Mechanistic aspects of carbon dioxide reforming of methane to synthesis gas over Ni catalysts

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A study of the kinetic isotope effect ($CH_4/CO_2 \rightarrow CD_4/CO_2$) for carbon dioxide reforming of methane to synthesis gas shows that an isotope effect exists with k_{CH_4}/k_{CD_4} ratio of 1.05–1.97, depending on reaction temperature and catalyst applied. The attainment of stable performance over Ni/La_2O_3 catalyst is found to be related to the strong chemisorption of CO_2, weak chemisorption of CH_4 and slow rate of CH_x formation, and fast rate for CH_x removal by oxidation.

Keywords: methane, reforming of; kinetics of methane reforming; carbon dioxide, reactions of; isotopic labeling; nickel, catalyst; lanthanum oxide, catalyst carrier; natural gas, utilization of

1. Introduction

Synthesis gas (CO/H_2) is an important feedstock for the production of methanol and synthetic fuels [1] which is currently produced by catalytic steam reforming of natural gas. However, the synthesis gas produced by the steam reforming process has a high hydrogen to carbon monoxide ratio which is undesirable for certain applications [2]. In this respect, the process of dry reforming of methane (with carbon dioxide) is superior to that of steam reforming, because it produces synthesis gas with a low hydrogen to carbon monoxide ratio. Furthermore, the former process has other important advantages over the latter [2–4] and, for this reason, it is receiving increasing attention in recent years.

Numerous materials have been tested as potential catalysts for reforming of methane with CO_2, while Ni-based catalysts [5–9], as well as supported noble metal catalysts [10–15] have been found to exhibit promising catalytic performance in terms of methane conversion and selectivity to synthesis gas. The catalysts which are based on noble metals are reported to be more active and less sensitive to coking than Ni-based catalysts. However, a recent study conducted in this laboratory [16] shows that when Ni is supported onto a La_2O_3 carrier and properly activated, it can exhibit good activity and excellent stability, in sharp contrast to other Ni-based catalysts, such as Ni/Al_2O_3. It has been observed that the stable performance of the Ni/La_2O_3 catalyst can even be obtained at temperatures as low as 550°C, a temperature at which even supported noble metal catalysts suffer carbon deposition and deactivation [17]. It has been shown that this is due to the formation of a new type of surface structure on the Ni/La_2O_3 catalyst which is resistant to catalyst deactivation [18]. In the present study, the kinetic behavior of the reforming reaction over the Ni/La_2O_3 and Ni/Al_2O_3 catalysts is compared. The kinetic isotope effect ($CH_4/CO_2 \rightarrow CD_4/CO_2$) for carbon dioxide reforming of methane to synthesis gas is, for the first time, investigated over these catalysts. Primary purpose is to reveal any differences in the mechanistic scheme concerning conversion of CH_4/CO_2 to H_2/CO.

2. Experimental

The 17 wt% Ni/La_2O_3 and 17 wt% Ni/Al_2O_3 catalysts were prepared by the method of wet-impregnation, using $Ni(NO_3)_2$ as the metal precursor. Detailed procedures of preparation of these catalysts have been described elsewhere [16].

Kinetic studies were conducted under differential reaction conditions, using a total feed flow rate of 300 ml/min which was found experimentally to be sufficient to eliminate interparticle mass transport resistances. The conversion of methane was controlled to be less than 10% by adjusting the amount of catalyst (1–5 mg), which was in the form of powder (< 0.02 mm) and was diluted with α-Al_2O_3 powder (one portion of catalyst was diluted with five portions of α-Al_2O_3). The catalyst particle size (< 0.02 mm) was found experimentally to be small enough so as to eliminate internal mass transport limitations. A quartz tube with inner diameter of 3 mm was used as the fixed-bed microreactor. Temperature was measured by two thermocouples placed inside a thermowell which was running along the reactor length. One thermocouple was placed just prior to the catalyst bed and the second one in the middle of the catalyst bed. Under the present experimental conditions, the temperature difference registered by the two thermocouples never exceeded 5°C. The reactor effluent was analyzed by on-line gas chromatography. H_2/D_2, O_2, N_2, CO, CH_4/CD_4 and CO_2 were separated and analyzed by a Carbosieve SII column connected to a TC detector. The concentration of water was estimated from hydrogen and oxygen mass balances.

The influence of the partial pressure of CH_4 or CO_2 in the feed mixture on the kinetic performance was investigated by variation of the initial partial pressure of CH_4 (10–500 Torr) at a constant initial pressure of CO_2 (152 Torr) and by variation of the initial partial pressure of CO_2 (10–500 Torr) at constant pressure of CH_4 (152 Torr). It was used to keep the total pressure at 1 bar. For the studies of the kinetic isotope effect on the reaction rate, a feed consisting of $CH_4(CD_4)/CO_2/He = 5/5/90$ vol% was used. Rate limitations by external or internal mass transfer resistances were proven to be negligible under the present reaction conditions, by applying suitable criteria.

3. Results and discussion

3.1. General observation

The reaction of CO_2 reforming of methane to synthesis gas was studied over Ni/La_2O_3 and Ni/Al_2O_3 catalysts in the temperature range of 580–750°C. Fig. 1 shows the variation of reaction rate with time on stream, obtained at 750°C. It is observed that the reaction rate over the Ni/La_2O_3 catalyst first increases with time on stream, during the initial 2–5 h of reaction, and then tends to be essentially invariable with time on stream. In contrast, the reaction rate over the $Ni/\gamma\text{-}Al_2O_3$ catalyst exhibits continuous deactivation with time on stream. However, the rate of deactivation decreases when time on stream exceeds 5 h. This reaction state can then be treated as pseudo-steady state. The reaction rates over the $Ni/\gamma\text{-}Al_2O_3$ and Ni/La_2O_3 catalysts after 5 h of reaction differ somewhat but are still of the same order of magnitude. After having run the reaction for 5 h at 750°C, the reaction temperature is varied in the range of 580–750°C and the respective rate is recorded. The apparent activation energy, estimated from the Arrhenius equation, is found to amount to 72.7 kJ/mol and 62.7 kJ/mol over the $Ni/\gamma\text{-}Al_2O_3$ and Ni/La_2O_3 catalysts, respectively. This leads to the suggestion that the reaction over the Ni/La_2O_3 catalyst proceeds through a pathway with somewhat lower apparent activation energy requirements.

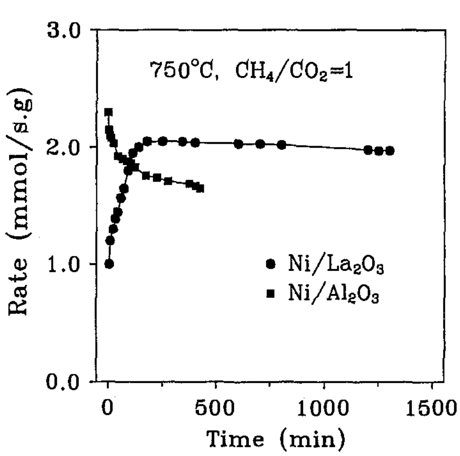

Fig. 1. Variation of reaction rate as a function of time on stream at 750°C over 17 wt% Ni/La_2O_3 and 17 wt% $Ni/\gamma\text{-}Al_2O_3$ catalysts. Reaction conditions: $F_{tot} = 300$ ml/min; $m_{cat} = 10$ mg; $CH_4/CO_2 = 1$, $P_{CH_4} = 152$ Torr, $P_{tot} = 760$ Torr, He as the balance gas.

3.2. Influence of partial pressure of CH_4 and CO_2 on rate of reaction

The influence of the partial pressure of CH_4 and CO_2 on the kinetics of carbon dioxide reforming of methane was studied over the $Ni/\gamma\text{-}Al_2O_3$ and Ni/La_2O_3 catalysts at 750°C, at atmospheric pressure. Prior to varying the individual partial pressures, the reaction was run for at least 5 h, under a constant feed composition ($CH_4/CO_2/He = 20/20/60$ vol%), so as to reach the stable performance of the Ni/La_2O_3 catalyst and the pseudo-stable performance of the $Ni/\gamma\text{-}Al_2O_3$ catalyst. It is observed that, within a fairly wide range of feed compositions (e.g. $CH_4/CO_2 = 0.5\text{–}2.0$), the rate of reaction changes rapidly upon increasing or decreasing the individual partial pressures and remains essentially invariable with time on stream between the measurements. However, when high partial pressure of methane ($CH_4/CO_2 > 2.0$) and high partial pressure of CO_2 ($CH_4/CO_2 < 0.5$) are used, the rate of reaction is found to decrease or increase with time on stream, respectively. These changes are much smaller and slower than the ones caused by changing feed composition. Therefore, the global behavior of the catalyst, as revealed by changing of the partial pressures of the reactants in the feed, is still valid even though the absolute experimental data suffer from small deviations.

Fig. 2 shows the influence of the initial partial pressure of CO_2 on the reaction rate obtained over the $Ni/\gamma\text{-}Al_2O_3$ and Ni/La_2O_3 catalysts at 750°C. The reaction rate is normalized with respect to the maximum rate observed over each of the two catalysts. Is is seen that the rate of reaction is rapidly increased with increasing CO_2 partial pressure at low P_{CO_2} and then tends to be almost constant at the high CO_2 partial pressure region. The rate of reaction over the Ni/La_2O_3 catalyst levels off at a relatively lower partial pressure of CO_2 (at 75–100 Torr) than the one over the $Ni/\gamma\text{-}Al_2O_3$ catalyst (at ca. 200 Torr), indicating that CO_2 chemisorption on the Ni/La_2O_3 catalyst is stronger than that on the $Ni/\gamma\text{-}Al_2O_3$ catalyst. This may be attributed to the basic nature of the La_2O_3 support which favors chemisorption of CO_2, in the form of, e.g. $La_2CO_2CO_3$. Fig. 3 shows the

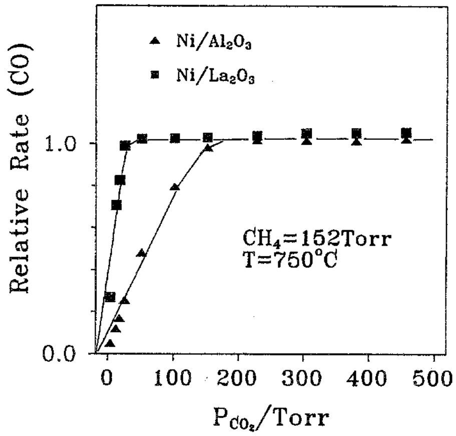

Fig. 2. Influence of the partial pressure of CO_2 on the reaction rate obtained over the Ni/γ-Al_2O_3 and Ni/La_2O_3 catalysts at 750°C. Reaction conditions: $F_{tot} = 300$ ml/min; $P_{CH_4} = 152$ Torr, $P_{tot} = 760$ Torr, He as the balance gas. The normalized reaction rate values refer to the maximum rate observed over the two catalysts.

influence of the initial partial pressure of CH_4 on the rate of reaction obtained over the Ni/γ-Al_2O_3 and Ni/La_2O_3 catalysts at 750°C. As in the previous case, the normalized rate is observed to rapidly increase with increasing CH_4 partial pressure at the low P_{CH_4} region and then to be constant at the high P_{CH_4} region. Although the kinetic differences between the Ni/γ-Al_2O_3 and Ni/La_2O_3 catalysts, shown in fig. 3, are not so significant as the ones shown in fig. 2, they are still quite discernible. It is noted that the reaction rate over the Ni/La_2O_3 catalysts starts to level off at higher partial pressures of CH_4 (ca. 220–300 Torr) than the one over the Ni/γ-Al_2O_3 catalyst (ca. 100–200 Torr). This observation suggests that the chemisorption of methane on the Ni/La_2O_3 catalyst is weaker than the one on the Ni/γ-Al_2O_3 catalyst.

The stronger chemisorption of CO_2 and weaker chemisorption of CH_4 on the working Ni/La_2O_3 catalyst, as compared to those on the Ni/γ-Al_2O_3 catalyst, should be related to the kinetic behavior of the two types of nickel catalyst (i.e. Ni/La_2O_3 and Ni/γ-Al_2O_3): the former offers a stable performance, while the latter exhibits continuous deactivation.

3.3. Kinetic isotope effect

The results of the kinetic isotope effect for the reaction of carbon dioxide reforming of methane to synthesis gas over the Ni/La_2O_3 and Ni/γ-Al_2O_3 catalysts are presented in table 1. Before switching the mixture from CH_4/CO_2/He to CD_4/CO_2/He, the reaction was run for at least 5 h to reach stable performance of the Ni/La_2O_3 catalyst and pseudo-stable performance of the Ni/γ-Al_2O_3 catalyst. It is shown in table 1 that the rate of CO formation (R_{CO}) over the Ni/La_2O_3 catalyst is significantly reduced upon replacing CH_4 with CD_4 in the feed mixture, indicating that breaking of the C–H bond of the CH_4 molecule is a slow step over the Ni/La_2O_3 catalyst. The value of the $R_{CO}^{CH_4}/R_{CO}^{CD_4}$ ratio over the Ni/La_2O_3 is found to be sensitive to the reaction temperature, increasing from 1.19 to 1.97 as temperature decreases from 750 to 650°C. The kinetic isotope effect for the rate of hydrogen formation (R_{H_2}) over the Ni/La_2O_3 catalyst is found to be weaker than the respective one for CO formation. While the $R_{CO}^{CH_4}/R_{CO}^{CD_4}$ ratio amounts to 1.31 at 700°C and 1.19 at 750°C, the respective values of the $R_{H_2}^{CH_4}/R_{D_2}^{CD_4}$ ratio amount to 1.12 at 700°C and 1.08 at 750°C. This might be attributed to the fact that the consumption of one methane molecule in the reaction results in the formation of one CO and two hydrogen molecules. As a consequence, the global observation of the kinetic isotope effect for H_2 formation is weaker than that for CO formation. In contrast to the case of the Ni/La_2O_3 catalyst, the rate of CO formation over the Ni/γ-Al_2O_3 catalyst is found to be only weakly affected by changing the CH_4/CO_2/He mixture to the CD_4/CO_2/He mixture (see table 1). A small but discernible reduction in the rate of CO formation over the Ni/

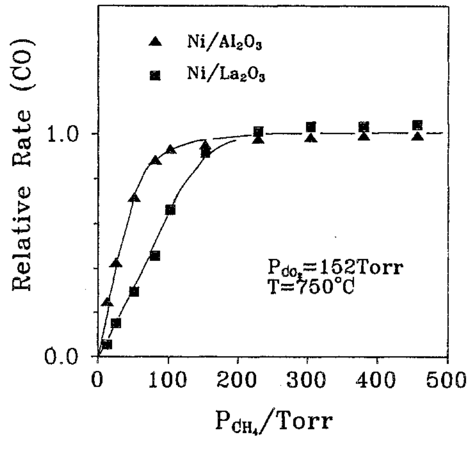

Fig. 3. Influence of the partial pressure of CH_4 on the reaction rate obtained over the Ni/γ-Al_2O_3 and Ni/La_2O_3 catalysts at 750°C. Reaction conditions: $F_{tot} = 300$ ml/min; $P_{CO_2} = 152$ Torr, $P_{tot} = 760$ Torr, He as the balance gas.

Table 1
Kinetic isotope effect for the reaction of carbon dioxide reforming of methane to synthesis gas over supported Ni catalysts

Catalyst 17 wt% Ni/	Temperature (°C)	k_{CH_4}/k_{CD_4} [a]	
		$R_{CO}^{CH_4}/R_{CO}^{CD_4}$	$R_{H_2}^{CH_4}/R_{D_2}^{CD_4}$
La_2O_3	650	1.97 ± 0.05	n.d. [b]
	700	1.31 ± 0.05	1.12 ± 0.05
	750	1.19 ± 0.05	1.08 ± 0.05
γ-Al_2O_3	580	1.08 ± 0.05	n.d.
	650	1.05 ± 0.05	n.d.
	700	1.04 ± 0.05	0.99 ± 0.05
	750	1.02 ± 0.05	1.02 ± 0.05

[a] k_{CH_4}/k_{CD_4} corresponds to the ratio of the rate obtained when using CH_4/CO_2 mixture to that when using CD_4/CO_2 mixture.
[b] n.d. implies that the concentration of H_2 and D_2 was too low to be accurately measured.

γ-Al_2O_3 catalyst is observed when CH_4 is replaced with CD_4, i.e. the value of the $R^{CH_4}_{CO}/R^{CD_4}_{CO}$ ratio amounts to 1.0–1.08. It is noted that this ratio is also temperature-dependent, increasing with decreasing temperature. However, no detectable kinetic isotope effect for the rate of hydrogen formation is observed over the Ni/γ-Al_2O_3 catalyst.

One of the major side-reactions of CO_2 reforming of methane is the reverse water–gas shift reaction ($CO_2 + H_2 \rightleftharpoons CO + H_2O$). This reaction involves the cleavage of H–H and H–O bonds, and is expected to be affected by replacing CH_4 with CD_4. Table 2 presents the results of the influence of the replacement of CH_4/CO_2/He with CD_4/CO_2/He on the product distribution, obtained over the Ni/La_2O_3 catalyst at 750°C. It is shown that the ratios $P_{CO}P_{H_2O}/P_{CO_2}P_{H_2}$ and $P_{CO}P_{D_2O}/P_{CO_2}P_{D_2}$ amount to 0.031 and 0.016, respectively, which are smaller than the corresponding thermodynamic equilibrium constants, which, at the stated conditions, are estimated to be equal to 0.80 and 1.11, respectively. These findings clearly demonstrate that the reverse water–gas shift reaction under the present conditions of CH_4 reforming with CO_2 is far away from thermodynamic equilibrium. Because of this, some kind of kinetic isotope effect for the reverse water–gas shift reaction is expected when CH_4 is replaced with CD_4. This is confirmed by the observation of a significant reduction in the concentration of water when CH_4 is replaced with CD_4, i.e. the ratio $P^{CH_4}_{H_2O}/P^{CD_4}_{D_2O}$ amounts to ca. 1.56. This implies that a significant kinetic isotope effect exists for the reverse water–gas shift reaction. Since the concentration of water produced under the conditions applied is one order of magnitude lower than the concentrations of H_2 and CO, i.e., the ratio of CO or hydrogen concentration to water concentration ranges from ca. 16 to ca. 23 (see table 2), the kinetic isotope effect for the reverse water–gas shift reaction is estimated to cause less than 5% alteration in CO and H_2 (or D_2) concentrations. Therefore, the global observation of the alteration of the formation rate of CO and H_2 (i.e. k_{CH_4}/k_{CD_4} in table 1) should not be due to the kinetic isotope effect for the side-reaction (reverse water–gas shift) but due to that of the major reaction of CO_2 reforming of methane to synthesis gas.

For the reaction of methane reforming with carbon dioxide, the most probable slow steps are those of methane activation to form CH_x ($x = 0$–3) species, and the reaction between CH_x species and the oxidant, either in the form of oxygen adatoms originated from CO_2 dissociation or CO_2 itself (including CO_2 activation). A previous FTIR study [15] showed that the surface carbon species on the working Ni catalysts contain no C–H bond, indicating that the surface carbon species are H-deficient (CH_x, x is equal to or close to zero). From the present kinetic isotope effect study, it becomes apparent that methane activation is the slow step over the Ni/La_2O_3 catalyst but is a relatively fast step over the Ni/γ-Al_2O_3 catalyst. Accordingly, it can be reasonably assumed that methane activation is the rate-determining step for the formation of synthesis gas over the Ni/La_2O_3 catalyst, while the reaction between surface carbon species (CH_x, $x = 0$) and the oxidant (including CO_2 activation) is the rate-determining step over the Ni/γ-Al_2O_3 catalyst. Considering the facts that the overall rates obtained over the Ni/La_2O_3 and Ni/γ-Al_2O_3 catalysts are of the same order of magnitude and that the apparent activation energy obtained over the Ni/La_2O_3 catalyst is smaller than that over the Ni/γ-Al_2O_3 catalyst, it can be further derived that the activation energy of the slow step, i.e. the reaction between the surface carbon species and the oxidant, over the Ni/γ-Al_2O_3 catalyst is larger than that over the Ni/La_2O_3 catalyst and that the energy for methane activation over the Ni/La_2O_3 catalyst is larger than that over the Ni/γ-Al_2O_3 catalyst. From the above assessment, it is clear that the step of CH_x formation is faster while the step of removal of the surface carbon species by reaction with the oxidant is slower over the Ni/γ-Al_2O_3, as compared to those over the Ni/La_2O_3 catalyst. This is also in line with the preceding results (figs. 2 and 3) which show that methane chemisorption is stronger and carbon dioxide chemisorption is weaker on the Ni/γ-Al_2O_3 catalyst than the respective processes on the Ni/La_2O_3 catalyst. Probably, this is the reason why the Ni/γ-Al_2O_3 catalyst exhibits continuous deactivation with time on stream, caused by excess carbon accumulation, while the Ni/La_2O_3 catalyst is capable of showing a stable performance, which may be due to establishment of equilibrium between the formation and the removal of the surface carbon species on the working catalyst surface [16].

Table 2
Influence of kinetic isotope effects on product distribution over the Ni/La_2O_3 catalyst at 750°C

$P^{CH_4}_{H_2}/P^{CH_4}_{H_2O}$	$P^{CD_4}_{D_2}/P^{CD_4}_{D_2O}$	$P^{CH_4}_{CO}/P^{CH_4}_{H_2O}$	$P^{CD_4}_{CO}/P^{CD_4}_{D_2O}$	$P^{CH_4}_{H_2O}/P^{CD_4}_{D_2O}$
15.9 ± 1.0	22.9 ± 1.0	17.9 ± 1.0	23.5 ± 1.0	1.56

4. Conclusions

The following conclusions can be drawn from the results of the present study.

(1) It is confirmed that the Ni/La_2O_3 catalyst exhibits good activity and excellent stability whereas the Ni/Al_2O_3 catalyst shows continuous deactivation with time on stream in the process of CO_2 reforming of methane to synthesis gas.

(2) The reaction rate is rapidly increased and then tends to be essentially constant with increasing partial pressure of CH_4 or CO_2 in the reaction mixture. CO_2 chemisorption is relatively stronger and CH_4 chemisorption is relatively weaker on the Ni/La_2O_3 catalyst as

compared to the respective processes on the Ni/Al_2O_3 catalyst.

(3) A reduction of the rate of CO formation, by a factor of 1.19–1.97, was observed over the Ni/La_2O_3 catalyst upon switching the reaction feed from CH_4/CO_2 to CD_4/CO_2, indicating that methane activation over the Ni/La_2O_3 catalyst is a slow step.

(4) Only a small reduction in the rate of CO formation, by a factor of 1.02–1.08, was detected over the Ni/Al_2O_3 catalyst upon switching CH_4/CO_2 to CD_4/CO_2, suggesting that methane activation over the Ni/Al_2O_3 catalyst is a fast step.

(5) The fact that the Ni/La_2O_3 catalyst exhibits stable performance while the $Ni/\gamma\text{-}Al_2O_3$ catalyst shows continuous deactivation by accumulation of excess carbon on its surface can be explained by the present results which show that the rate of CH_x formation is slower, and the rate of CH_x removal is faster while the adsorption of CO_2 is stronger, and the adsorption of CH_4 is weaker over the Ni/La_2O_3 catalyst compared to the respective parameters over the $Ni/\gamma\text{-}Al_2O_3$ catalyst.

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