MgO-promoted ruthenium catalysts

## 1. Introduction

The reaction between methane and carbon dioxide to syngas ($CO + H_2$) is a major issue in heterogeneous catalysis [1]. This reaction also finds application in chemical energy transmission systems due to the high reaction enthalpy of this process [2]. Most of the group VIII transition elements (Fe, Co, Ni, Ru, Rh, Pd, Ir and Pt) have been shown to catalyse this reaction [3]. Although noble metals may be too expensive for large-scale commercial use, catalysts based on them, especially Ru and Rh, have been proved to be carbon resistant, while non noble metals (Co and Ni) are prone to deactivation by coke [4,5]. On the other hand, the selection of the support can greatly modify the catalytic properties of a given metal under methane dry reforming conditions and give rise to changes in the activity in terms of turnover number or stability towards sintering and resistance to carbon deposition [6,7]. Metal–support interactions and/or the participation of basic sites of the support have also been found to play a specific role in the $CO_2/CH_4$ reaction [8–10].

Numerous papers have been devoted to the study of catalytic systems dispersed on a variety of oxides ($SiO_2$, $Al_2O_3$, $La_2O_3$, $ZrO_2$, $Y_2O_3$, $TiO_2$, $CeO_2$, MgO and CaO) [3,11–15] but little attention has been paid to carbonaceous materials as catalysts supports for this reaction [7,16,17]. Black carriers, due to their high ability to absorb radiation, are of particular interest for application in the storage of solar energy [18]. In the present paper a ruthenium catalyst supported on activated carbon in the reaction of $CH_4$ with $CO_2$ and the promoting effect of the basic oxide MgO is investigated by means of transient isotopic experiments carried out in a temporal analysis of products (TAP) reactor.

## 2. Experimental

A commercial high surface area activated carbon (ICASA, Spain) is used as support. Before use, it is treated with a HCl solution in order to remove inorganic materials, then washed and dried. The resulting support presents a specific surface area of 961 $m^2\,g^{-1}$ ($N_2$, 77 K). The catalysts are prepared by impregnating the activated carbon with an aqueous solution of $Ru(NO)(NO_3)_3$ to yield a nominal metal loading of 2 wt%. Once dried, a part of this specimen is impregnated with an aqueous solution of $Mg(NO_3)_2$ to obtain a Mg : Ru atomic ratio of 10 : 1. Before testing, the catalysts Ru/C and Ru–MgO/C are reduced *in situ* under pure hydrogen (2.1 $l\,h^{-1}$) at 673 K for 2 h.

The ruthenium dispersion ($D$) in each catalyst is determined by $H_2$ pulse chemisorption at 373 K. Activity tests are performed at atmospheric pressure in a fixed-bed quartz reactor operated at 823 K. The reacting mixture (10% $CH_4$ + 10% $CO_2$ + 80% He) is fed at a flow rate of 6 $l\,h^{-1}$ with a weight hourly space velocity of $4 \times 10^5$ $cm^3\,h^{-1}\,g^{-1}$. The individual flows of reactants and diluent are adjusted by mass flow controllers and the effluents are continuously analysed by gas chromatography. Freshly reduced catalyst and support samples are also submitted to a flow of 10% $CO_2$ + 90% He (6 $l\,h^{-1}$) at 823 K in order to determine the level of gasification of the activated carbon support occurring via the reverse Boudouard reaction ($CO_2 + C \rightarrow 2CO$).

Transient pulse experiments are carried out in a TAP-2 reactor described in [19]. The catalyst sample (0.050 g) is placed between two layers of quartz particles. Prior to

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the experiment the sample is reduced in pure hydrogen ($2.4\ l\,h^{-1}$) at 673 K for 1 h, outgassed in vacuum and heated to the reaction temperature (823 K). Two series of successive pulses of a mixture of 90% $^{12}CO_2 + 10\%$ Ar ($1.3 \times 10^{16}$ molecules/pulse) followed by two series of successive pulses of 10% $^{13}CH_4 + 90\%$ He ($5.3 \times 10^{16}$ molecules/pulse) are injected into the reactor via two high-speed valves. Then the sample is submitted to a sequence of $D_2$ pulses until no change in the TAP response is obtained and a new series of 10% $^{13}CH_4 + 90\%$ He is injected.

## 3. Results and discussion

Table 1 compiles the main characteristics of the Ru/C and Ru–MgO/C catalysts and their activity, selectivity and stability with time on stream at 823 K. Both samples have a similar metal surface area. The slightly higher Ru dispersion of the Ru–MgO/C catalyst can be considered as a promoter effect, which was shown elsewhere to limit the sintering of the metal during the reduction stage [20]. The turnover numbers estimated for $CH_4$ are also similar for both catalysts, while the net rate of CO production per surface metallic site is influenced by the extension of the reverse water–gas shift reaction ($CO_2 + H_2 \rightleftharpoons CO + H_2O$). For comparison of these values with others reported in the literature, let us take into account the uncertainty in the metallic dispersion. Firstly, because hydrogen chemisorption measurements have been carried out after reduction at 673 K and the catalytic performance has been measured at a rather higher temperature (823 K). On the other hand, it must be considered that these TON values can be overestimated due to the suppression of hydrogen adsorption on metals dispersed on carbon supports, as previously observed in similar catalysts [21]. The presence of interstitial carbon atoms at the surface of the metallic crystallites has been suggested to be the reason for a reduced $H_2$ uptake on carbon-supported metals [22]. Keeping this in mind, a comparison with the turnover number obtained by Bradford and Vannice for methane in the $CH_4 + CO_2$ reaction on a similar catalyst (4.8 Ru/C) [16] has been carried out by extrapolating it to our experimental conditions, i.e., $P_{CH_4} = P_{CO_2} = 76$ Torr and $T = 823$ K, according to the power rate law expresion: $TOF_{CH_4} = A\exp(-E_{CH_4a}/RT)P_{CH_4}^{\bar{\alpha}}P_{CO_2}^{\bar{\beta}}$, where the mean values of $\bar{\alpha}$, $0.52 \pm 0.36$, and $\bar{\beta}$, $0.21 \pm 0.40$, have been calculated on the values reported in the literature for $CH_4$ [3]. It results in an activity per surface metallic site of $0.3\ s^{-1}$, one order of magnitude lower than in our case. However, this value was calculated by assuming 100% in the catalyst dispersion, given the inconsistency found in the number of ruthenium atoms exposed to the surface estimated from the $H_2$ and CO uptakes (H/Ru = 0.085 and CO/Ru = 1.2). So, by assuming in our catalysts 100% dispersion we would obtain for the unpromoted and the promoted catalysts, 0.21 and $0.25\ s^{-1}$, respectively, these values being in good agreement with the one obtained in [16].

Table 1
Main characteristics and catalytic properties of the catalysts.[a]

| | Ru/C | Ru–MgO/C |
|---|---|---|
| Ru loading (wt%) | 2 | 2 |
| Mg : Ru atomic ratio | – | 10 |
| $D$ (%) | 6 | 9 |
| $X_{CH_4(t=1\ h)}$ (%) | 8.4 | 10.0 |
| $r_{CO(t=1\ h)}$ ($\mu mol\ g^{-1}\ s^{-1}$) | 88 | 94 |
| $r_{CO(t=6\ h)}/r_{CO(t=1\ h)}$ | 0.98 | 0.99 |
| $r_{CO(t=12\ h)}/r_{CO(t=1\ h)}$ | 0.95 | 0.97 |
| $TON_{CH_4}$ ($s^{-1}$) | 2.8 | 2.2 |
| $TON_{CO}$ ($s^{-1}$) | 7.3 | 5.2 |
| $S_{H_2}$ (%) | 57 | 82 |
| $S_{CO}$ (%) | 95 | 100 |

[a] Reactant mixture: 10% $CH_4$ + 10% $CO_2$ + 80% He, gas flow rate $6\ l\,h^{-1}$, reaction temperature 823 K, pressure 1 atm.

At similar level of conversion and activity, the MgO-promoted sample is found more selective towards hydrogen by 25% as compared to the unpromoted Ru/C, indicating that the reverse water–gas shift reaction is less favored in the presence of MgO. The slightly below 100% selectivity to CO (about 95%) noted on the Ru/C catalyst, i.e., the C unbalance, suggests that carbon deposition takes place during the reaction, which rules out any significant support gasification. This process may explain the slight deactivation, 2% after 6 h and 5% after 12 h, found by comparing with the activity measured after 1 h of reaction. For the Ru–MgO/C sample, a CO selectivity (or C balance) of 100% is found, in line with a higher stability of the catalyst.

In order to determine the ability of the support to react with $CO_2$, the activated carbon and the two ruthenium catalysts are tested in a diluted carbon dioxide stream at reaction temperature (823 K). The bare support appeared to be completely inert to $CO_2$ at that temperature. In contrast, a transient carbon dioxide conversion (about 4% on Ru/C and 2% on Ru–MgO/C) decreasing with time is observed for the Ru-containing samples (figure 1). The amount of

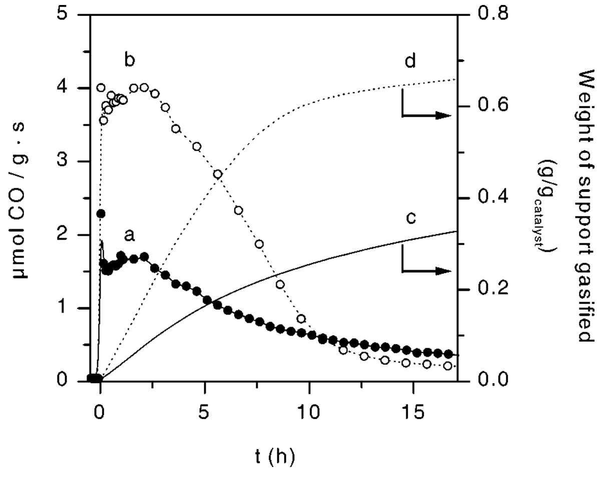


Figure 1. Carbon monoxide evolution from catalysts under diluted carbon dioxide at 823 K: (a) Ru/C and (b) Ru–MgO/C. Estimation of the amount of the support lost by gasification ($CO_{2(g)} + C_{(support)} \rightleftharpoons 2CO_{(g)}$): (c) Ru/C and (d) Ru–MgO/C. Reactant mixture: 10% $CO_2$ + 90% He, flow rate $6\ l\,h^{-1}$.

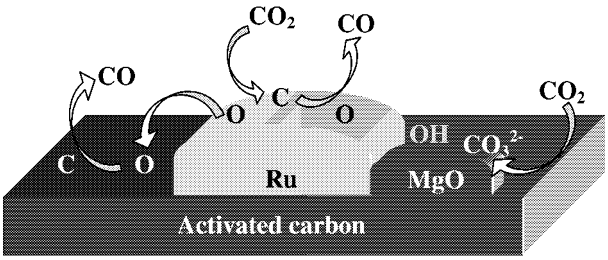


Figure 2. Schematic representation of the gasification of the support and the preventing role of magnesia.

carbon of the support that evolves as CO, also presented in figure 1, is estimated according to the gasification reaction: $CO_{2(g)} + C_{(support)} \rightleftharpoons 2CO_{(g)}$. These results demonstrate that metallic ruthenium catalyses carbon dioxide dissociation into carbon monoxide and active surface oxygen species that are able to react with the carbon support to yield CO. However, the presence of MgO limits significantly this process. This could be due to an intimate contact between Ru and MgO that reduces the concentration of interfacial sites between the metal and the support (figure 2). This tight interaction between Ru and MgO has also been deduced from temperature-programmed reduction (TPR) of these catalysts [20]. The TPR profiles showed an increase in the reduction temperature of ruthenium after MgO addition. According to the extensive studies on $CO_2$ activation on transition metals surfaces reviewed by Freund and Roberts [23], carbon dioxide is known to chemisorb on atomically rough metal surfaces, which contain a high defect density. The mechanism of $CO_2$ adsorption on metals has been usually connected with the formation of bent $CO_2^{\delta-}$ adspecies [24] that have been shown to be the essential precursor in the facile formation of the dissociation products, i.e., adsorbed oxygen and carbon monoxide, as in our case, or other compounds resulting from its reaction with coadsorbed species, such as carbonate, oxalate, formate, etc. In contrast, adsorption of $CO_2$ on oxides generally leads to the formation of surface carbonate structures rather than to the dissociation of the molecule [25]. Given the extensive gasification of the carbon support in these catalysts over a several hours period, the formation of a stable ruthenium oxide ($RuO_2$), which would be unable to dissociate $CO_2$, can be ruled out and therefore the presence of mobile oxygen species adsorbed on metallic ruthenium, which are active for the gasification of the active carbon used as support, can be postulated. The presence of MgO at the ruthenium–carbon interface would limit the rate of support oxidation as it is shown in figure 2.

Transient isotopic experiments are carried out in a temporal analysis of products (TAP) microreactor to obtain more detailed information about the processes taking place at the catalyst surface. In TAP experiments, the ratio between the number of pulsed molecules and the number of surface ruthenium atoms is between 0.01 and 0.09. This means that only a small part of the ruthenium sites is probed by each pulse during the experiment.

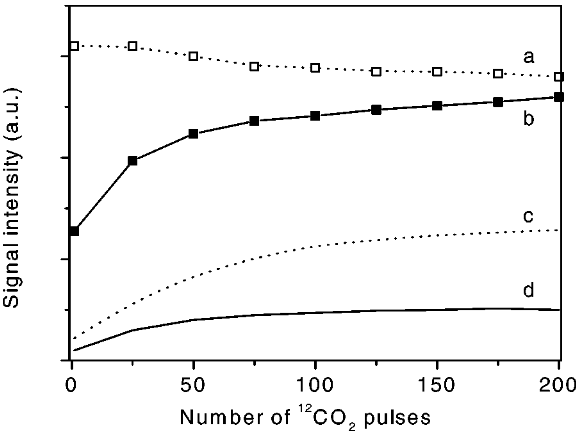
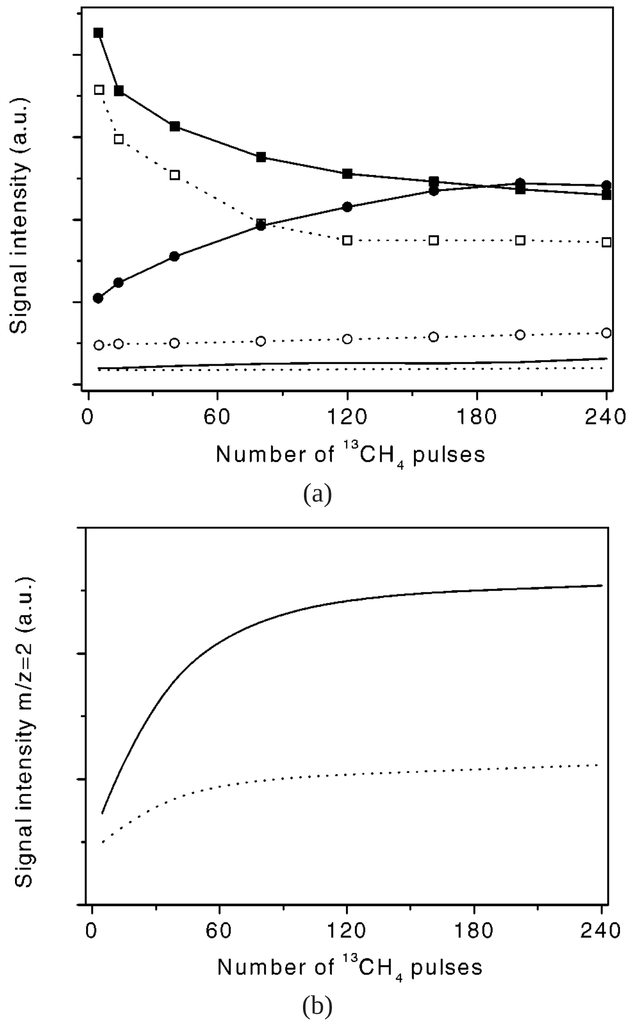


Figure 3. Intensity of TAP responses to a sequence of 200 pulses of 90% $^{12}CO_2 + 10\%$ Ar at 823 K: (a) $^{12}CO$ produced on Ru/C, (b) $^{12}CO$ produced on Ru–MgO/C, (c) $^{12}CO_2$ unreacted on Ru/C and (d) $^{12}CO_2$ unreacted on Ru–MgO/C.

Figure 3 displays the integrated areas of the $^{12}CO_2$ and $^{12}CO$ TAP responses obtained on the Ru/C and Ru–MgO/C catalysts during a sequence of 200 pulses of 90% $^{12}CO_2 + 10\%$ Ar. The amount of CO produced on the Ru/C catalyst is larger than on the Ru–MgO/C sample (curve (a) vs. curve (b)), though the amount of reacted $CO_2$ is larger for the promoted sample (curve (d) vs. curve (c)), in agreement with the previous results under continuous carbon dioxide flow. Further $CO_2$ pulsing leads finally to similar levels of CO production. The additional $CO_2$ uptake not leading to CO formation on the MgO-promoted sample indicates that part of $CO_2$ is retained on the catalyst. Species arising from carbon dioxide adsorption on MgO have been generally indentified as carbonate species, mainly surface bidentate adspecies and only a little part of monodentate ones [25,26]. Among them, the strongest bound species are stable up to 1000 K [27]. Thus, it seem plausible that a part of the pulsed $CO_2$ remains at the MgO surface in the form of bidentate surface carbonates.

After $^{12}CO_2$ pulsing, the catalytic surfaces are probed with a first series of 240 pulses of a 90% He + 10% $^{13}CH_4$ mixture. Figure 4 (a) and (b) shows the profiles obtained for $^{13}CH_4$, $^{12}CO$ and $^{13}CO$ (a) and $H_2$ (b) at the reactor exit. For the two samples, methane conversion is almost complete for each pulse. As for product formation over Ru/C there is initially a large production of $^{12}CO$ that decreases with time, while the amount of $^{13}CO$ formed directly from $^{13}CH_4$ is constant and much smaller (figure 4(a)). The amount of hydrogen initially produced is very low but gradually increases with the number of injected pulses (figure 4(b)). Over Ru–MgO/C a larger formation of $^{12}CO$ is observed but following a decreasing profile similar to that obtained over the unpromoted catalyst (figure 4(a)). A much larger production of $^{13}CO$ is also noted in the way that, finally, each $^{13}CH_4$ pulse yields equimolecular amounts of the isotopically labelled oxides: $^{13}CO$ and $^{12}CO$ (figure 4(a)). The same trend is observed for hydrogen production (figure 4(b)).



(a)

(b)

Figure 4. Intensity of TAP responses obtained on Ru/C (···) and Ru–MgO/C (—) by injecting 240 pulses of a mixture of 10% $^{13}CH_4$ + 90% He at 823 K over the catalysts previously submitted to $^{12}CO_2$ pulses. (a) $^{13}CH_4$ (no symbol), $^{13}CO$ (○, ●) and $^{12}CO$ (□, ■); (b) $H_2$.

The first clear trend revealed in figure 4(a) is that a rather large amount of $^{12}CO$ is still produced though only $^{13}CH_4$ is fed. This indicates that both catalysts accumulated $^{12}C$ and O during the previous series of $^{12}CO_2$ pulses. This pool of $^{12}C$ and O may be (i) under the form of adsorbed $CO_2$, which is most likely the case for the MgO-promoted sample, and (ii) as ruthenium chemisorbed oxygen (Ru–$O_{ads}$) for both samples, since this form of oxygen was found to be able to react with carbon of the support into CO. This pool of surface oxygen available initially on both catalysts explains the low initial production of hydrogen (figure 4(b)) since the probability for hydrogen formed from methane dissociative chemisorption to react with surface oxygen will increase when the concentration of the latter is high. The more the methane is pulsed, the more it reduces the surface ruthenium phase and the more the hydrogen can leave the reactor without secondary oxidation.

The second trend observed in figure 4 (a) and (b) is that a much larger amount of $^{12}CO$, $^{13}CO$ and $H_2$ is produced on the MgO-promoted sample. Again a rational explanation derives from the $^{12}CO_2$ accumulation on the promoted sample as magnesium carbonates. On this catalyst, the slow decomposition of carbonates in the vicinity of the Ru phase provides a continuous source of surface oxygen, which may react with the $^{13}C$ atoms issued from the methane dehydrogenation into $^{13}CO$. Thus, when the initial pool of Ru–$O_{ads}$ (present on both catalysts) is consumed, one $^{12}CO_2$ molecule decomposed from the carbonate pool will give one $^{12}CO$ molecule and one surface oxygen which will in turn react with a surface $^{13}C$ into one $^{13}CO$ molecule. This explains the isoproduction of $^{13}CO$ and $^{12}CO$ on the promoted sample after a large number of methane pulses. In addition, this source of oxygen which continuously "cleans" the Ru surface from the carbon arising from methane adsorption and decomposition, will also contribute to favor the methane activation process and, therefore, the hydrogen production, as observed in figure 4(b) and in the previous steady-state experiments with a higher $H_2$ selectivity (table 1). In contrast, only a residual production of $^{13}CO$ is observed on the unpromoted sample due to this absence of a permanent source of surface oxygen at the vicinity of the methane adsorption sites. However, considering that an almost complete $^{13}CH_4$ conversion is achieved on Ru/C, like on Ru–MgO/C (figure 4(a)), this means that a significant carbon deposition takes place on the unpromoted sample from $^{13}CH_4$ dehydrogenation, as attested by the lower but non negligible hydrogen production (figure 4(b)). This is in good agreement with the lower CO selectivity detected for this catalyst under steady-state reaction conditions (table 1). In this respect, the rapidly decreasing $^{12}CO$ production observed on the unpromoted sample (figure 4(a)) is likely to come from the support gasification due to the accumulated oxygen in the ruthenium phase. A side source of $^{12}CO$ arising directly from the decomposition of accumulated $^{12}CH_xO_y$ species (such as formate) on the carbon support during the previous $CO_2$ pulsing experiment cannot be excluded. That possibility should be checked by direct *in situ* IR observation.

Upon a subsequent injection of a series of $D_2$ pulses, $H_2$ and HD molecules are detected at the reactor outlet, indicating some isotopic exchange of $D_2$ with H-containing adspecies. The degree of exchange over Ru–MgO/C ($H_2$/HD = 0.30) is found to be much higher than over the Ru/C catalyst ($H_2$/HD = 0.023), as expected by the presence of surface OH groups on the magnesia phase that are difficult to remove at temperatures lower than 873 K even *in vacuo* [28]. Once the catalyst surface is in equilibrium with the $D_2$ concentration in the gas phase, a series of 10% $^{13}CH_4$ + 90% He pulses is injected. For similar $^{13}CH_4$ conversion, the intensity of the HD outlet pulses is measured (in arbitrary units) and values of 0.1 a.u. for Ru/C and 0.2 a.u. for Ru–MgO/C are determined. Given the high temporal resolution of the technique, the conditions of very low pressure in the reactor and the low residence time of the reactant gases in contact with the catalyst bed, secondary processes of hydrogen exchange can be neglected. The higher HD production after $^{13}CH_4$ reaction on the MgO-promoted catalyst also probes the participation of the hydroxyl species in the methane activation process. It may reasonably be speculated that these OH (OD) species, essentially magnesium hydroxyl groups, are located at the metal–promoter interface and/or can suffer migration processes towards the Ru particles, acting also as a source of oxidant able to limit the catalyst aging.

## 4. Conclusions

Ruthenium supported on an activated carbon has been tested for the dry reforming of methane at 823 K. The activated carbon is an inert material under carbon dioxide atmosphere. However, in the presence of ruthenium, gasification of the support takes place indicating the ability of the metal to catalyse carbon dioxide dissociation into CO and surface oxygen able to spillover to and react with the support.

The addition of MgO to the Ru/C catalyst is shown to promote the $CO_2$ reforming of $CH_4$ to syngas with (i) an improved selectivity to CO and $H_2$ and (ii) a higher resistance to deactivation by carbon deposition. The presence of magnesia limits the reverse water–gas shift reaction and the gasification of the support. The accumulation/decomposition of $CO_2$ as magnesium carbonate provides a continuous source of oxygen at the vicinity of the Ru particle which favours the oxidation of carbon arising from $CH_4$ adsorption and dehydrogenation on the ruthenium particles into CO. Therefore, the Ru surface is maintained clean enough to allow the methane reforming into CO and $H_2$ to proceed without serious aging. This source of oxygen is however sufficiently limited not to promote the secondary oxidation of adsorbed hydrogen. Hydroxyl groups present at the metal/promoter interface could also contribute to limit the catalyst aging. Thus, the promoted sample may be typical of a bifunctional catalysis for the $CO_2$ reforming reaction.

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