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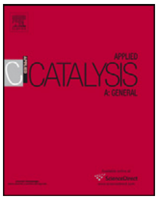

Microkinetic analysis of CH_4 CPO tests with CO_2-diluted feed streams

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ABSTRACT

Autothermal CH_4 catalytic partial oxidation (CPO) tests were performed in an adiabatic lab-scale reformer over 2 wt% Rh/α-Al_2O_3 catalysts supported on 600 cpsi cordierite honeycombs. The effect of adding either CO_2 or N_2 to CH_4/air mixtures was investigated at constant O_2/CH_4 ratio (0.56) and total flow rate (10 Nl/min). At increasing dilution the conversion of CH_4 and the gas temperatures decreased. Also, at equal CH_4 concentration, the addition of CO_2 decreased the temperatures and the conversion of CH_4 more importantly than N_2. Thus, in line with previous studies from this and other laboratories, no evidence of a direct dry reforming route was found; the observed thermal behavior appeared largely controlled by the heat capacity of the feed streams. However an important chemical effect of CO_2 addition, not previously appreciated in the literature, was shown by the evolution of the outlet H_2/CO ratio; at increasing N_2 dilution, the H_2/CO ratio slightly increased from about 2 to 2.5, but at increasing CO_2 dilution, the H_2/CO ratio decreased from about 1.7 to 0.7. These trends are in line with the thermodynamics of the reverse water gas shift (RWGS) reaction; such a reaction was thus extremely fast in all the experiments with CO_2, even at the highest values of dilution, while CH_4 conversion did not reach the equilibrium.

A C_1 microkinetic model was used to analyze the results. A close match between calculated and measured temperatures, conversions and syngas composition was obtained under all conditions. Notably, the present microkinetic scheme, which incorporates steps for CO_2 adsorption and reactivity, was able to account for the observed net consumption of CO_2 and for the lowering of the H_2/CO ratio in the experiments with CO_2 co-feed. Surface coverages were analyzed for the various investigated conditions and the effects on the kinetics of methane steam reforming were evaluated in detail; the factors which control the onset of a more kinetically controlled regime at high degrees of dilution were highlighted.

1. Introduction

Global climate changes and the need to reduce greenhouse gas emissions and pollution have stimulated growing interest towards alternative and clean fuels, together with the development of highly efficient and environmentally friendly energy systems. In this respect, syngas offers several opportunities for enhancing the performances of both traditional combustion processes and novel energy systems, such as fuel cells. However, these new applications ask, at least for the short-term period, for small-scale devices and thermal efficient syngas production from natural gas. As a consequence, the traditional steam reforming on Ni-based catalysts, which is an energy-intensive endothermic process, cannot be readily scaled down and alternatives are required.

In light of this, the catalytic partial oxidation (CPO) of methane (1) over Rh or Pt supported catalysts is a promising solution for novel, small-scale applications of syngas [1].

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H^{R}_{298\,K} = -36\,kJ\,mol^{-1} \tag{1}$$

The CPO reaction is mildly exothermic and can be carried out under autothermal conditions at very short contact times (10^{-2} to 10^{-4} s) with almost complete selectivity to H_2 and CO [2] even with the use of air; these features allow for the development of compact and simple reformers for on-board applications [3]. Such a high selectivity to syngas can be maintained also at high pressures, thus allowing for an easier integration with downstream pressurized equipment [4–7]. In the field of power generation, interest has recently grown in the conduction of CH_4 CPO in catalytic burners under ultra-diluted, O_2-lean conditions [8,9]: CH_4 and O_2 react in the presence of large amounts of H_2O and CO_2 recycled from exhaust streams, consequently avoiding NO_x production and moderating temperature gradients. Similar recycle may also take place in solid oxide fuel cells with direct internal reforming, where CPO can be exploited for the start-up and sustained in the presence of CO_2 and H_2O during low-power operations [10]. In general, the possibility of feeding H_2O and CO_2 to CPO reformers is

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extremely attractive, since it allows for modulating the balance between exothermic oxidation and endothermic steam and CO_2-reforming, as well as tuning the H_2/CO ratio of the syngas produced [11].

With respect to these applications, it is of interest to investigate the effect of CO_2 on CPO. In the literature, various research groups have addressed the role of CO_2 in the kinetic scheme of CH_4 partial oxidation on Rh in short contact time reactors. Most of the published works are experimental, and pieces of evidence were collected at various scales of investigation, ranging from isothermal microreactors to autothermal reactors. Numerical analyses have been reported to much less extent. Several authors agree that CO_2-reforming does not partake in the reaction mechanism [7,12–15]: it is commonly assumed that the rate of CH_4 consumption by CO_2-reforming is much slower than that of oxidative reforming and steam reforming, and therefore it does not occur in the presence of either H_2O or O_2. By means of spatially resolved temperature and composition profiles collected over Rh and Pt foam catalysts, Schmidt and co-workers [13] showed that CO_2 is produced in the presence of O_2, while it keeps unaltered when O_2 is depleted and CH_4 is being consumed at the expenses of H_2O. In a dedicated work on the effects of CO_2 and H_2O, the same group [14] provided direct evidence on the absence of CO_2-refoming in CH_4 CPO. It was concluded that H_2O is the preferential co-reactant of CH_4 even in the presence of large amounts of CO_2. Hence, CO_2 has no kinetic effect on the rate of CH_4 consumption, but only affects the distribution of the products by unbalancing the water gas shift equilibrium.

Mantzaras and co-workers [7,9,16–18] have also performed extensive work on the characterization of the steady state performance and the ignition/extinction dynamics of CH_4–O_2 reformers with EGR (exhaust gas recycle). Together with a wide experimental investigation, this group has, to our knowledge, first addressed the numerical analysis of the adiabatic reactor operating with large amounts of H_2O and CO_2. A single-channel, 2D model of the reactor was developed; the model incorporated both the detailed description of the gas-phase chemistry from Warnatz et al. [19] and the detailed catalytic scheme of Deutschmann and co-workers [20]. The adequacy of such scheme in reproducing the measured methane conversion and syngas yields in CPO of CH_4/air mixtures had been previously shown by the same authors [8]. In order to evaluate the impact of H_2O and CO_2 on the production of synthesis gas, Mantzaras and co-workers developed a numerical methodology which consists of simulating the presence of a fictitious species H_2O^* or CO_2^* that had the same thermodynamic and transport properties as H_2O and CO_2 but did not participate in any reaction. From this analysis, the authors concluded that while H_2O had a direct impact on CH_4 conversion and syngas composition, CO_2 had neither one of the two chemical effects. This means that a specific contribution from the reverse water gas shift (RWGS) reaction was not taken into account.

However, experiments with single co-feed of CO_2 were not performed; all data were obtained only by diluting CH_4 and O_2 with H_2O/CO_2 mixtures with a 2/1 ratio, thus largely favoring the water gas shift (WGS) thermodynamic driving force. On the other hand we do expect that CO_2 and RWGS may play a role in the CPO process when the exhaust gas recycle has a different composition, such as in the case of the exhaust mixture from an diesel engine where the H_2O/CO_2 ratio is close to 1 [3]. Thus, in our opinion, neither the experimental work, nor the numerical analysis (which did not account for a significant readsorption of CO_2) from previous works is conclusive about the role of CO_2 recycle in syngas catalysis.

The key role of the RWGS reaction has been shown in the literature. A number of kinetic studies performed over noble metal catalysts showed that a close similarity exists between CO_2-reforming and steam reforming rates, so that CO_2-reforming would rather proceed via a combination of RWGS and steam reforming [21–25]. Experimental and theoretical works by different groups concur to suggest that CH_4 reforming is kinetically controlled by methane activation and is insensitive to the co-reactant (CO_2 or H_2O), and that partial replacement of H_2O by CO_2 has no relevant effect on the mechanism [24,26]. WGS or the RWGS steps have been often found as equilibrated reactions. Some authors [23,27,28] also observe a moderate inhibiting effect of CO adsorption on CH_4 reforming rate, which becomes relevant in the case of CO_2-reforming, when CO is present in larger concentration on the metal surface.

In this work, we investigate the effect of CO_2 in CH_4 CPO under autothermal conditions. The experiments were simulated by means of a microkinetic scheme [29] incorporated in the detailed model of the adiabatic reactor [30]. Such scheme has been previously validated by comparison with isothermal kinetic data concerning the behavior of CH_4/O_2, CH_4/H_2O and CH_4/CO_2 feed streams [26,31]. In particular, differently from previous kinetic schemes proposed in the literature, this model can describe conditions wherein CO_2 adsorption may have a role.

2. Modeling

2.1. Reactor model

The experiments were analyzed by means of a 1D, heterogeneous, dynamic, fixed bed, single-channel model of the reactor [30,32]. The model consisted of mass, enthalpy and momentum balances for the gas phase and for the solid phase, which included axial convection, solid conduction and gas–solid transport terms. Following the results reported in Refs. [20,33,34], no contribution by homogeneous chemistry was accounted for under the operating conditions adopted. The heat and mass transport properties of the honeycomb monolith were accounted for with specific correlations [35]. Heat conduction in the solid was described with an effective axial thermal conductivity coefficient corrected by the addition of the radiative contribution according to the correlation of Lee and Aris [36]. Radiative dispersion effects at the back and front heat shield were also introduced in the boundary conditions.

2.2. Microkinetic heterogeneous scheme

A thermodynamically consistent C_1 microkinetic model for the conversion of CH_4 to syngas [29] was incorporated in the reactor model. The scheme consists of 82 elementary reactions and 13 surface species; it is able to predict mechanistic details of steam reforming, CO_2-reforming and CH_4 CPO over Rh catalysts [27,37] in full agreement with independent experimental studies (e.g. [24]).

In the scheme, the activation of the CH_4 molecule is assumed to occur via pyrolysis (2), leading to the production of C* species and CH_x* fragments [22,24,25,38]. Additionally, due to lower energy barriers compared to O-assisted processes [39,40], the OH* species results the favorite co-reactant of C* and CH_x* ((3) and (4)) instead of O* adatoms. This applies also to the case of CH_4/CO_2 feed steams that is for the CO_2-reforming process.

$$CH_{4}{*} + (4-x){*} \rightarrow CH_{x}{*} + (4-x)H{*} \tag{2}$$

$$C{*} + OH{*} \leftrightarrow CO{*} + H{*} \tag{3}$$

$$CH_{x}{*} + OH{*} \leftrightarrow CH_{x-1}{*} + H_2O{*} \tag{4}$$

The similarity between steam reforming and CO_2-reforming is established by considering that both reactions occur via a mechanism wherein OH* is the main oxidizing species: in steam reforming, OH* comes from the quasi equilibrated dissociation of H_2O, while in CO_2-reforming OH* is produced via activation of CO_2 [27]. Overall, experimental and modeling results [27,31] indicate