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Study of CO₂ and H₂O adsorption competition in the combined dry / steam reforming of biogas

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ABSTRACT

The combined dry-steam reforming (CDSR) of a model biogas (66 % CH₄ + 34 % CO₂) has been investigated under various feed compositions and reaction temperature conditions over a Ni-Rh/MgAl₂O₄ catalyst, with the objective to convert the excess of methane (compared to CO₂) by steam reforming (SR). Methane, however, appeared to react preferentially with H₂O rather than with CO₂, leading to an inhibition of the dry reforming (DR) reaction in the presence of steam. CO₂ and H₂O adsorption and co-adsorption studies revealed that H₂O was always adsorbed in much higher amounts than CO₂ on the catalyst surface. A Temkin adsorption model applied to temperature-programmed adsorption experiments (TPAE) showed that two different strongly adsorbed CO₂ and H₂O species were present on the catalyst surface at moderate temperature, but only one of each remained adsorbed at temperatures relevant to the reaction conditions (600–800 °C). H₂O was also shown to displace CO₂ from the catalyst surface, confirming that they compete, at least partially, for the same adsorption sites. At high temperature, the surface coverage by the most strongly adsorbed H₂O species was predominant. These results should contribute to the development of efficient catalytic processes for biogas valorization to produce syngas and hydrogen from renewable sources.

1. Introduction

Biogas is formed by microbial anaerobic digestion of biomass and contains essentially methane and carbon dioxide. Therefore, methane dry-reforming (DR, Eq. 1) is clearly the most advantageous option, in terms of CO₂ emissions mitigation, to convert biogas into syngas for hydrogen production or for Fischer-Tropsch synthesis. It can be reformed into syngas over Ni-based catalysts [1]. However, the CO₂/CH₄ ratio in biogas is generally <1, and full conversion of methane requires adding another reactant. It might ideally be obtained by combining steam reforming (SR, Eq. 2) and dry reforming reactions, which also allows tuning the outlet H₂/CO ratio.

The reforming reactions are always accompanied by the WGS/RWGS equilibrium (Eq. 3), which is displaced towards the RWGS reaction at

high temperature [2,3].

The combined dry-steam reforming (CDSR) has been investigated by Noronha et al. over Pt/ZrO₂ and Pt/Ce-ZrO₂ catalysts, from the standpoint of catalyst stability and coke deposition [4]. Addition of steam in the feed initially increased the CH₄ conversion over Pt/ZrO₂, but the catalyst deactivated more rapidly than under pure DR conditions, whereas the Pt/Ce-ZrO₂ catalyst was more stable in the presence of steam. Surprisingly, more coke deposits were formed on both catalysts under CDSR than under DR. In contrast, addition of small amounts of steam in a DR stoichiometric mixture has been reported to prevent the deactivation of a Ni-based catalyst by reducing coke formation [5]. However the effect of steam addition in a stoichiometric CH₄/CO₂ mixture on the outlet composition (H₂/CO ratio) was not reported nor investigated in details.

Wei and Iglesia [6] studied independently the kinetics of the steam and dry methane reforming reactions on Ni/MgO catalysts. They concluded that the methane C–H bond activation was the only kinetically relevant step, whereas CO₂ and H₂O activation was reversible and quasi-equilibrated during CH₄/CO₂ and CH₄/H₂O reactions. The forward CH₄ reaction rate constants and activation energies were identical

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using CO₂ or H₂O as co-reactant, and very similar to the initial methane decomposition rate in the absence of co-reactant. A sequence of common elementary steps involved in both DR and SR reactions was proposed: methane dissociates through cascade steps into adsorbed C* and H*. Theoretical calculations suggest that adsorbed C* reacts preferentially with adsorbed HO* groups to form CO and H₂, rather than with adsorbed O* species [7]. HO* species are formed directly from H₂O dissociative adsorption in the steam reforming reaction, whereas they are formed by reaction of CO₂ with H* in the case of dry-reforming.

The water-gas shift reactions are generally at thermodynamic equilibrium over a wide range of temperatures and reaction conditions [7,6].

The adsorption competition between CO₂ and H₂O in relation to the dry/steam reactions has been scarcely studied. It has been more intensively studied from the viewpoint of CO₂ separation and capture (therefore performed at low temperature compared to those relevant to DR and SR reactions) using various porous materials, notably MOFs and organic polymers, but a few studies on zeolites are also reported. Stevens et al. [8] showed that a 13X zeolite exhibited the highest CO₂ adsorption capacity among five different zeolites, but that exposure of 13X to H₂O before CO₂ totally blocked the CO₂ adsorption sites, since no adsorbed CO₂ species were detected. CO₂ and H₂O co-adsorption experiments also revealed that H₂O could displace adsorbed CO₂ species under a CO₂ partial pressure of 1013 Pa, indicating that CO₂ and H₂O compete for the same adsorption sites. The study of Wang and LeVan [9] on the adsorption equilibrium of CO₂/H₂O mixtures in zeolites 5A and 13X also concluded to a competitive adsorption in favor of H₂O over weakly adsorbed CO₂ species, but also pointed out that increasing the water partial pressure and temperature promotes CO₂ chemisorption as carbonates or bicarbonates. Ohlin et al. [10] investigated the effect of H₂O on the CH₄ and CO₂ adsorption properties of a Na-ZSM-5 zeolite with a high Si/Al ratio (Si/Al = 130, close to pure silica MFI), in view of application to CO₂ separation from CH₄ in biogas. H₂O was adsorbed in higher amounts than both CH₄ and CO₂, even when the CO₂ partial pressure was 47 times higher than that of H₂O. In this essentially silica framework zeolite, however, CO₂ and H₂O appeared to adsorb on different sites: only physisorbed CO₂ (adsorbed on hydrophobic sites of the pore walls) was detected at 35 °C, whereas H₂O adsorbed on polar silanol groups, therefore the adsorption was not competitive. In these studies, since CO₂ separation from gas mixtures is sought out, adsorption studies were performed at room or at low temperatures and involved mostly weakly adsorbed CO₂ species, which are not relevant to the species involved in the dry reforming reaction.

In the present study, the performances of a Ni-Rh/MgAl₂O₄ catalyst for DR, SR and CDSR were investigated under various reaction feed and temperature conditions, with the objective to assess the effect of steam on the DR reaction. This catalyst was previously studied in the auto-thermal reforming of model biogas to produce syngas, and it exhibited long-term performances (over 200 h) and resistance to carbon deposition and Ni oxidation [11,12]. However, in the autothermal reforming reaction CH₄ reacts only with O₂ and H₂O, while CO₂ present in the biogas is not utilized. Therefore, this study addressed specifically the reforming of biogas into syngas through the DR and CDSR reactions. The CO₂ and H₂O adsorption and co-adsorption properties were studied using transient experiments and reveal an adsorption competition between H₂O and CO₂ that leads to an inhibition of the DR reaction by steam.

2. Materials and methods

2.1. Catalyst preparation

The MgAl₂O₄ support was prepared by co-precipitation. An aqueous solution containing Mg and Al nitrates was drip-fed to an aqueous solution of ammonium carbonate in large excess (100 %) at room temperature under strong stirring. This excess was necessary to ensure complete precipitation of Mg cations [13]. The precipitate was aged for 3 h at 60 °C and pH 9. After filtration and washing with de-ionized water at room temperature, the powder was dried overnight at 100 °C, then calcined at 800 °C for 5 h in air. Chemical analysis of the support (analyzed by ICP-AES): 33.45 wt.% Al, 14.78 wt.% Mg.

Ni was deposited on the MgAl₂O₄ support by deposition-precipitation using nickel nitrate and urea in large excess (10 mol per mole Ni). The suspension was heated at 90 °C for 4 h under stirring. After cooling, the precipitate was filtered, washed several times with de-ionized water, dried at 100 °C and calcined at 550 °C for 4 h in air. Rh was deposited on NiO/MgAl₂O₄ by wet impregnation with an aqueous solution of rhodium nitrate. The solution was stirred for 4 h. After evaporation of water, the powder was dried at 100 °C and calcined at 550 °C for 4 h in air. Chemical analysis of final catalyst: 10.21 wt.% Ni, 0.05 wt.% Rh. BET surface area: 160 m². g⁻¹.

TEM micrographs (not shown) of fresh 10 %Ni-0.05 %Rh/MgAl₂O₄ catalyst, after reduction under 20 % H₂ at 700 °C, showed that Ni was homogeneously distributed on the support as rounded Ni particles in the 4–10 nm size range, with an average size around 6 nm. Rh could not be observed due to the low Rh loading.

2.2. Reaction studies

Dry-reforming (DR) and combined dry-steam reforming (CDSR) catalytic tests were performed at atmospheric pressure using a quartz fixed bed reactor. The catalyst was sieved beforehand to obtain particle sizes between 100 and 200 microns. The catalyst mass used was 80 mg, diluted with quartz powder (160 mg) with a similar particle size. A K-type thermocouple was inserted at the bottom of the catalyst bed, close to the quartz frit, to monitor the catalyst temperature. Before reaction, the catalyst was reduced at 700 °C for 3 h in a mixture of H₂ (20 %) in Ar. Catalytic tests were performed isothermally with a total reactants flow rate of 250 mL/min, which corresponded to a WHSV of 188 L.h⁻¹. g⁻¹. The typical DR feed composition consisted of 10 % CH₄, 10 % CO₂ and 10 % He diluted in Ar. Helium was used as internal standard for quantitative analysis of products, because the effluent flow rate was higher than the inlet flow rate, due to the net gas production resulting from the reforming reactions stoichiometry (Eq. 1 & 2). In SR and CDSR experiments, the liquid water flow rate was controlled by a calibrated HPLC pump (Shimadzu LC-20AD, liquid flow range 0.0001–5 mL/min) and dispensed through an evaporator heated at 200 °C. All gas lines and valves were heated at 130 °C to avoid steam condensation. The effluent from the reactor was analyzed online using a micro-gas chromatograph (Agilent 3000) equipped with two analytical modules (Plot U and MolSieve 5 Å columns with backflush) and TCD detectors, that allowed analyzing CH₄, CO₂, CO, H₂ and He. Steam was condensed in a cold trap at 5 °C at the reactor outlet to prevent any liquid condensation in the chromatograph micro-fluidic injection valves. The carbon balance was equal to 100 ± 0.02 % in all experiments. The HSC-Chemistry software version 4 (OUTOKUMPU, Finland) was used to calculate the equilibrium compositions, based on the minimization of the free Gibbs energy. It should be mentioned that the calculations were based on the presence of CH₄, CO, CO₂, H₂, H₂O and Ar in the gas phase, with exclusion of solid carbon. When carbon was included as possible product, the calculations predicted an extensive carbon formation over wide temperature and composition ranges, which was not relevant to the applied reaction conditions (short residence time) and to the observed 10 %Ni-0.05 %Rh/MgAl₂O₄ catalyst performances, notably the good closure of the carbon

balance with only CH₄, CO and CO₂. The catalyst composition, with its basic MgAl₂O₄ support and Rh as dopant, has been shown to exhibit long-term activity for methane autothermal reforming with marginal carbon deposition [11,12].

2.3. Adsorption studies

CO₂ and H₂O adsorption studies were performed on a bench equipped with two gas lines and two automated switching 4-way valves for transient experiments. The gases (CO₂, Ar as tracer and He as diluent) were supplied through calibrated mass flow controllers, with a total flow rate of 100 mL/min. Water was introduced using a saturator/condenser system where the gas bubbled first in two liquid water baths at 25 °C in series, before bubbling in a third vessel immersed in a thermostated bath at cooler temperature (5–15 °C), where the excess steam was condensed to ensure full saturation of the gas. The temperature of the condenser was regulated with an accuracy of ± 0.1 °C. After the saturator, all gas lines and valves were heated at 130 °C to avoid steam condensation. Gas analysis was monitored using a mass spectrometer (Pfeiffer Omnistar) with heated capillary and inlet assembly. Around 0.20 g of catalyst was placed in a U-shape reactor for adsorption experiments, with a thin thermocouple placed inside the catalyst bed to monitor the catalyst temperature. The catalyst was initially reduced at 700 °C under 20 % H₂ in He for 1 h, then desorbed and re-reduced at 500 °C between each adsorption measurement. A typical experiment involved switching the gas composition according to the sequence He → 2% CO₂ /2% Ar/He, repeated 3 times to provide in the first sequence the total amount of strongly and reversibly adsorbed CO₂ species, then in the next 2 sequences the amount of reversibly adsorbed species, the third one used to confirm the results of the second. After the adsorption equilibrium at a selected temperature, the temperature was increased linearly at 15 °C/min in the presence of CO₂ to perform a temperature-programmed adsorption equilibrium (TPAE) experiment [14], or under pure He to perform a classic temperature-programmed desorption (TPD) of strongly adsorbed species. Similar experiments were carried out with H₂O/Ar/He and CO₂/H₂O/Ar/He gas mixtures.

3. Results and discussion

3.1. Effect of steam addition on dry-reforming catalyst performances

The 10 %Ni-0.05 %Rh/MgAl₂O₄ catalyst was tested under DR and CDSR conditions at different temperatures (Fig. 1). Under DR conditions (H₂O/CH₄ = 0) the CO₂/CH₄ ratio was set to 1. The methane and carbon dioxide conversions increased with temperature, whereas the H₂/CO outlet ratio was 0.73 at 487 °C and increased with temperature up to 0.92 at 670 °C. The conversion of CO₂ was always higher than the conversion of CH₄, due to the contribution of the RWGS reaction that consumes CO₂ and H₂ and results in a H₂/CO ratio less than unity [7]. The conversions of CH₄ and CO₂ were always below the expected conversions at the thermodynamic equilibrium, due to the high WHSV (188 L.h⁻¹.g⁻¹) that resulted in a low contact time (0.019 g.s.mL⁻¹). Verykios [15] showed that the DR of a CH₄/CO₂ mixture with similar composition over a Ni/La₂O₃ catalyst reached equilibrium compositions only at contact times of 0.06 g.s.mL⁻¹ and above.

Under CDSR conditions, the CO₂/CH₄ ratio was set to 0.66 (10 vol.% CH₄ and 6.60 vol.% CO₂), therefore adding steam in the reactants mixture with a H₂O/CH₄ ratio of 0.34 represents a stoichiometric CO₂:H₂O:CH₄ 0.66:0.34:1 mixture, considering that methane is converted by both dry and steam reforming reactions (Eq. 1 & 2). Adding steam in the feed stream led to an increase in the conversion of methane at H₂O/CH₄ ratios of 1 and above (Fig. 1A), and to a strong increase in the H₂/CO ratio (Fig. 1C), as the SR and WGS reactions became favored. The contribution of the WGS reaction was particularly strong at 487 °C, since it is thermodynamically favored at low temperature and at high H₂O/CH₄ ratio, leading to an outlet H₂/CO ratio close to 10 at 487 °C for an

Fig. 1. 10 %Ni-0.05 %Rh/MgAl₂O₄ catalyst performances for DR and CDSR at different temperatures and H₂O/CH₄ ratios. Circles: equilibrium values. (A) CH₄ conversion; (B) CO₂ conversion; (C) H₂/CO ratio. Conditions: CO₂/CH₄ = 1 in the absence of H₂O (DR); CO₂/CH₄ = 0.66 in the presence of H₂O (CDSR).

inlet H₂O/CH₄ ratio of 2, while the H₂/CO ratio expected from the sole SR reaction (Eq. 2) is 3. The H₂/CO ratios were generally close to or slightly lower than the calculated equilibrium ratios (Fig. 1C), probably due to slight differences between the experimental conditions (temperature, feed composition) and the conditions defined for the calculations. In contrast with methane, the conversion of CO₂ (Fig. 1B) was strongly affected by the presence of steam and decreased steadily with increasing H₂O/CH₄ ratios. At 487 °C and H₂O/CH₄ $\geq$ 0.68, the conversion of CO₂ became apparently negative, since more CO₂ was found at the reactor outlet than in the inlet feed, as the result of CO conversion into CO₂ by the WGS reaction. At H₂O/CH₄ = 2 the conversion of CO₂ was equal to zero whatever the temperature.

Table 1 summarizes the methane activities measured at 487 °C under the different reactants compositions investigated. The rates are given only for the lowest temperature studied, in the low methane conversion range (15–32 %), because at high temperature and conversions the reaction was subject to external diffusion limitations, as evidenced by the Arrhenius plots displayed in Fig. 2.

Table 1CH₄ reaction rates under DR and CDSR conditions at 487 °C.

	CH ₄ reaction rate (mmol.s ⁻¹ .g _{cat} ⁻¹)
DR	0.033
CDSR H ₂ O/CH ₄ = 0.34	0.042
CDSR H ₂ O/CH ₄ = 0.68	0.048
CDSR H ₂ O/CH ₄ = 1	0.060
CDSR H ₂ O/CH ₄ = 2	0.067

Fig. 2. Arrhenius plots of CDSR reaction rates at 487, 577 and 670 °C.

3.2. Effect of carbon dioxide addition on steam-reforming catalyst performances

Fig. 3 shows the effect of CO₂ addition to a stoichiometric SR feed at H₂O/CH₄ = 1. The methane reaction rate measured at 587 °C under pure SR conditions was 0.083 mmol.s⁻¹.g⁻¹, slightly slower than the CH₄ reaction rate measured at 577 °C under pure DR conditions (0.103 mmol.s⁻¹.g⁻¹, **Table 1**). The methane conversion (**Fig. 3A**) was only slightly affected by the introduction of CO₂ in the feed, changing from 41.2 % at CO₂/CH₄ = 0–46.5 % at CO₂/CH₄ = 1. These conversions were well below the calculated equilibrium conversions. In contrast, the H₂/CO ratio decreased strongly with CO₂ addition in the feed, which displaces the WGS equilibrium towards the RWGS reaction. Compared to methane, CO₂ appeared very moderately converted (7.4 and 11.9 % at CO₂/CH₄ = 0.6 and CO₂/CH₄ = 1, respectively), nevertheless this conversion can be attributed to both DR and RWGS reactions. In **Fig. 3B**, the H₂ and CO production rates at CO₂/CH₄ = 0, 0.6 or 1 are plotted as a function of the methane conversion reported in **Fig. 3A**. The CO production increased from 0.25 mmol/min at CO₂/CH₄ = 0 to 0.61 mmol/min at CO₂/CH₄ = 1 and the H₂ production decreased from 1.44 mmol/min to 1.28 mmol/min, while the methane conversion increased by ≈ 5%. Therefore, the CO production rate increased by 0.36 mmol/min when the H₂ production rate decreased by 0.16 mmol/min, which suggests that the RWGS reaction cannot account by itself for the conversion of CO₂ and that the DR reaction also contributes to the conversion of CO₂. These results, and particularly the reaction of the CO₂:H₂O:CH₄ 1:1:1 mixture in **Fig. 3A**, suggest that methane (or more specifically adsorbed carbon formed by methane decomposition) reacts preferentially with H₂O rather than with CO₂ over 10 %Ni-0.05 %Rh/MgAl₂O₄, in spite of the slower reaction kinetics, which is probably related to different adsorption properties of the two co-reactants on the catalyst and suggests an adsorption competition when both are present in the feed stream.

In the experiments displayed in **Fig. 3**, the temperature measured in the catalyst bed was 600 °C when the reactor was swept with Ar. Switching to the reaction conditions led to an immediate drop in the catalyst temperature, which translates the reforming reactions endothermicity (Eqs. 1 and 2): under pure SR conditions, the catalyst

Fig. 3. 10 %Ni-0.05 %Rh/MgAl₂O₄ catalyst performances for SR and CDSR at different CO₂/CH₄ inlet ratios. (A) Conversion of CH₄ and CO₂ and H₂/CO outlet ratio; (B) H₂ and CO production versus CH₄ conversion. Conditions: H₂O/CH₄ = 1 (SR and CDSR), CO₂/CH₄ variable (CDSR). Catalyst temperature: T = 587 °C at CO₂/CH₄ = 0; T = 584 °C at CO₂/CH₄ = 0.6; T = 583 °C at CO₂/CH₄ = 1.

temperature decreased to 587 °C, and to 584 and 583 °C under CDSR with CO₂/CH₄ = 0.6 and 1, respectively, in agreement with the higher endothermicity of DR compared to SR. This thermal behavior supports the contribution of the DR reaction, despite its limited extent, under these conditions (H₂O/CH₄ = 1). With the same catalyst temperature of 600 °C under Ar, the catalyst temperature dropped to 577 °C under the pure DR conditions shown in **Fig. 1**.

3.3. CO₂ adsorption studies

CO₂ undergoes dissociative chemisorption on Ni and on Rh, with formation of anionic CO₂⁻ species through electron transfer [2]. On Ni, the chemisorption properties were also shown to depend on the type of surface planes considered [16]. However, due to its acidic character, CO₂ also interacts strongly with the basic MgAl₂O₄ support. IR [17] and DRIFTS studies of CO₂ adsorption on Mg_xAl_yO_z mixed oxides with Mg/Al = 0.1–0.3 [18] evidenced the presence of 3 types of adsorbed species: bicarbonates HCO₃⁻ that form with surface OH groups, bidentate carbonates bridging Mg²⁺ and O²⁻ ions, and monodentate carbonates chemisorbed on O²⁻. The bicarbonate species desorbed below 100 °C, whereas both bidentate and unidentate carbonates were present up to 300 °C, but only unidentate carbonates were detected above 350 °C [17]. CO₂ adsorption on Ni/MgAl₂O₄ or on Rh/MgAl₂O₄ led to similar adsorbed species [19,20]. Basic supports such as La₂O₃ and MgAlO_x mixed oxides derived from hydrotalcites have been proposed to participate in the DR reaction mechanism through the formation of surface carbonate species that react with adsorbed carbon formed by decomposition of methane or propane [20–22].

The adsorption properties of the 10 %Ni-0.05 %Rh/MgAl₂O₄ catalyst for CO₂ were studied in transient experiments in which diluted CO₂ was adsorbed on the catalyst at different temperatures and partial pressures. Fig. 4 displays an example of sequence in which the gas composition was switched according to: He → 2% CO₂ / 2% Ar / He (Fig. 4A), followed by 2% CO₂ / 2% Ar / He → He (Fig. 4B) and again He → 2% CO₂ / 2% Ar / He (Fig. 4C). Ar was used as tracer since it does not adsorb on the catalyst, and the area between the CO₂ and Ar signals represents the amounts of CO₂ adsorbed or desorbed. The difference between total and reversible CO₂ gives the amount of strongly adsorbed species at the applied adsorption/desorption temperature, which is additionally confirmed using either TPAE or TPD experiments. Similar experiments were run at different temperatures (25–350 °C range) and CO₂ partial pressures.

Adsorption of CO₂ at room temperature followed by TPAE also revealed the presence of both weakly and strongly adsorbed CO₂ species. The inset in Fig. 5 shows the initial CO₂-adsorption/He-desorption sequence at 25 °C, in which 188 μmol/g of CO₂ adsorb (total CO₂) while 64 μmol/g desorb under He (weakly adsorbed species). After re-adsorption of CO₂ at 25 °C, Fig. 5 shows the evolution of CO₂ and Ar molar fractions at increasing adsorption temperatures under quasi-equilibrium conditions (TPAE procedure, [14]). The poorly resolved CO₂ peaks below 130 °C (total amount 68 μmol/g) are due to the decrease in the adsorption equilibrium coverage of the weakly adsorbed species, which are not relevant to the reaction conditions. The broad CO₂ peak between 140 and 500 °C (≈103 μmol/g) is due to the net desorption rate of the strongly adsorbed CO₂ species. The final switch 2% CO₂/2% Ar/He → He (not shown) at 500 °C leads to the desorption of ≈23 μmol/g of CO₂, indicating that there is a coverage in CO₂ species at 500 °C under P_{CO2} = 2 kPa. The total amount of strongly adsorbed species at 140 °C is 126 μmol/g.

The CO₂ peak at T>140 °C during the TPAE provides the experimental average coverage of the strongly adsorbed species (black circles in Fig. 6), considering that they are present at full coverage at T = 140 °C under P_{CO2} = 2 kPa (see Supplementary information), since the Ar and CO₂ molar fractions are equal at 130–140 °C (Fig. 5). This experimental curve can be fitted according to a modeling procedure described previously [23 and Supplementary information], based on (a) the Temkin adsorption model, which assumes a linear decrease in the heat of adsorption when the surface coverage increases and (b) localized adsorbed species for the expression of the adsorption coefficient. The

Fig. 5. TPAE on 10 %Ni-0.05 %Rh/MgAl₂O₄ under 2% CO₂/2% Ar/He in the 25–500 °C adsorption temperature range. Inset: Initial adsorption of 2% CO₂/2% Ar/He followed by desorption under He at 25 °C.

experimental data could not be modeled if only one CO₂ species was considered, but they were adequately fitted (Fig. 6, curve a) assuming two CO₂ adsorbed species A and B, with different heats of adsorption and ratios at saturation (Table 2). Curves b and c provide the individual coverages of the two CO₂ species under P_{CO2} = 2 kPa, and show that only species B is present on the catalyst surface in the temperature range relevant to DR and CDSR conditions (600–700 °C).

3.4. H₂O adsorption studies

Ni surfaces have been shown to display different reactivities towards water: H₂O adsorbs reversibly on relatively unreactive closed-packed (111) and (100) surfaces, whereas it can chemisorb or fully dissociate, depending on the conditions, on more open (110) surfaces and on stepped surfaces [24]. Water adsorption on alumina and on titania is generally considered non-dissociative and leads to the formation of similar adsorbed species: weakly physisorbed species and more strongly bound species chemisorbed on surface OH groups or on basic O²⁻ anions through hydrogen bonds, or coordinated to Al³⁺ or Ti⁴⁺ Lewis acid sites through the oxygen atom [25,26].

Fig. 4. Adsorption / desorption sequence of 2% CO₂/2% Ar/He on 10 %Ni-0.05 %Rh/MgAl₂O₄ catalyst at 250 °C. (A) Total CO₂ adsorbed; (B) CO₂ reversibly desorbed; (C) CO₂ reversibly adsorbed.

Fig. 6. Coverage of strongly adsorbed CO_2 species as a function of the adsorption temperature under $P_{\text{CO}_2} = 2$ kPa. Black circles: experimental data; red line: model fit assuming two different adsorbed species A and B; blue and magenta lines: individual calculated coverages of the two species A and B. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 2

Heats of adsorption of CO_2 and H_2O strongly adsorbed species on 10 %Ni-0.05 %Rh/ MgAl_2O_4 catalyst at full and zero coverage, and ratio of each species at surface saturation.

	E_A ($\theta = 1$) kJ/mol	E_A ($\theta = 0$) kJ/mol	Ratio at saturation
CO_2 species A	75	108	0.75
CO_2 species B	110	180	0.25
H_2O species A	78	105	0.55
H_2O species B	105	173	0.45

Fig. 7 displays an adsorption/desorption sequence with H_2O at 250°C , in which the gas composition was switched according to: $\text{He} \rightarrow 1.8\% \text{H}_2\text{O} / 2\% \text{Ar} / \text{He}$ (Fig. 7A), followed by $1.8\% \text{H}_2\text{O} / 2\% \text{Ar} / \text{He} \rightarrow \text{He}$ (Fig. 7B) and $\text{He} \rightarrow 1.8\% \text{H}_2\text{O} / 2\% \text{Ar} / \text{He}$ (Fig. 7C). The amounts of steam adsorbed were significantly higher than those of CO_2 , and the rate of water desorption decreased very slowly during the desorption. Moreover, a small H_2 peak was observed at the first introduction of steam on the catalyst (Supplementary data, Fig. 1), which was formed by dissociation of H_2O on surface metallic Ni sites.

Fig. 8 shows a TPAE performed on the reduced 10 %Ni-0.05 %Rh/ MgAl_2O_4 catalyst under $0.87\% \text{H}_2\text{O} / 0.87\% \text{Ar} / \text{He}$, where the initial adsorption temperature was set to 150°C to prevent the contribution of weakly adsorbed H_2O species. The total amount of water adsorbed was $290 \mu\text{mol/g}$, with also a small hydrogen production ($5 \mu\text{mol/g}$, not shown).

The temperature increase leads to a broad H_2O peak, which corresponds to the decrease in the adsorption equilibrium coverages of strongly adsorbed species. The total amount was $240 \mu\text{mol H}_2\text{O/g}$ at $T_a = 515^\circ\text{C}$, indicating that $290 - 240 = 50 \mu\text{mol/g}$ remained adsorbed at this temperature. Assuming full coverage of the H_2O species at 150°C ,

Fig. 8. TPAE on 10 %Ni-0.05 %Rh/ MgAl_2O_4 under $0.87\% \text{H}_2\text{O} / 0.87\% \text{Ar} / \text{He}$ in the $150\text{--}500^\circ\text{C}$ adsorption temperature range.

Fig. 7. Adsorption / desorption sequence of $1.8\% \text{H}_2\text{O} / 2\% \text{Ar} / \text{He}$ on 10 %Ni-0.05 %Rh/ MgAl_2O_4 catalyst at 250°C . (A) Total H_2O adsorbed; (B) H_2O reversibly desorbed; (C) H_2O reversibly adsorbed.

Fig. 9. Coverage of strongly adsorbed H₂O species as a function of temperature at $P_{\text{H}_2\text{O}} = 0.87$ kPa. Black circles: experimental data; red: model fit assuming two different adsorbed species; blue and magenta: calculated individual coverages of molecularly (A) and dissociatively (B) adsorbed species. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Fig. 9 provides the evolution of the experimental adsorption equilibrium coverage with the increase in the adsorption temperature under quasi-isobaric conditions. Again, the Temkin adsorption model described the data adequately if two species were considered (Fig. 9, curve a). Since H₂O adsorption experiments revealed, through the formation of hydrogen, that a small fraction of water dissociated on reduced Ni, these two species were assumed to be molecular and dissociated H₂O species. The heats of adsorption of the two species at high and low coverage and their ratios at full surface coverage are reported in Table 2. In the temperature range relevant to DR and CDSR conditions (600–700 °C), only the dissociated species B is present on the catalyst surface, and therefore involved in the reaction pathway.

3.5. CO₂ and H₂O competitive adsorption

Fig. 10 compares the amounts of total (QT) and strongly (QS) adsorbed CO₂ and H₂O at 150, 250 and 350 °C. Whatever the temperature, QT(H₂O) was roughly 3 times higher than QT(CO₂), while QS

Fig. 10. Amounts of CO₂ and H₂O adsorbed at 150–350 °C on 10 %Ni-0.05 % Rh/MgAl₂O₄.

(H₂O) was 2.5–4.5 times higher than QS(CO₂). At similar adsorption pressures, the adsorption of water is clearly favored over that of CO₂. This can be due in part to a difference in the nature of some adsorption sites for CO₂ and H₂O.

The competitive CO₂-H₂O adsorption was evidenced through the sequence displayed in Fig. 11. CO₂ was first adsorbed alone at 250 °C, then H₂O was added in the gas mixture and subsequently removed. At each H₂O addition, a CO₂ desorption peak corresponding to 45 ± 5 mmol/g was observed while H₂O adsorbed on the catalyst, i.e. before the onset of the H₂O signal. These results might involve both CO₂ and H₂O strongly adsorbed species evidenced previously, however at higher temperature the detectable amounts of CO₂ displaced by H₂O decrease rapidly.

A deeper insight in the competitive adsorption between CO₂ and H₂O adsorbed species relevant to the DR and CDSR reactions was obtained using a competitive Temkin model [27,28] and the heats of adsorption calculated for CO₂-B and for dissociatively adsorbed H₂O-B species (present on the catalyst surface in the 600–800 °C temperature range). Fig. 12 shows the calculated evolution of the surface coverage of each species with temperature, considering the adsorption of single H₂O or CO₂ species (no competition) or their competitive co-adsorption.

The model predicts that the CO₂-B coverage strongly prevails up to 500 °C, but at $T > 600$ °C it decreases faster than the H₂O-B coverage and the surface becomes predominantly covered by dissociated H₂O-B species. Although this result is calculated and should be confirmed by direct identification of the different CO₂ and H₂O adsorbed species, i.e. using IR spectroscopy, it provides a plausible explanation to the catalyst behavior observed in CDSR experiments.

4. Conclusion

Combined dry-steam methane reforming was applied to convert a model biogas into syn-gas over a 10 %Ni-0.05 %Rh/MgAl₂O₄ catalyst. The effect of CO₂ addition to a steam reforming feed steam, and conversely the effect of H₂O addition to a dry reforming feed stream, evidenced an adsorption competition between CO₂ and H₂O that led to an inhibition of the dry-reforming reaction in the presence of steam. CO₂ and H₂O adsorption studies at different temperatures showed that H₂O was always adsorbed in much higher amounts than CO₂ on the catalyst surface. A Temkin-based model applied to quasi-equilibrium adsorption data showed that two different strongly adsorbed CO₂ and H₂O species were present on the catalyst surface at moderate temperature, but only one of each remained adsorbed at temperatures relevant to reaction conditions (600–800 °C). H₂O was also shown to displace CO₂ from the catalyst surface, confirming that they compete, at least partially, for the same adsorption sites. At high temperature, the surface coverage by the

Fig. 11. Transient response to successive gas switches 2% CO₂/2% Ar /He → 2% CO₂/1.8 % H₂O /2% Ar /He over 10 %Ni-0.05 %Rh/MgAl₂O₄ catalyst at 250 °C.

Fig. 12. Comparison of the calculated coverages of CO₂-B and H₂O-B species in the absence of competition (dotted lines) or in competitive co-adsorption (full lines) at a CO₂ and H₂O partial pressure of 2 kPa.

most strongly adsorbed H₂O species was predominant.

Credit author statement

N. Guilhaume: adsorption studies, HSC calculations, writing, editing the paper.

R. Wandawa, W. Yin: dry-reforming and combined DSR measurements.

D. Bianchi: modelling adsorption data, editing.

Y. Schuurman: project supervision, editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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