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Kinetic study of the catalytic reforming of methane with carbon dioxide to synthesis gas over Ni/La_2O_3 catalyst

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Abstract

The kinetic behavior of the Ni/La_2O_3 catalyst in the reforming reaction of methane with carbon dioxide was investigated as a function of temperature and partial pressures of CH_4 and CO_2. The apparent activation energy of the reforming reaction was estimated to be 13.2 kcal/mol. It was also found that increase of the H_2 partial pressure leads to a continuous enhancement of the rate of CO formation, due to the simultaneous occurrence of the water-gas shift reaction. The mechanism of the CH_4/CO_2 reaction has been investigated using steady-state isotopic tracing and transient experiments, as well as FTIR, XRD, XPS and HR-TEM techniques. Based on the mechanistic results, a kinetic model was developed, which was found to predict satisfactorily the kinetic measurements. Methane cracking and the surface reaction between C and oxycarbonate species, are suggested to be the rate determining steps of the CH_4/CO_2 reaction over the Ni/La_2O_3 catalyst.

Keywords: Catalytic reforming; Natural gas; Ni/La_2O_3 catalyst; Carbon dioxide; Synthesis gas

1. Introduction

The reforming reaction of methane with carbon dioxide to synthesis gas has received significant attention in the last few years as it constitutes a promising alternative route for the production of synthesis gas. Although steam reforming is the dominant method for synthesis gas production, it produces syngas with high H_2/CO ratio, which is not suitable for methanol and Fischer–Tropsh synthesis. The reforming of methane with carbon dioxide has also been proposed as a means of storing and transporting solar and atomic energy [1,2]. Worner and Tamme [3] have studied the CO_2 reforming of methane in a solar driven volumetric receiver-reactor, demonstrating this concept of solar energy harvesting.

The reaction has been investigated over both, noble metal [4–9] and Ni-based [10–18] catalysts dispersed on different carriers. A major problem associated with both types of catalysts is continuous deactivation with time on stream due to carbon deposition. In the case of noble metals, efforts to alleviate this problem have centered around the use of additives and promoters [4], while in the case of Ni catalysts the support seems to play a major role in this respect [9,10,15].

Kinetic and mechanistic studies have been performed over noble metal and Ni-based catalysts. Ross and co-workers [8], observed that both methane and carbon dioxide dissociate independently of one another over Pt/ZrO_2. The dissociation of carbon dioxide acts as an oxygen supplier while the decomposition products of methane scavenge the oxygen from the catalyst surface [5,6,8]. Lercher and co-workers [9] also studied the CO_2 reforming of CH_4 over the same catalyst and concluded that catalytic activity is determined by the accessibility of Pt on the $Pt–ZrO_2$

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perimeter. The perimeter concentration can be altered by calcination.

The kinetics of CO_2 reforming of methane over Pt supported on TiO_2, ZrO_2, Cr_2O_3 and SiO_2 as well as over Ni-based catalysts were studied by Bradford and Vannice [19,20]. The kinetic behavior was explained by a mechanism which involves dissociative CH_4 adsorption and CH_xO decomposition as slow kinetic steps. CO_2 participates in the reaction mechanism through the reverse water-gas shift to produce OH groups. Surface OH groups react with adsorbed CH_x intermediates to yield a formate-type intermediate, CH_xO, which decomposes to yield H_2 and CO [20]. It was also suggested that the support may serve as a sink for surface hydroxyl groups, such that the active site for CH_xO formation and subsequent decomposition may be at the metal–support interface. The kinetics of elementary surface reactions involved in the reforming of methane to synthesis gas over supported Ni catalysts were also studied by Aparicio [18]. The model developed suggests that there is no single rate-determining step in methane reforming with either steam or CO_2 and that under some conditions the availability of surface oxygen may play a key role in determining the rate.

Detailed mechanistic studies have been performed in this laboratory over the Ni/La_2O_3 catalyst, which exhibits unique behavior in the methane reforming reaction in the sense that its activity initially increases with time on stream and subsequently remains constant for extended periods of time [21–24]. In the present study, kinetic measurements over the Ni/La_2O_3 catalyst were performed in the temperature range 650–750°C. The conclusions from the previous mechanistic studies are combined with the present kinetic results to derive a mechanistic scheme and a kinetic model for the reaction.

2. Experimental

2.1. Catalyst preparation

Ni/La_2O_3 catalyst, containing 17 wt.% Ni, was prepared by the wet impregnation method, using nitrate salt ($Ni(NO_3)_3{\cdot}5H_2O$) as the metal precursor [21]. The residue was then dried at 110°C for 24 h and then was heated at 500°C under N_2 flow for 2 h for complete decomposition of the nitrate. After this treatment, the catalyst was reduced at 500°C in H_2 flow for at least 5 h. A further reduction at 750°C for 1 h in H_2 flow was performed before any experiment.

2.2. Kinetic apparatus and measurements

The apparatus employed for the kinetic measurements consists of a flow measuring and control system, a heated quartz tube reactor and an on-line analytical system. Feed flow rates were measured and controlled by thermal mass flow meters. Weighted amounts of catalyst (5–10 mg) were placed in the middle of the reactor supported by quartz wool. The internal reactor diameter is 4 mm, while the catalyst bed height is 2.5 mm. A chromel–alumel thermocouple, inside a thermowell which run through the catalyst bed was used for temperature measurement and control. Analysis of the feed and of the reaction mixtures was performed by a gas chromatograph connected on-line to the reactor apparatus via a gas sampling valve. The TC detector was used to analyze H_2, O_2, CO, CH_4, CO_2, and H_2O, separated by a carbosieve S-II 100/120 mesh column. Kinetic measurements were performed under differential conditions in the temperature range 650–750°C, employing dilute CH_4/CO_2/He feeds. The total feed flow rate was 300 ml/min, while the catalyst particle was in the range 0.18–0.22 mm.

3. Results and discussion

3.1. Mass and heat transport effects

Reliable kinetic data can only be obtained in the absence of mass and heat transport resistances. The effects of interface and intraparticle heat and mass transport resistances on kinetic parameters were determined employing theoretical and experimental procedures. The effect of feed flow rate and catalyst particle size of the Ni/La_2O_3 catalyst on reaction rate was determined experimentally with a feed mixture composed of CH_4/CO_2/He (=10/10/80 vol.%) at 750°C.

The effect of variation of flow rate under constant W/F ratio on the reaction rate at 750°C is presented in Fig. 1a. It can be seen that the reaction rate is rather invariant to flow rate when it exceeds 200 ml/min. Therefore, employment of a flow rate of 300 ml/min

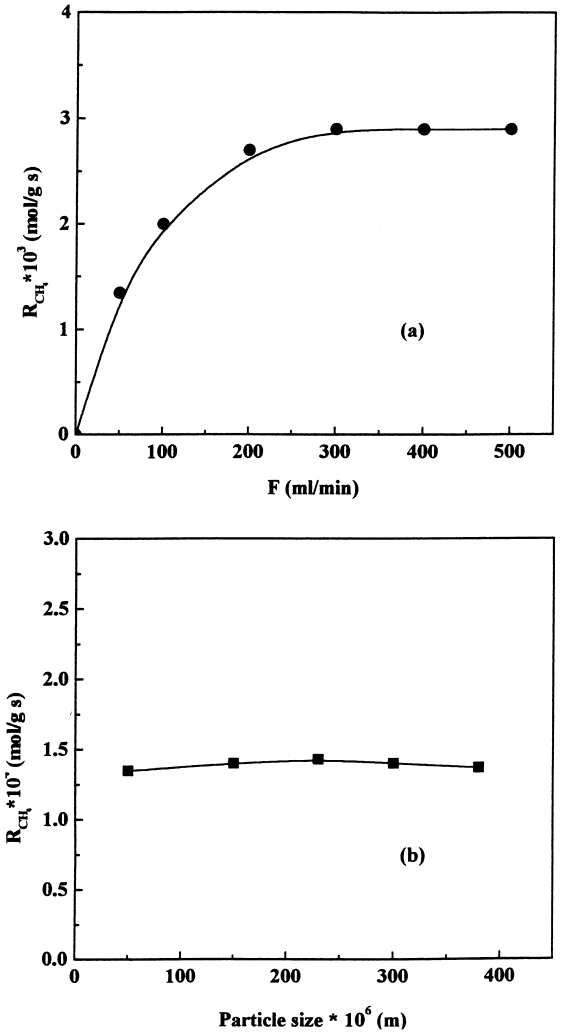

Fig. 1. (a) Effect of volumetric feed flow rate on the rate of methane consumption during reforming reaction over the Ni/La_2O_3 catalyst at constant $W/F = 1.25 \times 10^{-2}$ g s/ml. (b) Effect of catalyst particle size on the reaction rate observed over Ni/La_2O_3 catalyst at constant *W/F* ratio.

in the kinetic experiments seems to be adequate for operation in the kinetic regime, taking into account the fact that the kinetic experiments are conducted at even lower temperature, in the range 650–750°C.

The effect of the catalyst particle size on the reaction rate at 750°C is shown in Fig. 1b. All measurements were conducted with a flow of 300 ml/min using catalyst particles of diameter in the range 0.05–0.4 mm. It can be seen that the rate of methane conversion is invariant to the average diameter of the particles, within the particle size range investigated. Therefore, employment of particles with average diameter of 0.2 mm appears to be sufficient for operation in the kinetic regime.

3.2. Kinetic studies

Kinetic studies of the CH_4/CO_2 reaction were carried out at the temperature of 750°C. Fig. 2 presents the variation of reaction rate with time on stream, expressed in units of mmol/g s, obtained under differential reaction conditions over Ni dispersed on various carriers such as La_2O_3, $A1_2O_3$, YSZ (yttria-stabilized zirconia), SiO_2 and CaO. It is shown that the Ni/YSZ catalyst exhibits higher initial reaction rate, as compared with the other Ni-based catalysts, but its deactivation rate is very rapid. In fact, all catalysts, with the exception of the Ni/La_2O_3 catalyst, deactivate considerably with time of exposure to the reaction mixture. The rate of deactivation is very high during the initial 4–5 h and decreases at longer times on stream. As has been discussed previously, the deactivation of these catalysts is due to carbon accumulation on the surface of Ni, which originates from cracking of CH_4.

In contrast to the kinetic behavior of most of the Ni-based catalysts, the Ni/La_2O_3 catalyst exhibits a

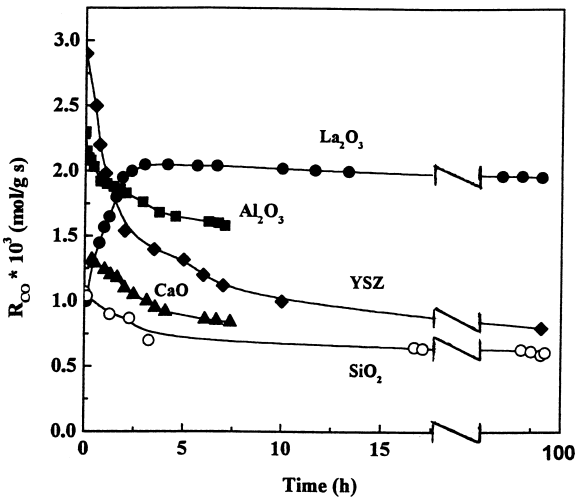

Fig. 2. Alteration of the reaction rate as a function of time on stream over Ni/La_2O_3, Ni/Al_2O_3, Ni/YSZ, Ni/CaO, and Ni/SiO_2 catalysts at 750°C.

unique kinetic performance. The reaction rate is observed to increase with time on stream for the initial 2–5 h of reaction and remains stable during 100 h of operation. The above reported behavior has already been discussed by Zhang et al. [21–24]. It has been shown that the unique performance of the Ni/La_2O_3 catalyst is due to the fact that particles of LaO_x are deposited onto the Ni crystallites where they react with CO_2 to form carbonates and oxycarbonates. These species, in turn, react with the accumulated carbon at the interface of the Ni and La_2O_3 particles, thus restoring the Ni surface to its original state. As long as the rate of carbon deposition is equal to the rate of carbon scavenging, a stable catalyst results. Furthermore, only a small fraction of the Ni particles is participating in the catalytic process, which is the fraction at the interface with the lanthanum oxycarbonate particles. The remaining Ni surface is covered with carbon and is catalytically inactive.

The unique kinetic performance of the Ni/La_2O_3 catalyst leads to the suggestion that new catalytic sites, which are more active and stable towards the CH_4/CO_2 reaction, are formed on the Ni/La_2O_3 catalyst surface, following exposure to the reaction mixture, as discussed above. For this reason, detailed mechanistic studies of the surface and bulk structure as well as characterization of carbon accumulated during reaction, has been conducted over the Ni/La_2O_3 catalyst [21–24]. The results of these studies are related to the present kinetic study from which a mechanistic kinetic model is derived.

3.2.1. Temperature sensitivity of reaction rate

The temperature sensitivity of the CH_4/CO_2 reaction rate over the Ni/La_2O_3 catalyst was investigated in the temperature range 500–800°C, employing a feed mixture consisting of CH_4/CO_2/He at the ratio of 10/10/80. The experiments were conducted after the performance of the catalyst was stabilized at 750°C. Results in the form of an Arrhenius plot are shown in Fig. 3. The apparent activation energy, as determined from the results of Fig. 3, is 13.2 kcal/mol, a value which is lower than the respective activation energy which has been reported for noble metal catalysts, which is in the range 20–30 kcal/mol [6]. Bradford and Vannice [20] report activation energies for CO formation over Ni catalysts supported on C, SiO_2, TiO_2 and MgO carriers which range between 19 and

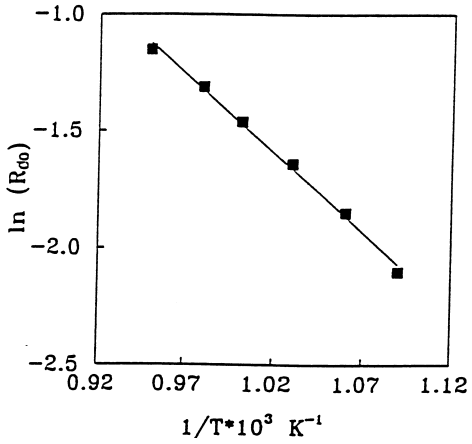

Fig. 3. Influence of the reaction temperature on the rate of CO formation. Experimental conditions: CH_4/CO_2/He = 10/10/80 vol.%, $Q = 300$ ml/min.

44 kcal/mol. It is apparent that the support of Ni crystallites may influence significantly the activation energy, probably by altering the rate-controlling step in the reaction sequence. This has been established by a kinetic isotope effect study [23] which showed that over Ni/La_2O_3 methane cracking is the rate determining step while over Ni/Al_2O_3 methane cracking is a fast step. Aparicio et al. [25] report values of the apparent activation energy of 17.5 and 16.5 kcal/mol for Ni/Al_2O_3 and Ni/SiO_2 catalysts, respectively. The value of the activation energy estimated in the present study is lower than those reported previously. This is probably due to the unique mechanistic scheme, which is offered by this catalyst, which is described in a subsequent section.

3.2.2. Effect of CH_4 and CO_2 partial pressures on intrinsic rate

The influence of the partial pressures of CH_4 and CO_2 on the rate of CO_2 reforming of methane was studied over the Ni/La_2O_3 catalyst at atmospheric pressure in the temperature range 650–750°C, under differential conditions. The Ni/La_2O_3 catalyst was activated as follows. It was first exposed to pure H_2 at 750°C for 2 h and then to the CH_4/CO_2/He (10/10/80 vol.%) mixture at 750°C. The reforming reaction was followed for 5 h, until the catalyst had reached the stable level. After this treatment, the variation of CH_4 or CO_2 partial pressure was conducted.

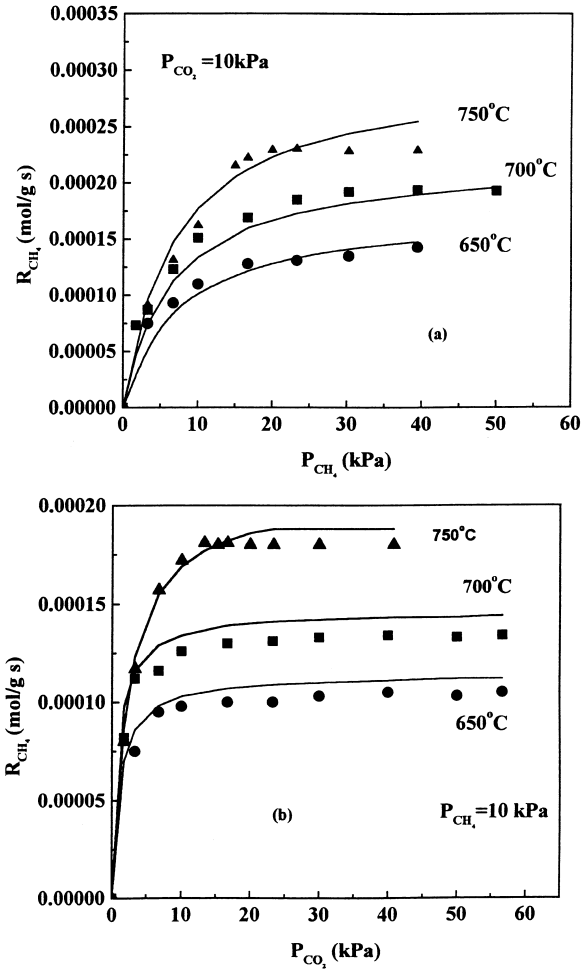

Fig. 4. Effect of alteration of partial pressures of (a) CH_4 and (b) CO_2 at constant P_{CO_2} and P_{CH_4}, respectively, on the reaction rate over Ni/La_2O_3 catalyst at 650, 700 and 750°C. Solid symbols: experimental results, solid lines: model prediction.

A constant CH_4 partial pressure of 10 kPa was used as the CO_2 partial pressure was varied between 2 and 58 kPa, and a constant partial pressure of CO_2 equal to 10 kPa was used when the CH_4 partial pressure was varied between 2 and 50 kPa. The effect of the variation of the methane partial pressure on the rate of methane consumption is presented in Fig. 4a. It is shown that the reaction rate is strongly affected by the partial pressure of methane for CH_4 partial pressures lower than 20 kPa. Further increase of partial pressure of CH_4 up to 50 kPa, does not seem to affect measurably the rate of reaction. The alteration of the rate of methane consumption with partial pressure of CO_2 and reaction temperature, at a constant methane partial pressure of l0 kPa, is shown in Fig. 4b. A very strong influence is observed as the CO_2 partial pressure is varied in the range 0–l0 kPa. However, a stable performance is observed as the CO_2 partial pressure is varied in the range 13–60 kPa. Comparison of Fig. 4a and b suggests that the reaction rate is more sensitive to CO_2 partial pressure, than to CH_4 partial pressure, at low CO_2 and CH_4 partial pressures, respectively. This result indicates that CO_2 adsorption on the Ni/La_2O_3 catalyst is stronger than that of CH_4, which can be attributed to the stronger interaction of the CO_2 molecule with the La_2O_3 support, due to the basic nature of La_2O_3. It is well known that CO_2 reacts with La_2O_3 and produces $La_2O_2CO_3$ species, which play an important role in the kinetic mechanism and the stability of the Ni/La_2O_3 catalyst [21].

The effect of alteration of CH_4 and CO_2 partial pressures at constant CO_2 or CH_4 partial pressures of 5, 15 and 20 kPa, on the rate of reaction at 750°C is shown in Fig. 5 (a and b). It is apparent that a strong influence of both reactants on the reaction rate is observed at low CH_4 and CO_2 partial pressures. The influence becomes stronger as the concentration of CO_2 or CH_4, respectively, in the reaction mixture increases.

3.2.3. Effects of H_2 and CO_2 partial pressures on intrinsic rate

Fig. 6 demonstrates the alteration of the rates of CH_4 and CO_2 consumption as well as the rate of CO production with variation of H_2 partial pressure, as the CH_4 and CO_2 partial pressures were kept constant at 10 kPa, at the reaction temperature of 750°C. It can be observed that H_2 has essentially no effect on the reforming activity of the Ni catalyst, as evidenced by the invariance of the rate of methane consumption, with H_2 partial pressure. The rates of CO formation and of CO_2 consumption, on the other hand, increase considerably with increase of hydrogen pressure. This result can be attributed to the occurrence of the inverse water-gas shift reaction. Thus, increase of H_2 partial pressure leads to a further CO_2 consumption via the reaction

$$CO_2 + H_2 \rightarrow CO + H_2O$$

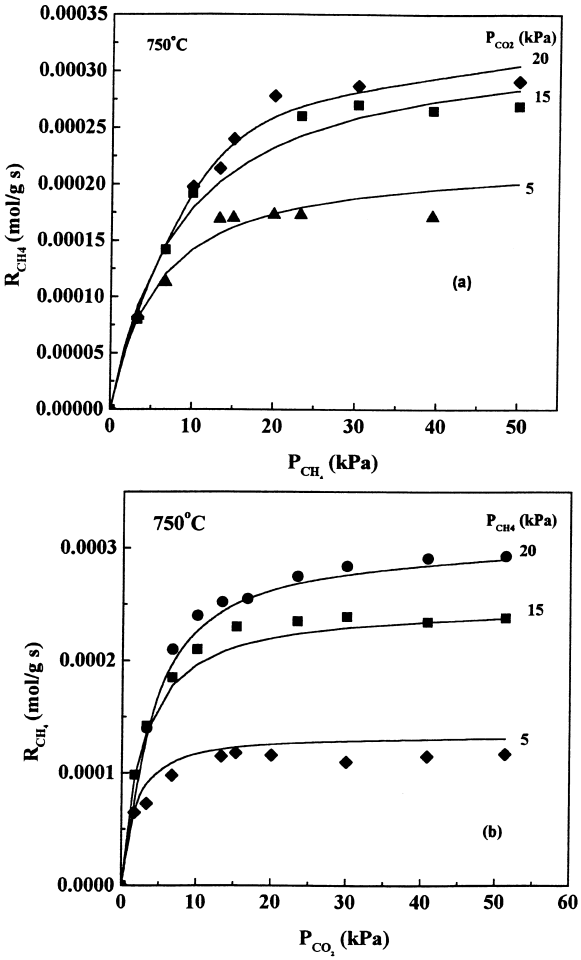

Fig. 5. Effect of alteration of partial pressures of (a) CH_4 and (b) CO_2 on the reaction rate over Ni/La_2O_3 catalyst as the partial pressures of CO_2 and CH_4, respectively, are kept constant at 5, 15 and 20 kPa. Solid symbols: experimental results, solid lines: model prediction.

which occurs in parallel with the CO_2 reforming of CH_4 reaction.

In addition, the influence of CO partial pressure on the reaction rate was studied in the temperature range 650–750°C. It was found that the rate of reforming reaction was slightly influenced by the partial pressure of CO, decreasing with increasing P_{CO} up to 4 kPa, and remained more or less stable for further increases of P_{CO}.

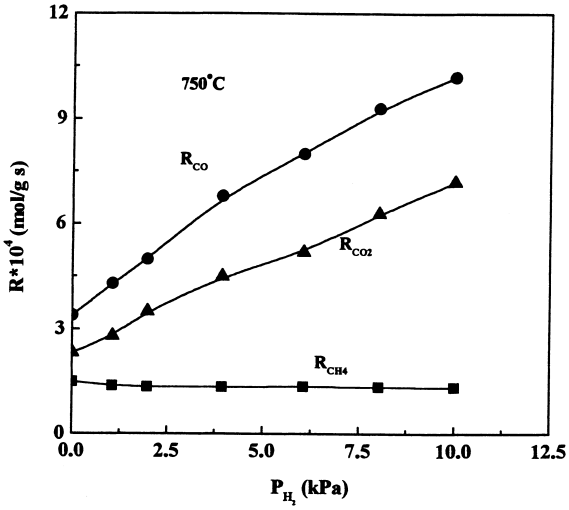

Fig. 6. Effect of hydrogen partial pressure on the rates of methane and CO_2 consumption and CO production at 750°C.

3.3. Proposed mechanism

The mechanism of the methane reforming reaction with CO_2, over the Ni/La_2O_3 catalyst has been investigated employing a number of different techniques [21–24] and the most important observations, upon which the proposed mechanism is based, are the following:

- A certain fraction of the Ni content of the catalyst is visible by XPS and SIMS, following the reforming reaction even under integral conditions. This implies that portion of Ni is free of carbon deposits under reaction conditions [24].
- Methane was detected (by steady-state isotopic tracing kinetic analysis) to exist on the surface of the catalyst under reaction conditions [27].
- Transient studies have shown that the rate of dissociation of CO_2 on Ni crystallites is not significant as compared to that of CH_4. Naturally, the carbon which accumulates onto Ni crystallites, derives mostly from the CH_4 molecule [28].
- A strong interaction exists between CO_2 and the La_2O_3 support leading to the formation of stable $La_2O_2CO_3$ species, which are detected by FTIR and XRD [22].
- Transient studies employing isotopically labelled molecules indicate that the La_2O_3 support or the

$La_2O_2CO_3$ species which are formed behave as a dynamic oxygen pool under reaction conditions, participating in the formation of CO [27].

- In contrast to the Ni/Al_2O_3 catalyst, over the Ni/La_2O_3 catalyst, cracking of methane on Ni is a slow step [23].
- The active carbon-containing species which exist on the catalyst surface under reaction conditions consist exclusively of carbon, and not of CH_x, $x > 0$, species [28].
- HR-TEM has revealed that islands of La_2O_3 exist on the surface of the Ni particles under reaction conditions. This structure is probably formed during preparation of the catalyst [26].

Based on these observations, the following mechanistic steps, which lead to the production of CO and H_2 are proposed:

1. Reversible adsorption of methane on the surface of Ni which leads to cracking of methane and production of carbon deposits and hydrogen. Methane cracking is a slow step while methane adsorption is at equilibrium:

$$CH_4 + S \overset{K_1}{\leftrightarrow} S\text{–}CH_4 \quad \text{equilibrium} \tag{1}$$

$$S\text{–}CH_4 \overset{k_2}{\rightarrow} S\text{–}C + 2H_2 \quad \text{RDS} \tag{2}$$

2. A strong interaction exists between CO_2 and La_2O_3 which leads to the formation of $La_2O_2CO_3$ species. This is a fast step, considered to be at equilibrium

$$CO_2 + La_2O_3 \overset{K_3}{\leftrightarrow} La_2O_2CO_3 \quad \text{equilibrium} \tag{3}$$

3. $La_2O_2CO_3$ species react with carbon deposited onto Ni particles at the interface between Ni and $La_2O_2CO_3$. In this way the methane cracking activity of Ni (at the periphery of the $La_2O_2CO_3$ particles) is restored and the catalyst exhibits good stability. Therefore, the active portion of the catalyst is the interfacial area between Ni and oxycarbonate particles. The remaining surface of Ni is covered by carbon deposits. This step is also considered to be a slow step in the sequence

$$La_2O_2CO_3 + C\text{–}S \overset{k_4}{\rightarrow} La_2O_3 + 2CO + S \quad \text{RDS} \tag{4}$$

4. Adsorbed hydrogen, at very low surface coverage, may also exist and interact with other surface species. This adsorbed hydrogen originates from the sequential cracking of the methane molecule and it is assumed to be at equilibrium with gas phase hydrogen

$$H_2 + 2S \leftrightarrow 2S\text{–}H \quad \text{equilibrium} \tag{5}$$

The following steps are assumed to be fast steps in comparison with slow steps 2 and 4 above:

$$La_2O_2CO_3 + H\text{–}S \leftrightarrow La_2O_3 + CO + S\text{–}OH^- \tag{6}$$

$$S\text{–}OH^- + C\text{–}S \leftrightarrow S\text{–}CO + S\text{–}H\ (s) \tag{7}$$

$$S\text{–}OH + S\text{–}H \leftrightarrow H_2O + 2S \tag{8}$$

$$S\text{–}CO \leftrightarrow CO + S \tag{9}$$

5. Simultaneously, the inverse water-gas shift reaction takes place, which may be described by the following sequence of reaction steps:

$$CO_2 + S \leftrightarrow S\text{–}CO_2 \tag{10}$$

$$S\text{–}CO_2 + H\text{–}S \leftrightarrow S\text{–}CO + OH\text{–}S \quad \text{slow} \tag{11}$$

$$S\text{–}OH + H\text{–}S \leftrightarrow H_2O + 2S \tag{12}$$

3.4. Kinetic model

A rate expression for the CO_2 reforming of methane is developed, based on the mechanism illustrated above, assuming that steps 2 and 4 are both rate-controlling. It is further assumed that the Ni surface at the periphery of the oxycarbonate particles, which is the catalytically active surface, is either covered with carbon or it is vacant. Alternatively, it is assumed that the surface coverage of other species, such as H or CO, is negligible. Under these assumptions, the rate of methane conversion is of the form

$$R_{CH_4} = \frac{K_1 k_2 K_3 k_4 P_{CH_4} P_{CO_2}}{K_1 k_2 K_3 P_{CH_4} P_{CO_2} + K_1 k_2 P_{CH_4} + K_3 k_4 P_{CO}}$$

where K_1 is the equilibrium constant of methane adsorption and k_2 the rate constant of the decomposition (cracking) of methane on the surface of Ni. The two constants could not be determined individually but only their product which was found to be: $K_1 k_2 = 2.61 \times 10^{-3} \exp(-4300/T)$ (mol/g s) $(\text{kPa})^{-1}$. The value of -4300 represents the sum of the activation energy of methane cracking and the enthalpy of methane adsorption on Ni. The constant

K_3 which is the equilibrium constant of the reaction between CO_2 and La_2O_3 was found to be $5.17 \times 10^{-5} \exp(8700/T)\,(\mathrm{kPa})^{-1}$ while the rate constant of the reaction between the oxycarbonate species and carbon deposited on the surface of Ni, k_4, was found to be $5.35 \times 10^{-1} \exp(-7500/T)\,(\mathrm{mol/g\,s})$.

The predictions of the model, i.e. the rate of methane consumption as a function of CH_4 and CO_2 partial pressures and temperature are shown in Figs. 4 and 5. In Fig. 4(a), the experimental results (symbols) along with the model predictions (solid lines) are shown for the experiment in which the methane partial pressure was varied at a constant CO_2 partial pressure of 10 kPa, within the temperature range 650–750°C. In Fig. 4(b), the experimental results (symbols), along with the model predictions (solid lines), are shown for the experiment in which the CO_2 partial pressure was varied at a constant CH_4 partial pressure of 10 kPa within the same temperature range. It can be seen that in both cases, the fitting obtained by the model is very good and the main features of the reaction are adequately described. In Fig. 5(a) the experimental data and the model predictions are presented for the cases which the partial pressure of CO_2 is constant at 5, 15 and 20 kPa while the partial pressure of CH_4 is varied. Similarly, in Fig. 5(b) the experimental data and model predictions are presented for the cases in which the partial pressure of CH_4 is constant at 5, 15 and 20 kPa, while P_{CO_2} is varied. It is obvious that the kinetic model predicts satisfactorily the kinetic results. The success of the prediction of the kinetic data by the model is not fortuitous. No other kinetic model, among those which were tested could predict satisfactorily the kinetic results. The good model prediction is due to the fact that the development of the kinetic model is based on detailed mechanistic studies.

4. Summary and conclusions

The kinetics of the reaction of CO_2 reforming of methane over the Ni/La_2O_3 catalyst, were investigated in the temperature range 650–750°C by variation of the partial pressures of CO_2 and of CH_4. Based on detailed mechanistic studies, a mechanistic model is proposed from which a kinetic model is derived. The mechanistic scheme assumes adsorption of CH_4 on Ni, followed by cracking and carbon deposition, as a slow step. CO_2 reacts with La_2O_3 to form $La_2O_2CO_3$ (fast step) and the oxycarbonates react with carbon at the interface of the Ni–$La_2O_2CO_3$ particles (slow step) to produce CO. The inverse water-gas shift reaction occurs simultaneously. The kinetic model which is based on this mechanism predicts satisfactorily the kinetic results.

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