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Catalytic partial oxidation of methane over a 4% Rh/α-Al_2O_3 catalyst
Part II: Role of CO_2 reforming

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Abstract

A kinetic study of the CO_2 reforming of CH_4 over a 4 wt% Rh/α-Al_2O_3 catalyst was performed in a short contact time annular reactor. Experiments were carried out under nearly isothermal conditions, at high space velocity (2×10^6 Nl/K g_{cat}/h), within the temperature range 300–800 °C, at varying feed composition. CO_2/CH_4 tests with excess CO_2 showed a strong similarity with previous H_2O/CH_4 tests. At $CO_2/CH_4 = 1$ (an experiment characterized by negligible amount of H_2O in the product mixture), the measured conversion of methane was significantly lower. Additional experiments with co-feed of O_2 or H_2 indicated that H_2O had a limiting role on the conversion of CH_4. A quantitative analysis of data was performed by means of a 1D heterogeneous model of the reactor, by assuming that steam reforming and reverse water gas shift were uniquely active and proceeded according to kinetics that were estimated on the basis of independent data. Though neglecting the rate of CO_2 reforming, all the observed trends could be well described as a cycle of H_2O reforming and RWGS (initiated by a trace amount of H_2O in the feed) wherein the rate determining step (either SR or RWGS) depends on the gas-phase composition. Finally, experiments confirmed that the addition of CO to the reaction mixture partly slowed down the kinetics of methane activation, which had been indirectly postulated in Part I of this work on the basis of CH_4 CPO data at varying reactant concentrations.

Keywords: CO_2 reforming of CH_4; Reverse-WGS; Steam reforming of CH_4; CH_4 CPO; Rh/α-Al_2O_3; Annular reactor; Kinetic study

1. Introduction

The present work is the second part of a two-paper series on the development of a molecular kinetic scheme for the catalytic partial oxidation of CH_4 over 4 wt% Rh/α-Al_2O_3 catalysts. In Part I [1], the results of an extensive experimental study performed with a short contact time annular reactor are reported and rationalized on the basis of an indirect kinetic scheme, consisting of six molecular rate expressions (the oxidation of CH_4, the post-combustions of H_2 and CO, the steam reforming of CH_4, the WGS and its reverse reaction). Part II of the work is focused on the role of CO_2-reforming in the kinetics of the CPO process.

Since the early paper of Fischer and Tropsch [2], the reforming of CH_4 with CO_2 over group VIII metal catalysts has been studied as a valuable route to produce synthesis gas with lower H_2/CO ratio than that produced by steam reforming. Since then an extensive literature on dry-reforming has been published and reviews are available [3–5]. The formation of coke, the mechanism of CH_4 and CO_2 activation, the role of the support, the identification of the rate determining step (or steps) and the derivation of kinetic expressions are some widely treated issues [6–22].

A less treated aspect, which is especially important for understanding of the role of CO_2 reforming within the complex process of CH_4 partial oxidation, is represented by the relationship between CO_2 and H_2O reforming. On the basis of kinetic and isotopic tracer methods, Wei and Iglesia [10] proposed a unique mechanism for the reforming of CH_4 with both CO_2 and H_2O and speculated that the CO_2 and H_2O reforming rates were identical to that of CH_4 decomposition. Accordingly, both CO_2 and H_2O reforming are kinetically equal since the only relevant step is the activation of the first C–H bond of the CH_4 molecule.

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A unifying rate expression was adopted, proportional to CH_4 pressure and independent of the co-reactant pressures. This interpretation applies to Ni and other noble metals catalysts (Pt, Pd, Ir, and Ru) supported on different metal oxides [11].

Other authors have observed that the rate of CO_2 reforming is lower than that of H_2O reforming. Using Ni film, Bodrov and Apel'baum [7] found that the rate of CO_2 reforming was comparable to the rate of steam reforming in the presence of some steam in the feed stream, thus H_2O was interpreted as the preferential co-reactant of CH_4; in the absence of any H_2O in the feed stream, the rate of CO_2 reforming decreased significantly, which was explained by assuming that the formation of H_2O passed through the slow decomposition of methane to produce H_2 and the reaction between H_2 and CO_2. Rostrup-Nielsen and Bak Hansen [6] have compared the rate of CO_2 reforming with that of steam reforming over several supported metals and concluded that replacement of steam by carbon dioxide had no significant impact on the reforming mechanism of CH_4. The authors proposed that in both cases two irreversible steps control the kinetics, namely methane activation and the surface reaction of C with adsorbed oxygen atoms, which would originate by the dissociation of adsorbed H_2O in the case of steam reforming and by the dissociation of adsorbed CO_2 in the case of CO_2 reforming. The observed moderate decrease of rate passing from steam to CO_2 was related to kinetic effects (e.g., an inhibiting effect of CO adsorption, being CO present in larger concentration in the case of CO_2 reforming). Also, the authors pointed out that H_2O production on the catalyst is critical during CO_2 reforming experiments since, once RWGS makes steam available on the surface, a fast route of CH_4 consumption by H_2O reforming is established. Bradford and Vannice [13] contributed to reconcile previous literature data with further investigations on the rate of dry reforming over Ni. They proposed a reaction scheme wherein CH_x species react with surface hydroxyls, originated by the reverse-WGS reaction and derived a molecular kinetic expression by assuming that both CH_4 dissociation and the decomposition of the CH_xO intermediate were rate determining; such expression retains dependences on both CH_4 and CO_2 partial pressure and explained well their observations on the existence of a negligible effect of CO_2 concentration on the rate of CH_4 conversion, except for extremely small concentrations of CO_2 (in which case the rate of methane consumption was negatively affected).

Few works have treated the role of CO_2 reforming in the short contact time CPO of CH_4 (and mostly dealing with non isothermal reactor operation), and general agreement exists about the lack of importance of this route. The absence of CO_2 reforming was reported both for fuel rich CH_4/air mixtures and for CH_4/O_2 mixtures highly diluted in H_2O and CO_2 [23–27]. Numerical detailed analysis and experimental data confirmed that the addition of CO_2 has a minor impact on the system and affects only the WGS equilibrium, but not the fuel conversion.

In this work, the annular reactor [1] was applied to investigate the CO_2 reforming of CH_4 over a 4% Rh/Al_2O_3 catalyst. The aim of the research was to identify the relative role of CO_2-reforming and steam reforming of methane within the CH_4-CPO process. Experiments were performed with diluted CO_2/CH_4 mixtures, under comparable operating conditions as those used for investigating the kinetics of steam reforming. CO_2/H_2 tests were also performed to evaluate the rate of the reverse water gas shift reaction, that is the rate of H_2O supply during CO_2 reforming experiments. Data were quantitatively analyzed by a 1D model of the reactor and the results of the analysis were verified by comparison with CH_4 CPO data.

2. Experimental

The testing apparatus and the flow system, as well as the preparation and the characterization methods of the present $Rh/\alpha\text{-}Al_2O_3$ catalysts have been already described in detail in the first part of the work [1]. The experiments herein reported were carried out on a catalytic layer 8.6 mg in weight, 2 cm long, and 23 μm thick.

The catalytic tests were carried out at atmospheric pressure and at a GHSV of $2 \times 10^6\ \mathrm{Nl/K\,g_{cat}/h}$. This value of GHSV was chosen to better compare the CO_2 reforming tests with the CPO and the H_2O reforming ones, shown in Part I. To avoid axial thermal gradients, diluted gas mixtures were fed (balance $N_2 > 90\%$ v/v); axial gradients were always within 10 °C/2 cm for all the experiments and lower than 5 °C/2 cm for most of them.

A standard kinetic test was used and it consisted of varying the reaction temperature from 300 °C up to 850 °C with step-wise increments of 50–70 °C. At each temperature, conversions and selectivities were estimated by repeated analysis and showed stable values within 15–20 min. As mentioned in Part I, prior to the kinetic investigation the catalyst underwent a standard conditioning procedure which consisted of repeated runs at GHSV of $8 \times 10^5\ \mathrm{Nl/K\,g_{cat}/h}$, feeding a gas mixture with 4% CH_4 v/v, $O_2/CH_4 = 0.56$, N_2 to balance. The catalyst conditioning was complete when stable performances were reached in the whole temperature range. CO_2-reforming experiments were performed at 1% CH_4 v/v and varying CO_2 inlet fraction. Additional experiments were carried out with co-feed of O_2 (0.1%) and H_2 (0.1 and 1%). CO_2/H_2 tests (also with co-feed of H_2O and CO) were performed to estimate the RWGS reactivity. The steam reforming data, illustrated and analyzed in Part I of this work, represent a reference for evaluating the reactivity of CH_4 in the presence of CO_2. CPO tests under standard operating conditions (1% CH_4 v/v, $O_2/CH_4 = 0.56$, N_2 to balance, at a GHSV of $2 \times 10^6\ \mathrm{Nl/K\,g_{cat}/h}$) were repeated throughout the experimental study to verify the absence of catalyst deactivation. It must be emphasized that also after the most risky tests for carbon formation, the activity remained almost unaltered, so that there was no uncertainty in regarding the observed effects as truly kinetic.

3. Experimental results

3.1. RWGS tests

Experiments of reverse water gas shift reaction (RWGS) were performed by varying the CO_2 and H_2 inlet fractions.

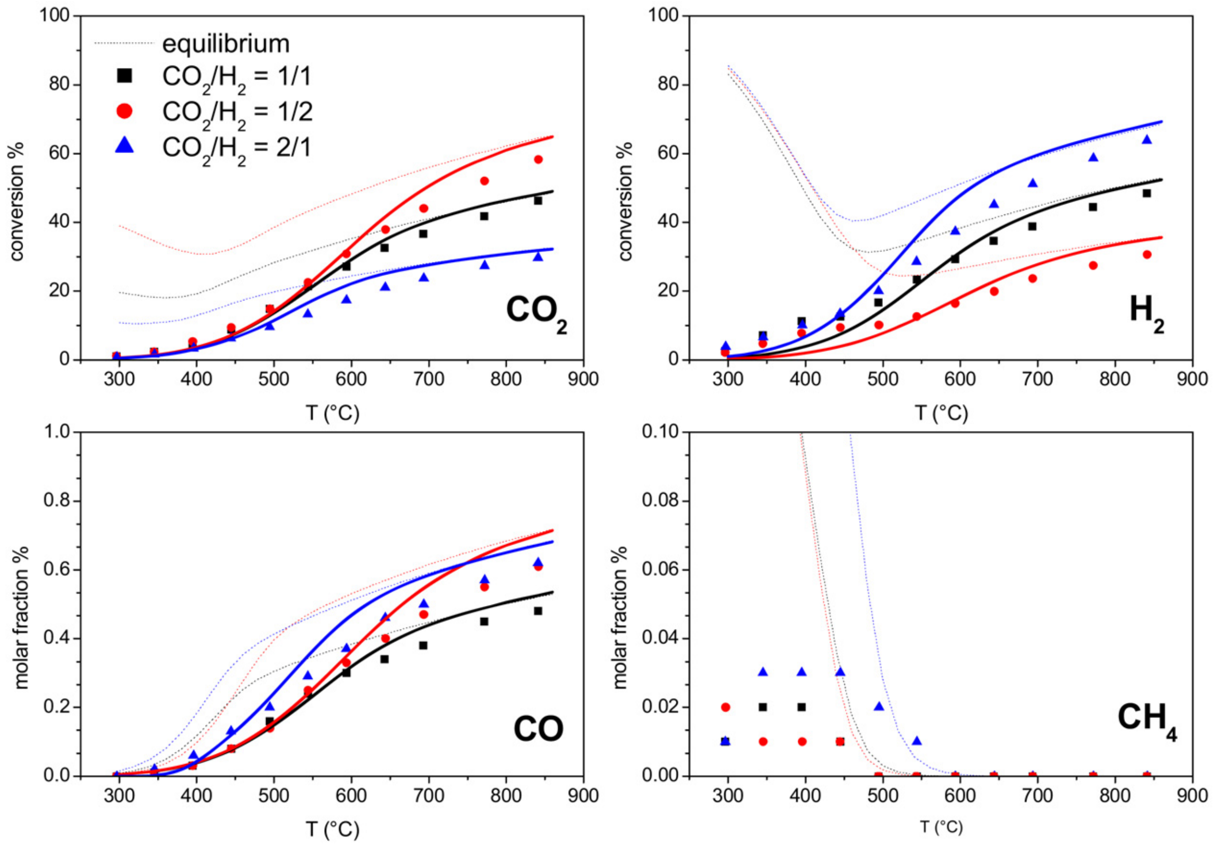

Fig. 1. Effect of reactants concentration in RWGS reaction. Experimental (symbols) and calculated (solid lines) results are reported. (■) $CO_2/H_2 = 1/1$, (●) $CO_2/H_2 = 1/2$, (▲) $CO_2/H_2 = 2/1$. N_2 to balance, $GHSV = 2 \times 10^6\ Nl/Kg_{cat}/h$, atmospheric pressure.

Fig. 1 reports in symbols the results. The conversion of reactants started at 300 °C, it steadily grew with temperature and closely approached the thermodynamic equilibrium trends at the highest investigated temperatures. The temperature range from 300 to 450 °C (wherein the reactor operated close to differential conditions) was regarded as kinetically relevant. Within such temperature range, CO_2 conversion did not change upon either increasing H_2 inlet concentration or increasing CO_2 content.

An inspection of the product distribution reveals that for temperatures lower than 550 °C a peak in methane concentration was always present and indicated that a methanation reaction was taking place, with likely stoichiometry:

$$CO + 3H_2 \rightarrow CH_4 + H_2O. \qquad (2)$$

Additional tests with CO and H_2O cofeed were performed in order to refine the kinetic analysis of the reaction. A CO-enriched run was carried out by feeding a mixture of CO_2 (1%), H_2 (3%), and CO (0.5%) in N_2. Results are reported in Figs. 2a and 2b; it is shown that CO had a small delaying effect on the conversion of CO_2 at low temperatures ($T < 500\,°C$), and a promoting effect at higher temperatures, but these trends are likely associated to the thermodynamic driving force as the measured conversions paralleled the calculated conversions at equilibrium. H_2O addition was tested by feeding excess H_2 and O_2; thus, H_2O was produced in situ on the catalyst, exploiting its high oxidation activity [1]. Results are reported in Figs. 2c and 2d; below 500 °C no kinetic effect was appreciable.

3.2. CO_2 reforming tests: Effect of CO_2 concentration

Fig. 3 reports the results of experiments at constant CH_4 concentration and varying CO_2 concentration. The conversion of reactants became appreciable at 300 °C and grew with temperature. In the runs with $CO_2/CH_4 > 1$, CH_4 conversion was little affected by the CO_2 inlet fraction: the conversion of CH_4 amounted to 50% at about 550 °C and was almost complete at the highest investigated temperatures. Data compared well with the analogous steam reforming data, reported in Part I: the extent of CH_4 conversion was comparable and the independence from the concentration of the co-reactant was a common feature. Concerning the product distribution, the production of H_2 and CO was accompanied by the formation of H_2O (which increased at increasing amount of CO_2), as expected by the tested reverse-WGS reactivity.

Quite differently, when feeding a stoichiometric CO_2/CH_4 mixture, CH_4 conversion was considerably lower in the whole temperature range; it reached 50% at about 640 °C and amounted to only 80% at 850 °C. Thus, the conversion of methane in the present CO_2-reforming test was significantly lower than that observed in the dual H_2O-reforming test [1,28]. Besides, only trace amounts of H_2O were detected in the product mixture.

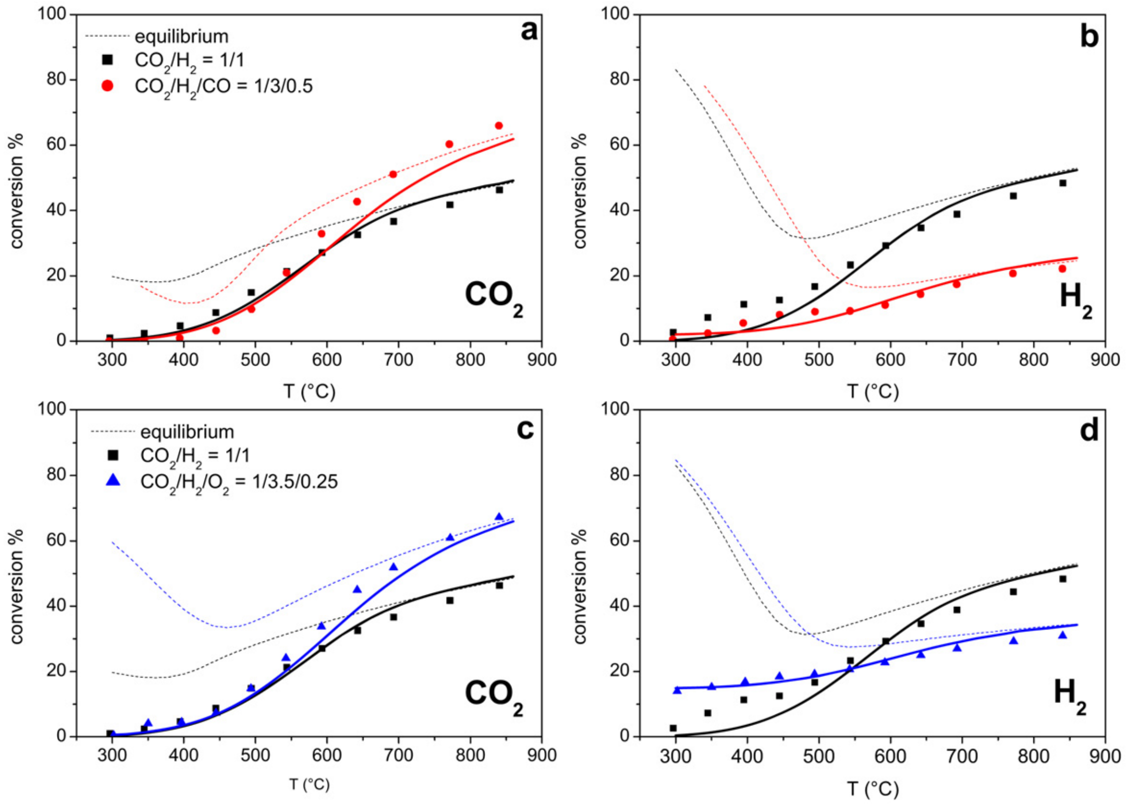

Fig. 2. Effect of CO addition and H_2O addition on reactants conversion in RWGS reaction. Experimental (symbols) and calculated (solid lines) results are reported. Panels (a) and (b): (■) $CO_2/H_2 = 1/1$, (●) $CO_2/H_2/CO = 1/1/0.5$. Panels (c) and (d): (■) $CO_2/H_2 = 1/1$, (▲) $CO_2/H_2/O_2 = 1/3.5/0.25$. N_2 to balance, $GHSV = 2 \times 10^6\ Nl/K\,g_{cat}/h$, atmospheric pressure.

Notably, a relatively small but non negligible concentration of H_2O is predicted at equilibrium (Fig. 4).

3.3. CO_2 reforming tests: Effect of O_2 enrichment

A small amount of O_2 (0.1%) was added to the same CH_4/CO_2 mixtures previously used; the aim was to perturb the reaction system and specifically the surface amount of H_2O (or surface hydroxyls) in order to investigate the role of water in the CO_2 reforming of CH_4. Fig. 4 shows that at $CO_2/CH_4 = 1$, the conversion of CH_4 was remarkably enhanced in the whole temperature range and water was present in the product mixture. It must be noted that the increase of conversion cannot be simply explained by the additional reaction of CH_4 with the co-fed O_2, given its little amount.

Fig. 5 compares the results of the three experiments with O_2 addition. At $CO_2/CH_4 > 1$, the O_2 co-feed produced a moderate enhancement of CH_4 conversion with respect to the corresponding CO_2/CH_4 tests. As a result, the values of CH_4 conversion at varying CO_2 concentration became comparable. A residual promoting effect of CO_2 could be observed above 500 °C. Though, below 400 °C, under nearly differential conditions, the three curves showed equal CH_4 conversion.

3.4. CO_2 reforming tests: Effect of H_2 enrichment

The reaction system was also perturbed by cofeeding H_2, which was also expected to affect the surface amount of H_2O, through the reverse-WGS reaction. Amounts of 0.1 and 1% were added to the $CO_2/CH_4 = 1$ mixture (N_2 to balance). Fig. 6 shows that the addition of H_2 had no effect either on the consumption of the reactants or on the distribution of the products (not reported). Since no increase was detected in H_2O production, it can be speculated that the RWGS reaction was delayed with respect to CH_4 activation (which remained the primary source of H_2).

3.5. $CH_4/O_2/CO$ mixtures: Effect of CO enrichment

$CH_4/O_2/CO/N_2$ mixtures were fed with 1% CH_4 molar fraction, 0.6% O_2 molar fraction and varying CO inlet fraction from 1 to 3%. Starting from about 250 °C, the combustion of CO occurred prior to that of CH_4, resulting in the in situ production of 1% (or 1.2%) CO_2 (depending on the inlet concentration of CO). Thus, the reacting mixtures behaved like $CH_4/CO_2/O_2/CO/N_2$ mixtures with varying CO amount. Aim of the experiments was to testing the CO_2-reforming of methane in the presence of added CO, thus verifying the existence of an inhibiting effect of CO adsorption on methane activation, which had been previously assumed on the basis of indirect pieces of evidence [1,28]. Fig. 7 reports the measured outlet composition against the catalyst average temperature. In all the runs O_2 conversion was complete above 400 °C.

In the experiment with $CH_4/CO/O_2 = 1/1/0.6$ (equivalent to a $CH_4/CO_2/O_2 = 1/1/0.1$ mixture), the conversion

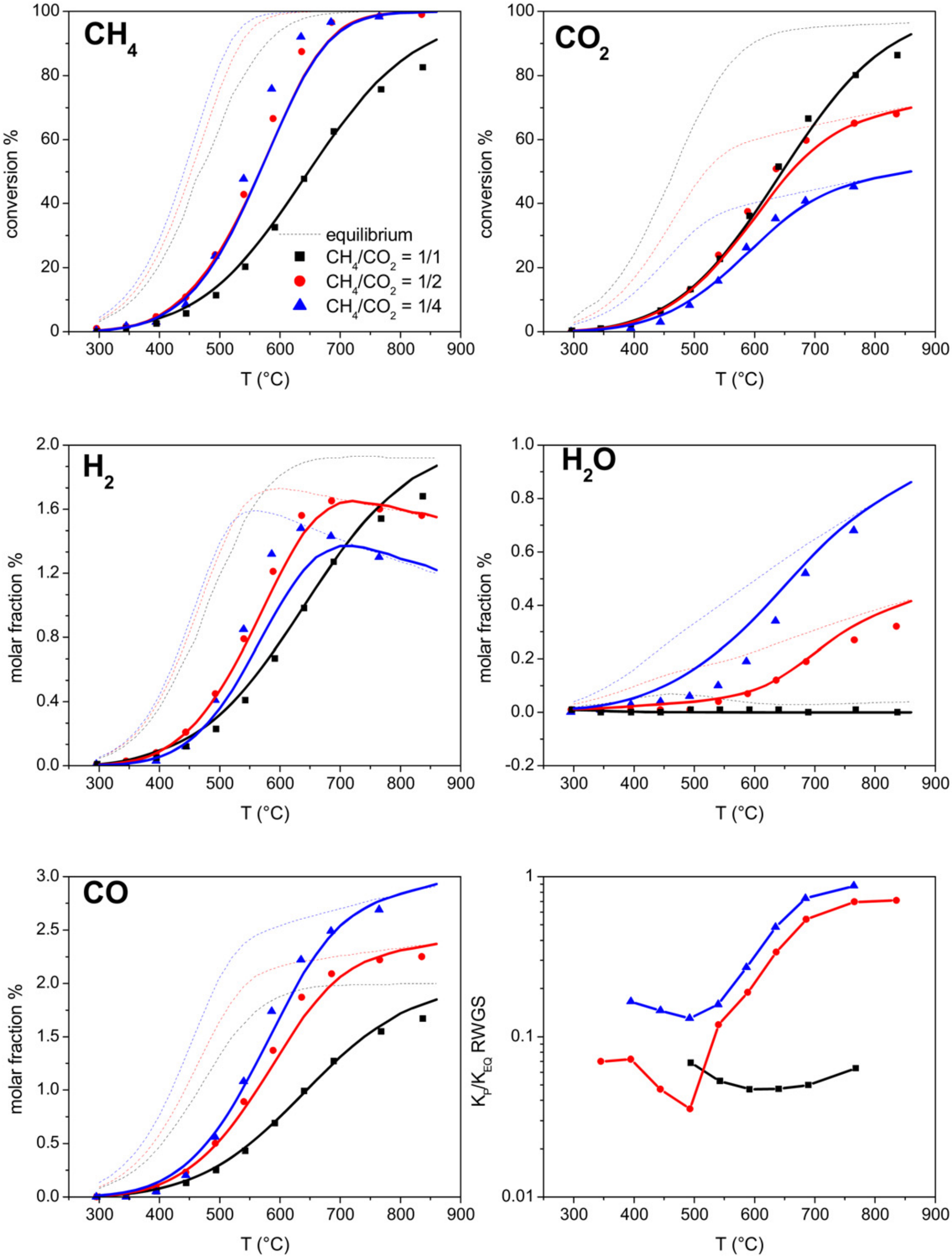

Fig. 3. Effect of CO_2/CH_4 molar ratio on reactants conversions and product molar fractions. Experimental (symbols) and calculated (solid lines) results are reported. (■) $CO_2/CH_4 = 1$, (●) $CO_2/CH_4 = 2$, (▲) $CO_2/CH_4 = 4$. Feed composition: $CH_4 = 1\%$ v/v, CO_2/CH_4 variable, N_2 to balance, $GHSV = 2 \times 10^6$ Nl/K g_{cat}/h, atmospheric pressure.

of CH_4 was fully comparable with that measured in the $CH_4/CO_2/O_2 = 1/1/0.1$ experiment reported in Fig. 4, and also comparable with that measured in the H_2O-reforming experiments (Fig. 10, Part I). The experiments with increasing amount of CO showed an important delaying effect on CH_4 conversion. In the series of experiments, CH_4 initial activation was progressively shifted from 300 to 350 to 450 °C. Upon increasing the temperature, the gap among the conversion curves was still present but progressively reduced. Above 750 °C, independently of the CO inlet fraction, all CH_4 was converted and the products reached the equilibrium. CO_2 activation and H_2 production were also inhibited by CO, whereas the CO molar fraction was much less affected.

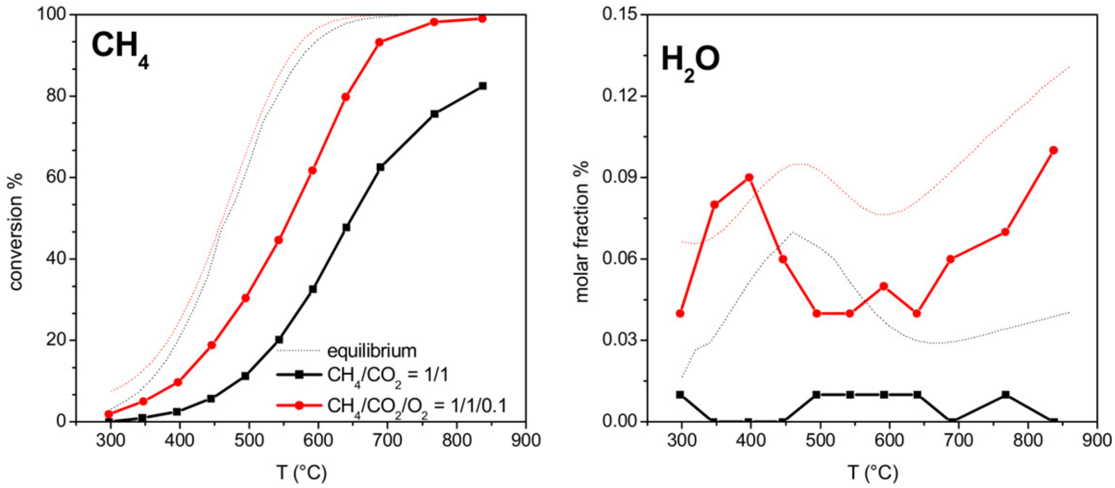

Fig. 4. Effect of O_2 addition on CH_4 conversion and H_2O molar fraction on CO_2 reforming tests at $CO_2/CH_4 = 1$. Experimental (symbols) and calculated (solid lines) results are reported. (■) No O_2 added, (●) 0.1% O_2 added. Feed composition: $CH_4 = 1\%$ v/v, $CO_2/CH_4 = 1$, N_2 to balance, GHSV $= 2 \times 10^6$ $\text{N l}/\text{K g}_{\text{cat}}/\text{h}$, atmospheric pressure.

4. Discussion

4.1. $CH_4 + CO_2$ tests

The previous H_2O/CH_4 experiments (presented in Part I) and the CO_2/CH_4 experiments with excess CO_2 herein reported confirmed that the rate of CH_4 activation is independent of the nature and amount of the reforming co-reactant, in line with the recent findings by Wei and Iglesia [10,11]. Though, the stoichiometric CO_2/CH_4 test yielded lower CH_4 conversion and, a unique feature, no appreciable H_2O production, whereas H_2O was always present in different amounts in the other experiments. However, when co-feeding a small amount of O_2, which resulted in a non nil concentration of H_2O, the conversion of CH_4 in the stoichiometric CO_2/CH_4 run reached comparable values with those of steam reforming and of the other non stoichiometric CO_2 reforming tests. The observed acceleration of the reaction rate by water is fully in line with the results by Bodrov and Apel'baum [7], Rostrup-Nielsen and Bak Hansen [6], Bradford and Vannice [13]. In line with the interpretation by Bradford and Vannice, it is proposed that, in the CO_2/CH_4 tests, H_2O was the effective co-reactant of CH_4, being H_2O produced by the reverse-WGS reaction. In order to verify whether this hypothesis could explain all the observed effects, a quantitative analysis of the data was addressed.

First, a kinetic expression for the RWGS reaction was estimated. The form:

$$r_{\text{RWGS}} = k_{\text{RWGS}} P_{CO_2} (1 - \eta_{\text{RWGS}}) \sigma_{H_2} \qquad (3)$$

described at the best the data reported in Figs. 1 and 2. Experiments were in fact coherent with a first-order dependence on CO_2, zero order dependence on H_2 and with the absence of any effect from the products. The limiting roles of thermodynamic equilibrium and of the co-reactant (H_2) were taken into account by including in the rate equation the terms $(1 - \eta_{\text{RWGS}})$ and σ_{H_2}, defined as in Part I of this work. Optimal estimates of the kinetic parameters are reported in Table 2 of Part I. It is observed that, at this stage, we neglected the kinetics of methanation; though detected during the CO_2/H_2 tests, the role of this reaction is expected to be negligible within the CH_4-CPO reaction process.

A rate expression identical to (3) was proposed in [29,30] for $Rh/\gamma\text{-}Al_2O_3$ catalysts under methane-rich mixtures, but a distinct kinetic form was assumed when deducing it from methane-free tests. The authors associated this difference to the role of CH_4, which, when present in the environment, dissociates on the surface and modifies the RWGS reaction pathway. In our case, no need of such a distinction was encountered. Notably the estimated value of the activation energy (72 kJ/mol) is in good accordance with the present one (62 kJ/mol).

Next, the kinetics of RWGS and steam reforming (the same developed in Part I on the basis of dedicated experiments) were incorporated in the 1D model of the annular reactor and applied to simulate the CO_2 reforming experiments. It must be noted that, if we assume that CO_2 reforming is only an apparent stoichiometry resulting from the linear combination of steam reforming and RWGS:

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO \qquad \text{true,} \qquad (4)$$

$$CO_2 + H_2 \rightleftarrows H_2O + CO \qquad \text{true,} \qquad (5)$$

$$CH_4 + CO_2 \rightleftarrows 2H_2 + 2CO \qquad \text{apparent,} \qquad (6)$$

then initiation of the cycle requires the presence of either H_2O or H_2, which were not co-fed in the CO_2/CH_4 tests of Fig. 3. However, trace amounts of humidity (up to 3 ppm) are reasonable for most of the high-purity gases used in the experiments. Simulations of the CO_2/CH_4 tests were thus performed by assuming that 1 ppm of H_2O was present in the feed. Such a small amount was enough to initiate steam reforming since its rate was assumed independent of H_2O partial pressure down to $p_{H_2O} < 10^{-6}$ atm [1].

The molecular reaction scheme (4)–(6) implies that the "CO_2-reforming" passes through the elementary steps:

$$CO_2{}^* + H^* \rightarrow CO^* + OH^* \quad \text{and}$$

$$C^* + OH^* \rightarrow CO^* + H^*,$$

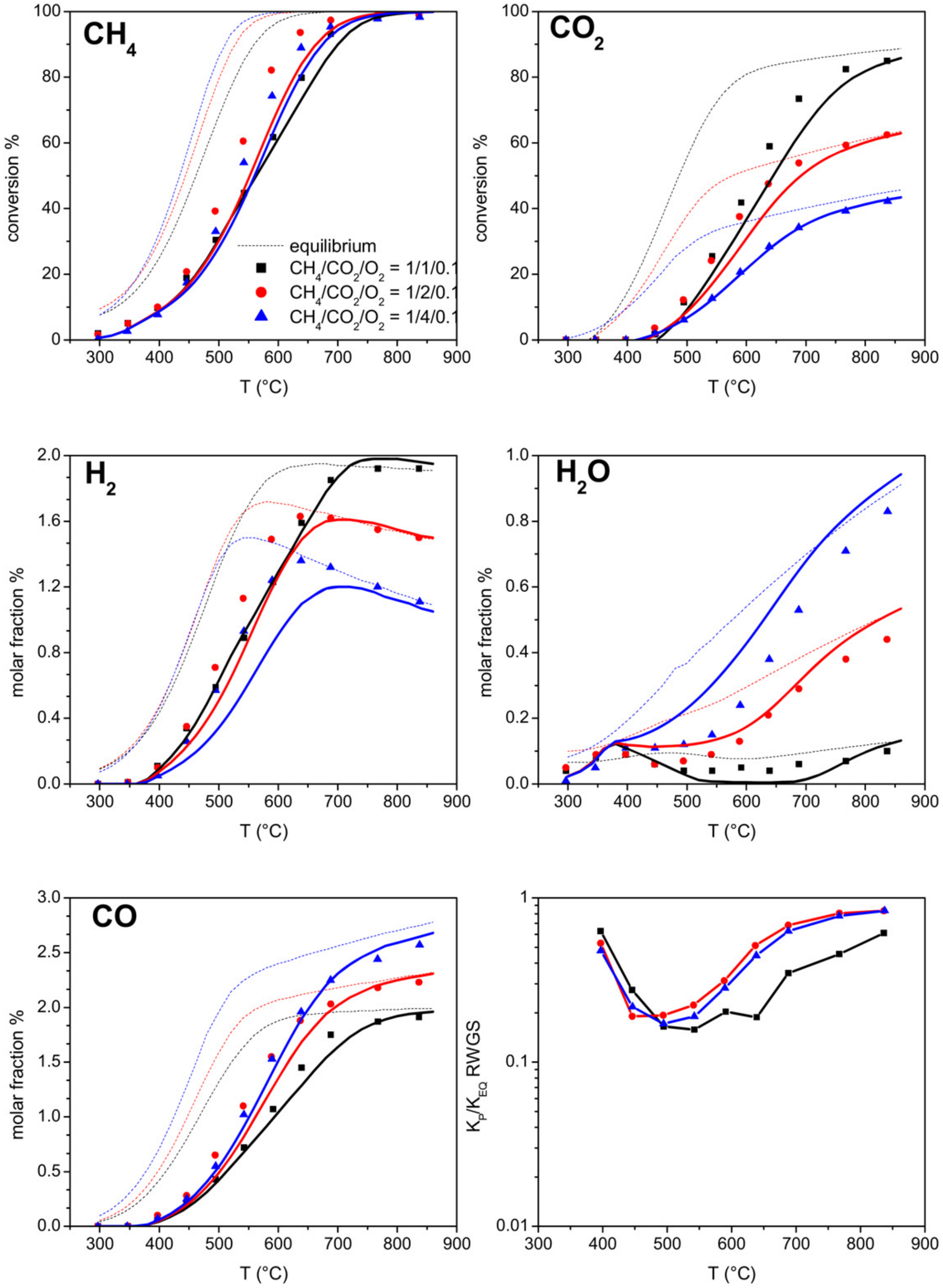

Fig. 5. Effect of 0.1% O_2 addition on reactants conversions and product molar fractions. Experimental (symbols) and calculated (solid lines) results are reported. (■) $CO_2/CH_4 = 1$, (●) $CO_2/CH_4 = 2$, (▲) $CO_2/CH_4 = 4$. Feed composition: $CH_4 = 1\%$, $O_2 = 0.1\%$ v/v, CO_2/CH_4 variable, N_2 to balance, GHSV $= 2 \times 10^6$ $Nl/Kg_{cat}/h$, atmospheric pressure.

whereas the elementary steps:

$CO_2^* \rightarrow CO^* + O^*$ and

$C^* + CO_2^* \rightarrow 2CO^*$

are excluded, as also suggested in [13,31].

The model predictions are represented by solid lines in Fig. 3. A remarkably good match was found between model predictions and experiments: the effect of the CO_2 content on the conversion of methane and the product distribution was very well reproduced. The model predicted that, with excess CO_2, the conversion of methane was independent of the inlet

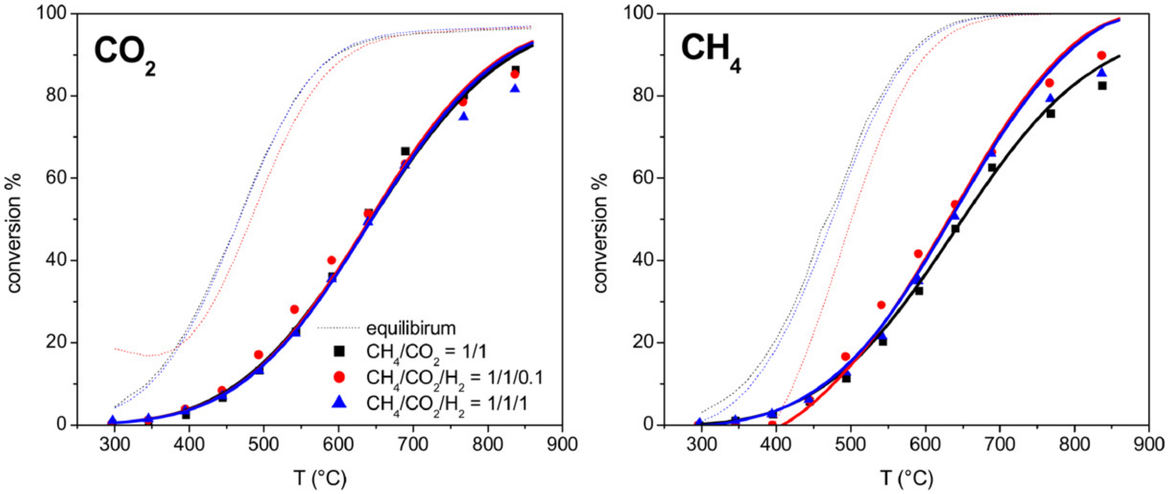

Fig. 6. Effect of H_2 addition on reactants conversion. Experimental (symbols) and calculated (solid lines) results are reported. (■) No H_2, (●) $H_2 = 0.1\%$, (▲) $H_2 = 1\%$. Feed composition: $CH_4 = 1\%$, $CO_2 = 1\%$ v/v, N_2 to balance, GHSV $= 2 \times 10^6$ Nl/K g_{cat}/h, atmospheric pressure.

CO_2 concentration. Furthermore it well reproduced that at stoichiometric CO_2/CH_4 feed ratio, the conversion of methane was significantly lower.

The model analysis supports the following interpretation:

(1) At stoichiometric amount of CO_2, the rate of RWGS was lower than the rate of steam reforming at all temperatures. Thus, the amount of H_2O produced by RWGS was promptly consumed by steam reforming and, as a result, the gas phase concentration of H_2O was zero and CH_4 conversion turned out to be limited by the rate of RWGS (which, in fact, was not equilibrated, as shown by the estimate of the experimental K_P/K_{EQ} ratio in Fig. 3) through a stoichiometric control.

(2) At higher CO_2 concentrations, the rate of RWGS increased. The reaction was kinetically controlled at low-medium temperatures (<600 °C) and its rate overcame that of steam reforming. At higher temperatures, the approach to thermodynamic equilibrium became close. The experimental K_P/K_{EQ} ratio increased toward unity at increasing temperature (Fig. 3). Thus, both at low and at high temperatures, steam reforming became the rate controlling step. H_2O was now present in the product mixture and CH_4 conversion presented the same values and trends as in the steam reforming experiments, including the independence from the amount of the co-reactant.

The main difference between the present data and those reported in the literature is the fact that under certain operating conditions herein realized (very high space velocity, moderate temperatures, diluted feed streams and equimolar CO_2 and CH_4 amounts) the reverse-WGS reaction was not equilibrated. Under these conditions a CO_2-dependence of methane conversion rate was manifest and reflected the kinetics of the RWGS reaction. At sufficiently high temperature and CO_2 concentration, the RWGS reaction was equilibrated and the CO_2-dependence of methane reforming rate became negligible. This latter situation is a common feature or assumption in most studies in the literature.

4.2. $CH_4 + CO_2$ tests with O_2 or H_2 enrichment

The O_2-enriched CO_2 reforming tests were also simulated, by accounting for the whole set of reactions listed in Table 2 of Part I of this paper. The calculated curves are represented by solid lines in Fig. 5. In the cases of $CO_2/CH_4 > 1$, the addition of oxygen had negligible effect according to both experiments and model predictions. Within the RWGS-SR sequence, the additional formation of H_2O via the oxidation reactions allowed for higher concentrations of surface hydroxyls, which favoured the approach of the RWGS reaction to the thermodynamic equilibrium. In fact, K_P/K_{EQ} values close to 1 were measured even at low temperatures. The kinetic effect on the rate of methane conversion was negligible, since the kinetic control of steam reforming was confirmed. Only in the case of $CO_2/CH_4 = 1$, the effect of O_2 addition was important; again, the most important consequences of enhancing H_2O concentration were the weakening of steam reforming dependence on the availability of H_2O by RWGS and the equilibration of RWGS in the whole temperature range, which made steam reforming the unique kinetically relevant step for methane conversion. Thus a change of the rate determining step from RWGS to steam reforming occurred; this explains why also at stoichiometric CO_2 content, comparable values of CH_4 conversions were observed and predicted as those of steam reforming.

It is worth noting that the fact that high methane conversions were observed during the O_2-enriched tests is an important indication that no irreversible deactivation due to C-accumulation occurred during the stoichiometric CO_2/CH_4 experiment.

Concerning the effect of H_2 addition, model predictions confirmed the observation that methane conversions and product distributions were unaltered (in line with the findings of Rostrup-Nielsen and Bak Hansen [6]). Simulations were performed assuming the presence of 1 ppm of water in the feed stream; since at $CO_2/CH_4 = 1$, steam reforming is faster than

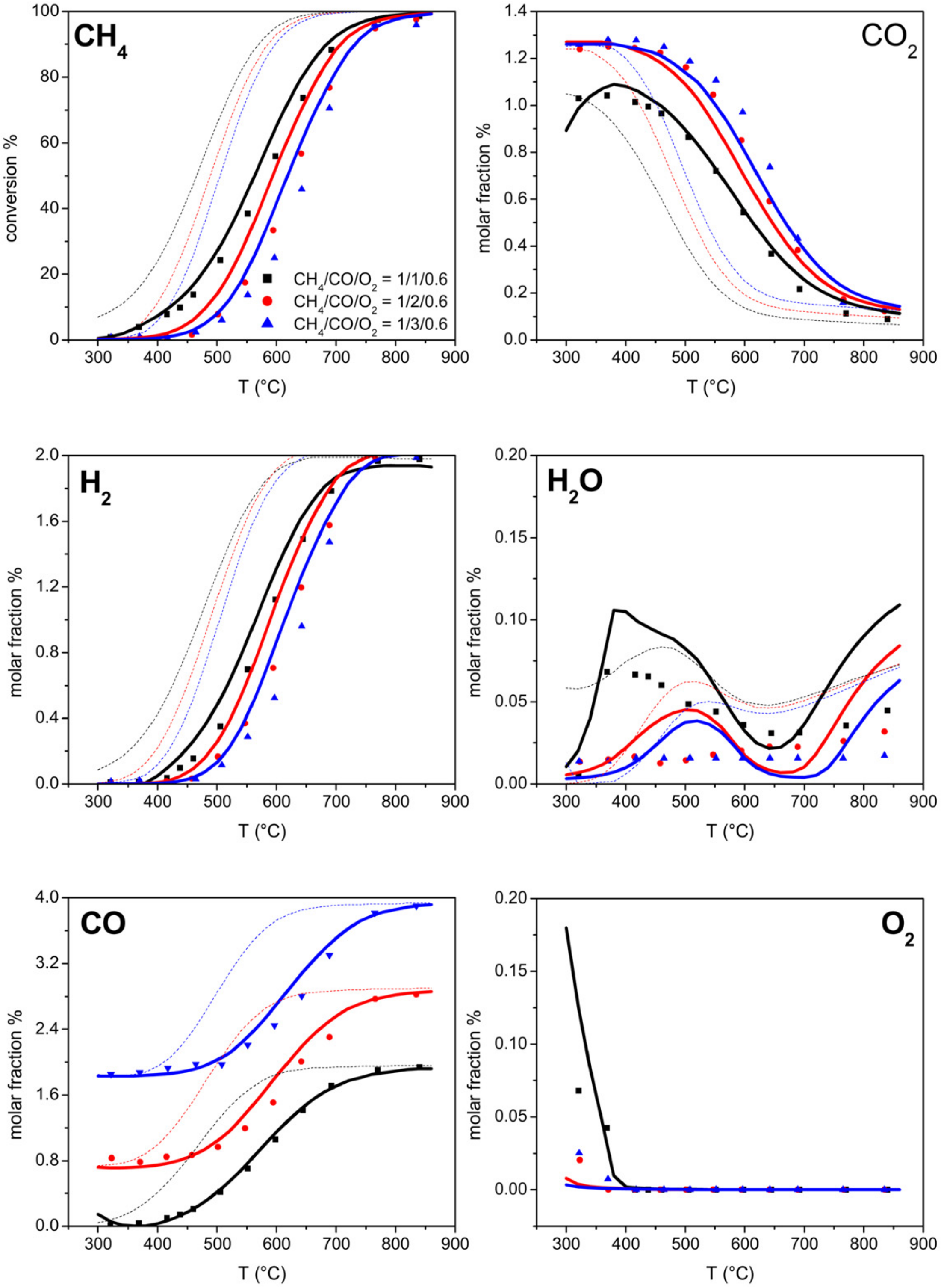

Fig. 7. Effect of CO addition on products and molar fractions in $CH_4/O_2/CO/N_2$ tests. Feed composition: (■) $CH_4/CO/O_2 = 1/1/0.6$ v/v, (●) $CH_4/CO/O_2 = 1/2/0.6$ v/v, (▲) $CH_4/CO/O_2 = 1/3/0.6$ v/v, N_2 to balance, GHSV $= 2 \times 10^6$ N l/K g_{cat}/h, atmospheric pressure.

the RWGS, then H_2O is the real initiator of the cycle, despite the addition of H_2. In this respect, it is important to note that the rate of the RWGS is independent on the amount of H_2. A condition where the RWGS was the rate controlling step was thus re-established and the reproducibility of the tests at stoichiometric conditions was confirmed.

4.3. $CH_4 + CO + O_2$ tests

The reference run with a $CH_4/CO/O_2 = 1/1/0.6$ feed composition was simulated and model calculations were practically coincident with the simulation of a $CH_4/CO_2/O_2 = 1/1/0.1$ composition. Experiments and model predictions were characterized by the kinetic control of steam reforming, since the RWGS was quasi equilibrated at all temperatures. Thus, the delaying effect of feeding larger amounts of CO on the rate of methane conversion was associated with the kinetics of steam reforming. Accordingly, an inhibiting term due to CO adsorption was included in the kinetic expression of steam reforming, which reflects one of the conclusions of Rostrup-Nielsen and Bak Hansen [6]. The extent of such a term (e.g., the adsorption constant at reference temperature and the adsorption enthalpy of CO) was estimated both on the basis of the data reported in Fig. 7 and on the basis of the whole experimental study reported in Part I. The introduction of such negative dependence on CO partial pressure allowed the satisfactory description of the $CH_4/CO/O_2$ data (Fig. 7), and was crucial for correctly describing the effect of dilution on CH_4 CPO runs (Fig. 7, Part I).

5. Conclusion

Rostrup-Nielsen and Bak Hansen [6] suggested that the mechanism of CO_2 reforming over metal-based catalysts is unlikely to differ significantly from that of steam reforming. The same authors proposed that in both processes CH_4 activation is followed by the reaction with a surface O species, originated by either CO_2 or H_2O. Bradford and Vannice [13] extended this picture and proposed for Ni-catalysts a generalized reaction scheme wherein surface hydroxyls (originated by the reverse water gas shift) react with CH_x species, thus emphasizing the analogy between CO_2 and steam reforming. Using Ni and noble metals, Wei and Iglesia [11] found a complete identity between the two processes, both being limited by methane activation.

The present work, that addresses the kinetic role of CO_2 reforming in the catalytic partial oxidation of methane over Rh/Al_2O_3 at very short contact time, largely confirms such previous studies and yields some novel conclusions. A wide variety of data and effects could be very well described by assuming that CO_2-reforming is actually a combination of steam reforming and reverse water gas shift (that is by assuming that surface hydroxyls are the effective co-reactants of adsorbed CH_x species). Independent kinetic investigations showed that the rate of steam reforming is proportional to methane concentration, while the reverse-WGS is proportional to CO_2 concentration. The kinetics of the methane conversion process is thus expected to depend on the kinetics of both the single reactions. However, under most of the investigated conditions, the reverse water gas shift was equilibrated and the CO_2-reforming of methane showed identical kinetic behavior as steam reforming. In the specific case given by the combination of high space velocity and low CO_2 concentration, the reverse-WGS reaction was nonequilibrated and controlled the rate of methane conversion.

It is worth emphasizing that the surprisingly good match between calculated and experimental data was obtained on a purely predictive basis, since the intrinsic rates of RWGS and steam reforming were independently estimated.

Also, this interpretation is fully in line with the kinetics of CH_4 CPO; by excluding the route of CO_2-reforming, and accounting for only steam reforming and reverse-WGS, an extensive set of CH_4 CPO data could be well described, as shown in Part I of this work.

A theoretical analysis is presently on-going, which aims at verifying the thoroughness of the proposed molecular interpretation of results by the means of micro-kinetic modeling.

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