

Kinetic study on the CH₄/CO₂ reforming reaction: Ni–H in Ni/α-Al₂O₃ catalysts greatly improves the initial activity

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Abstract

The Ni–H is proved to be formed in Ni/α-Al₂O₃ corresponding to the high temperature desorbed H in its H₂-TPD. Ni–H can be generated in Ni/α-Al₂O₃ either by the hydrogen reduction above 500 °C or during the in situ CH₄/CO₂ reforming reaction and it can also be eliminated by the treatment above 900 °C. Kinetic experiments show that the activity of the reforming reaction is initially increased with the amount of Ni–H in Ni/α-Al₂O₃ and finally it reaches one constant value due to the in situ regeneration of Ni–H. Pulse results indicate that Ni–H in Ni/α-Al₂O₃ is prone to form CH_x species with higher *x* value, which have higher activity for the reaction with CO₂. The catalysts with plentiful Ni–H show higher reaction rate and lower apparent activation energy (77 kJ/mol versus 143 kJ/mol) than those of the catalyst without Ni–H for the pulse of CO₂ after CH₄.

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Keywords: Ni–H; CO₂ reforming of CH₄; Initial activity of reforming reaction; CH_x reaction activity

1. Introduction

The CO₂/CH₄ reforming reaction is widely used to produce synthesis gas (CO and H₂), which can be further utilized in chemical energy transmission systems [1,2] or the Fischer–Tropsch reaction to produce liquids [3,4]. Industrial practice relies on Ni-based catalysts for their low cost and availability compared to the noble metals [5,6]. Due to Ni⁰ as the active center of the reaction, the Ni-based catalysts generally need to be reduced by hydrogen before the reactions [5,7]. It was always found the H species desorbed above 400 °C from the reduced Ni-based catalysts during the temperature program desorption (TPD) [8,9]. Then some questions come out here whether these hydrogen species in the reduced Ni also participate the reforming reaction and whether the hydrogen species influence the catalytic activity of Ni for the reforming reaction.

In fact, the high temperature desorbed H from the reduced Ni catalysts has been noticed before. Some groups consider the high temperature desorbed hydrogen as spillover H since they noticed

that hydrogen dissociated by Ni metal spills over the supports and involves the formation of hydroxyl groups on the surface of supports [10–12]. These supports are usually γ-Al₂O₃ or 5 Å molecular sieves and the formed hydroxyl groups promote the CH₄/CO₂ reforming reaction by activating CO₂. Our inspiration comes from that the used catalytic center Ni is actually one of the excellent metals used for storage hydrogen [13,14]. Once hydrogen is dissolved in Ni metal, Ni-vacancy–hydrogen is formed as Ni–H [15,16]. The formation of Ni–H will change the electronic property of Ni [17], which is different from the spillover H forming the surface hydroxyl groups. Therefore, there might be the different catalytic properties for the CH₄/CO₂ reforming reaction over the Ni catalyst involving Ni–H. Then we want to know whether the Ni–H can also be generated in the supported Ni catalysts during the H₂ reduction before reaction and whether the high temperature desorbed H species are also originated from the formed Ni–H in Ni-based catalysts.

Considering that both the spillover H and Ni–H show the high temperature desorbed H in the H₂-TPD, the spillover H over the Ni-based catalysts should firstly be avoided in order to investigate the influence of Ni–H on the reforming reaction. The formation of spillover H over catalysts is based on the support having big surface with plentiful surface hydroxyl groups, such as γ-Al₂O₃ [10–12]. Therefore, α-Al₂O₃ was selected as support

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for preparing Ni/ α -Al₂O₃ due to its much inert, small surface (2.1 m² g⁻¹) and few surface hydroxyl groups [18].

In this work, Ni–H is proved to generate in the reduced Ni/ α -Al₂O₃, accompanying with high temperature desorbed H species in H₂-TPD-MS. The formed Ni–H greatly improves the initial reaction rates for CH₄/CO₂ reforming reaction: Ni/ α -Al₂O₃ containing Ni–H shows the initial CH₄ conversion rate of 1.28×10^{-4} mol s⁻¹ g⁻¹, much higher than 0.54×10^{-4} mol s⁻¹ g⁻¹ for the same catalyst without Ni–H. Ni–H can also be in situ regenerated during the reforming reaction, therefore the latter rate is gradually increased to constant 1.28×10^{-4} mol s⁻¹ g⁻¹. The pulse results further reveal that the Ni–H improves the reforming reaction by increasing the x value of the intermediate CH_{*x*} species. However, the influence of Ni–H on the reforming reaction is usually not easy to be detected out during the steady state research. The higher reaction rate and lower activation energy for the CH₄/CO₂ pulse through Ni/ α -Al₂O₃ with plentiful Ni–H further demonstrate that the Ni–H improves the reforming reaction.

2. Experimental

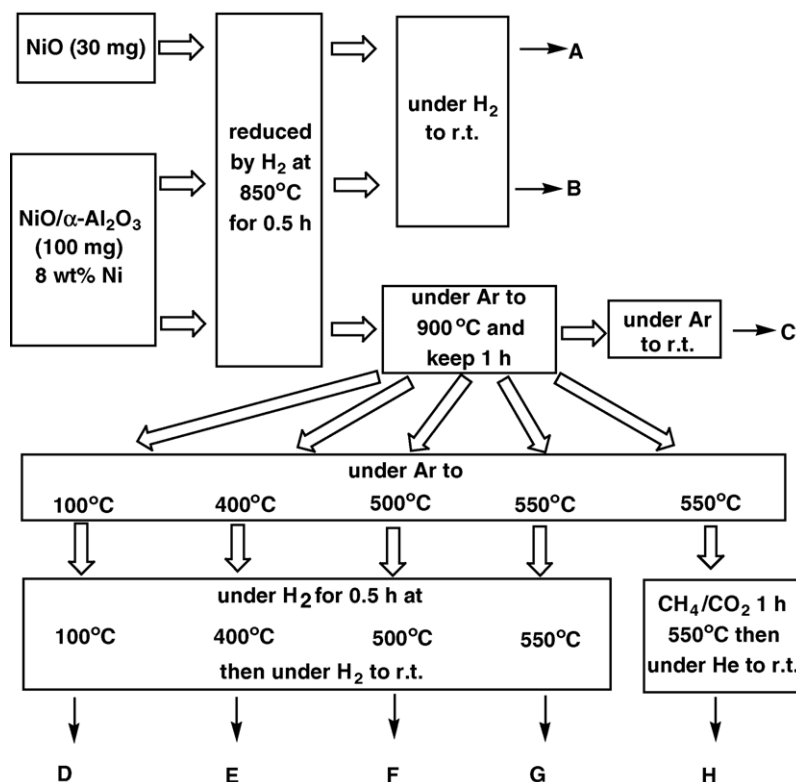
2.1. Catalysts and feed gases

All the catalysts were prepared by impregnating α -Al₂O₃ (2.1 m² g⁻¹, 100–160 meshes) with aqueous Ni(NO₃)₂·6H₂O for 12 h at room temperature (RT). Then the catalysts were dried at 120 °C for 3 h and calcined in air at 800 °C for 6 h. The

catalysts used for the CO₂/CH₄ reforming reaction are 8 wt% Ni/ α -Al₂O₃. CH₄ (99.995% purity), CO₂ (99.98% purity), N₂ (99.95% purity), He (99.99% purity), Ar (99.99% purity) and H₂ (99.99% purity) are used for the studies.

2.2. H₂-TPD

All the samples A–H below were analyzed by H₂-TPD-MS with an Ar flow of 30 ml/min and a rising temperature rate of 10 °C/min. The effluents from the reactor were on-line analyzed by GC–MS (GC Model 6890, carbon sieve as column, TCD as detector; MS 5973, three channels to detect H₂, H₂O and O₂). The sample A and catalysts B–H used for H₂-TPD tests are treated according to Scheme 1. Sample A is prepared by reduction of NiO (30 mg) by H₂ at 850 °C for 30 min then to RT under H₂. Catalyst B is obtained by the reduction of NiO/ α -Al₂O₃ (100 mg, 8 wt% Ni) by H₂ at 850 °C for 30 min then to RT under H₂. Catalysts C–H are treated as follows. All the NiO/ α -Al₂O₃ were first reduced by H₂ at 850 °C for 30 min then under Ar to 900 °C and kept for 1 h then: to RT under Ar to offer catalyst C; to 100 °C, 400 °C, 500 °C and 550 °C under Ar then reduced by H₂ for 30 min then to RT under H₂ to, respectively, give catalysts D–G; to 550 °C under Ar then treated by CH₄/CO₂ reforming reaction at 550 °C for 1 h then to RT under He to give catalyst H. All the sample A and catalysts B–H were tested by H₂-TPD-MS with Ar flow of 30 ml/min and the rising temperature rate of 10 °C/min. The TPD profiles of sample A and catalysts B–H are, respectively, shown as curves a–h in Fig. 1.



Scheme 1. The treatments of the sample A and catalysts B–H used for H₂-TPD.

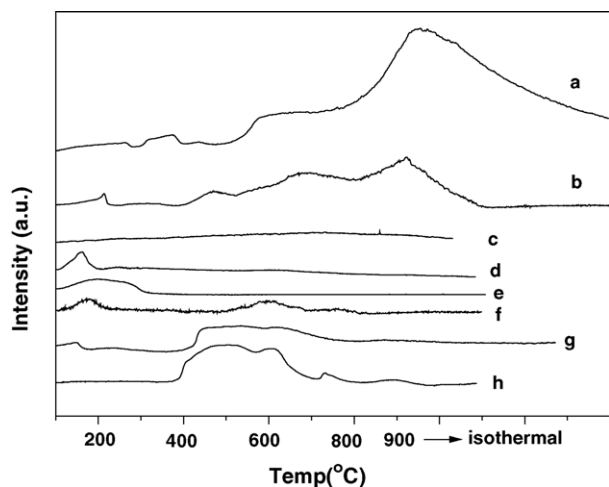


Fig. 1. The H₂-TPD of sample A and catalysts B–H.

2.3. X-ray diffraction (XRD) and H₂ chemisorption

XRD patterns were obtained with a Philips X'Pert Highscore powder diffractometer (Cu K α , 20° < 2 θ < 80°). The particle size of Ni can be calculated based on Scherrer equation. The exposed outer surface of Ni in Ni/ α -Al₂O₃ was measured by H₂ chemisorption at room temperature by assuming H/Ni atomic ratio of 1. The samples 8 wt% Ni/ α -Al₂O₃ were reduced at 850 °C for 0.5 h then decreased to 100 °C under Ar and kept for 20 min, and then further decreased to RT for in situ H₂ chemisorption measurements.

2.4. Kinetic studies

The apparatus employed for the kinetic measurements consists of a flow measuring and control system, a heated quartz tube differential reactor and an on-line gas chromatograph (Model 1102, TCD detector, carbon sieve as column). Feed flow rates were measured and controlled by mass flow meters. Reaction mixture of CH₄, CO₂ and N₂ in 5:5:90 (v/v/v) with a total flow rate of 360 ml/min (space velocity ca. 2,160,000 h⁻¹) was plugged into the quartz tube differential reactor containing 10 mg of catalyst at 550 °C under 1 atm. These catalysts were all treated with a He flow for 5 min at 550 °C before reactions in order to eliminate the influence of low temperature hydrogen species in H₂-TPD. The Con% (CH₄ and CO₂) and Sel% (H₂) was calculated based on the C, H and O balances. The Con% of CH₄ and CO₂ are kept in 4–10% (kinetic control), being far from the thermodynamic value of 60%. The reaction rates (shown as Fig. 4) are obtained using the initial rate method:

$$\text{For CH}_4 \text{ or CO}_2 : \text{ Reaction rate} = \frac{\text{Con\%} \times \text{flow rate}}{\text{catalyst mass}};$$

$$\text{For CO} : \text{ Reaction rate} = 2 \times \text{Rate}(\text{CO}_2) - 2 \times \text{Rate}(\text{CH}_4) \\ \times (1 - \text{Sel\%}(\text{H}_2)).$$

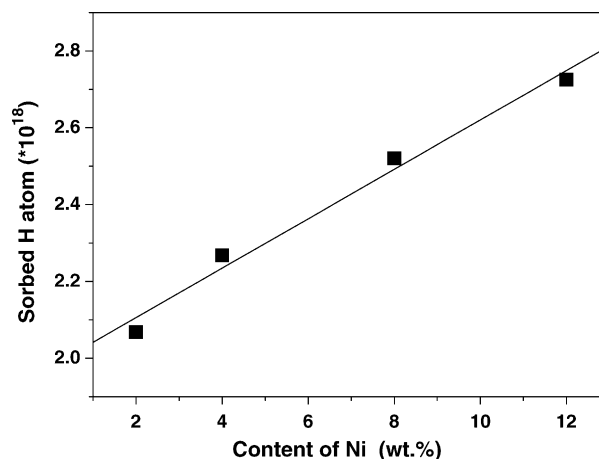


Fig. 2. The amount of H atoms sorbed in Ni/ α -Al₂O₃ is increased with the Ni content.

2.5. High temperature H₂ pulse and CH₄/CO₂ pulse reactions

A quartz tube of dimension of 6 mm o.d. \times 4 mm i.d. \times 40 cm length was used as a reactor. A thermocouple was introduced from the top of the reactor to measure the temperature of the catalyst bed. The H₂ pulse through 10 mg Ni/ α -Al₂O₃ (2 wt%, 4 wt%, 8 wt% and 12 wt% Ni) was carried out as follows. The fresh catalyst was used in every pulse. The catalysts were first reduced by H₂ at 850 °C for 30 min then to 900 °C under Ar and kept for 1 h then to 550 °C under Ar. Then H₂ was pulsed through these catalysts at 550 °C until H₂ sorption reaches the equilibrium. The total equilibrated amount of the sorbed H (Ni–H) in each catalyst can be calculated by summing the sorbed H in every H₂ pulse. The relationship between the H (Ni–H) amount and Ni content is shown in Fig. 2. Similarly, 10 mg Ni/ α -Al₂O₃ (8 wt% Ni) without Ni–H was pulsed by H₂ at different temperature (550 °C, 575 °C, 625 °C and 850 °C) until H₂ sorption reaches the equilibrium. The amount of H (Ni–H) versus the pulse temperature is shown in Fig. 3.

The catalysts (5 mg) and the high-purity Ar flow rate of 22 ml/min were used in order to keep the reforming reaction far away from the thermal equilibrium. All the catalysts were pre-treated by He at 550 °C for 5 min before the pulse reactions. The reactants and products were analyzed by an on-line GC (Model 103, TCD detector, carbon sieve as column) and the conversions (Tables 1 and 2) were calculated with N₂ as internal standard:

$$\text{Con\%}(\text{CH}_4) = \frac{(\text{CH}_4/\text{N}_2)_{\text{before pulse}} - (\text{CH}_4/\text{N}_2)_{\text{after pulse}}}{(\text{CH}_4/\text{N}_2)_{\text{before pulse}}} \\ \times 100\%;$$

$$\text{Con\%}(\text{CO}_2) = \frac{(\text{CO}_2/\text{N}_2)_{\text{before pulse}} - (\text{CO}_2/\text{N}_2)_{\text{after pulse}}}{(\text{CO}_2/\text{N}_2)_{\text{before pulse}}} \\ \times 100\%.$$

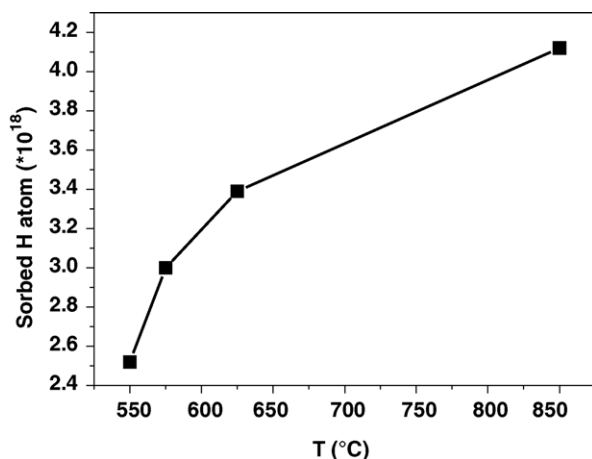


Fig. 3. The amount of H atoms sorbed in Ni/α-Al₂O₃ (8 wt%) is increased with the H₂ pulse temperature.

Table 1

The conversions for the pulse of CH₄ then CO₂ on catalysts B, G and C with different amount of Ni–H^a

Catalyst	Pulse	Conv. CH ₄ (%)	Conv. CO ₂ (%)
B	CH ₄	22.4	–
	CO ₂	–	19.0
G	CH ₄	21.5	–
	CO ₂	–	11.2
C	CH ₄	23.1	–
	CO ₂	–	0.0

^a Three catalysts are pulsed by CH₄ and then CO₂ with Ar as a carrier gas with a flow rate of 22 ml/min at 550 °C and the conversions are calculated according to the difference in its amount before and after the pulse.

2.6. Calculation of E_a

The conversions of CO₂ for the pulse CO₂ after CH₄ were tested in the range of 550–625 °C. The catalysts (5 mg) and the high-purity Ar flow rate of 22–33 ml/min were selected to keep the reforming reaction far away from the thermal equilibrium. The CO₂ reaction rates for the CO₂ pulse through the catalyst bed that has pulsed by CH₄ can be achieved from the conversions

Table 2

The conversions for the pulse of CO₂ then CH₄ and CO₂ again on catalysts B, G and C with different amount of Ni–H^a

Catalyst	Pulse	Conv. CH ₄ (%)	Conv. CO ₂ (%)
B	CO ₂	–	2.4
	CH ₄	23.9	–
	CO ₂	–	21.7
G	CO ₂	–	2.2
	CH ₄	23.2	–
	CO ₂	–	14.5
C	CO ₂	–	1.9
	CH ₄	22.5	–
	CO ₂	–	1.2

^a Three catalysts are pulsed by CO₂ then CH₄ and CO₂ again with Ar as a carrier gas with a flow rate of 22 ml/min at 550 °C and the conversions are calculated according to its difference in the amount before and after the pulse.

of CO₂ divided by contact time. Then the rates versus the different reaction temperature is shown as Fig. 5. The rate expressions for the reaction of CO₂ with adsorbed CH_x are shown as Eqs. (1)–(4). The apparent activation energy (E_a) for the reaction of CO₂ and adsorbed CH_x species on Ni sites was obtained by plotting the $\ln(\text{CO}_2 \text{ rates} \times \text{H}_2 \text{ chemisorption amount}/\text{CH}_4 \text{ conversion})$ versus the reciprocal of the pulse temperature (Fig. 6).

$$R_{\text{CO}_2} = A \exp\left(-\frac{E_a}{RT}\right) (P_{\text{CO}_2})^n C_{\text{CH}_x} \quad (1)$$

$$C_{\text{CH}_x} = \frac{\text{Conv. CH}_4\% \times \text{mol}_{\text{CH}_4}}{S_{\text{exposed Ni area}}} \quad (2)$$

$$S_{\text{exposed Ni area}} = 2 \text{mol}_{\text{H}_2 \text{ chemisorption}} \times S_{\text{Ni mol cross area}} \quad (3)$$

$$\ln R_{\text{CO}_2} = \text{Constant} - \frac{E_a}{RT} + \ln\left(\frac{\text{Conv. CH}_4\%}{\text{mol}_{\text{H}_2 \text{ chemisorption}}}\right) \quad (4)$$

3. Results and discussion

3.1. The formation of Ni–H in Ni/α-Al₂O₃

Fig. 1 shows the H₂-TPD profiles of sample A and catalysts B–H corresponding to the curves a–h. The hydrogen desorption temperature from the reduced pure Ni metal ranges from 400 °C to 900 °C (curve a), which is due to the formed Ni–H in Ni metal has high desorption temperature. The NiO/α-Al₂O₃ is reduced by H₂ to form Ni/α-Al₂O₃, which also gives the similar TPD profile with that of the Ni metal (curve b). Comparing the two TPD patterns of Ni metal and Ni/α-Al₂O₃, the areas of desorption peaks are almost consistent with the amount of Ni in Ni metal and Ni/α-Al₂O₃. These results indicate that the high temperature desorbed H from Ni/α-Al₂O₃ is greatly contributed to the amount of metal Ni.

Further experiments were also carried out to confirm where the high temperature H species come from. Firstly, the NiO/α-Al₂O₃ catalysts (8 wt% Ni) was pre-reduced by H₂ at 850 °C then was flowed by a Ar flow at 900 °C for 1 h and then kept under Ar to RT to form catalyst C. Its TPD profile (curve c in Fig. 1) shows that all the high temperature H species on catalysts have been eliminated. Then catalyst C without H species were pulsed H₂ again at 550 °C till saturation. The total amount of the sorbed H in catalyst C (8 wt%) can be determined as about $4.1 \times 10^{-4} \text{ mol g}^{-1}$. According to the results of H₂ chemisorption and XRD of Ni/α-Al₂O₃, the α-Al₂O₃ surface occupied by spherical Ni nano-particles is estimated $1.6 \text{ m}^2 \text{ g}^{-1}$. Then the left exposed α-Al₂O₃ surface is about $0.5 \text{ m}^2 \text{ g}^{-1}$ and the surface exposed oxygen atom is less than $3.8 \times 10^{-5} \text{ mol g}^{-1}$. Even if all the oxygen atoms are attached with H atoms, however, this case hardly happens because of the inert support surface of α-Al₂O₃, only $3.8 \times 10^{-5} \text{ mol g}^{-1}$ (<9%) H is sorbed on the support. Then we can conclude that the high temperature desorbed H species originated from the metal Ni.

Another series of experiments were also carried out to further confirm what the high temperature H species are. The NiO/α-Al₂O₃ catalysts with different Ni content (2 wt%, 4 wt% and 12 wt%) were also treated under the same conditions as that

of 8 wt%. Then the four catalysts (2 wt%, 4 wt%, 8 wt% and 12 wt%) without H species were again sorbed H₂ by H₂ pulses at 550 °C till the H₂ sorption saturation, where the sorbed H in the catalyst reaches its equilibrated amount. The amount of the sorbed H in every catalyst was found to linearly increase with the Ni content of Ni/α-Al₂O₃ (Fig. 2). The atom ratio of the sorbed H to the total Ni in catalysts was calculated as 0.3–0.4 for the pulse at 550 °C. And these four saturated catalysts show the high temperature desorbed H in their H₂-TPD. The ratio of the peak area almost agrees with the results of the H₂ pulse. Therefore, it can be experimentally confirmed that the high temperature desorbed H comes from Ni, rather than from the spillover H on the support, and these H species can be named Ni–H, which means presence of some interaction between Ni and H.

It should be mentioned here that Ni/α-Al₂O₃ (8 wt%) pulsed by H₂ at 550 °C till sorption equilibrium contains 4.1×10^{-4} mol g⁻¹ H, while the exposed Ni atom amount can be calculated as 2.4×10^{-4} mol g⁻¹. It is generally accepted that one exposed Ni atom adsorbs one H atom and this theory is especially used in the H₂ chemisorption measurement. Therefore, the Ni–H should also be present in the Ni nanoparticles of Ni/α-Al₂O₃. The linear relationship between the Ni–H amount and the total Ni amount in catalysts further proves the presence of Ni–H in the Ni particles. The influence of the pulse temperature (550 °C, 575 °C, 625 °C and 850 °C) on the equilibrated Ni–H amount was also investigated (Fig. 3). The Ni–H amount in Ni/α-Al₂O₃ catalyst (8 wt%) was found to increase with the increasing the pulse temperature.

The regeneration of the Ni–H was studied by a reduction of Ni/α-Al₂O₃ without Ni–H (corresponding to curve c in Fig. 1) by H₂ at 100 °C, 400 °C, 500 °C or 550 °C for 30 min. When the temperature is 100 °C or 400 °C, no Ni–H is observed from the TPD profiles of catalysts D and E (curves d and e in Fig. 1). It is found that the Ni–H appears again in the catalyst F with the reduction at 500 °C (curve f, Fig. 1), but the amount of Ni–H is lower than that of catalyst G reduced at 550 °C (curve g). The tendency is consistent with that of the H₂ pulse at different temperature (Fig. 3). If the catalyst without Ni–H is used to catalyze the CH₄/CO₂ reforming reaction at 550 °C for an hour, the Ni–H can be detected out again in catalyst H (curve h Fig. 1). This shows that the Ni–H can be regenerated either by the H₂ reduction at high temperature or during the reforming reaction itself.

3.2. Ni–H promotes the reforming reaction

The presence of Ni–H in Ni/α-Al₂O₃ will affect the electronic property of the catalyst, which might further affect the CH₄/CO₂ reforming reaction. Then the Ni/α-Al₂O₃ catalysts containing different amount of Ni–H (catalysts B–G) were tested for the CH₄/CO₂ reforming reaction by kinetic method. The CH₄ reaction rates for the reforming reaction over the different catalysts are shown in Fig. 4 CH₄. A constant rate of ca. 1.3×10^{-4} mol g⁻¹ s⁻¹ (b in Fig. 4 CH₄) is obtained for Ni/α-Al₂O₃ with plentiful Ni–H (catalyst B) corresponding to curve b in Fig. 1. When all the Ni–H was eliminated from the catalyst C just as curve c in Fig. 1, the initial rate of CH₄ conversion is greatly decreased to 0.54×10^{-4} mol g⁻¹ s⁻¹ at the initial 5 min (c in Fig. 4 CH₄). It is noticed that the rate is then slowly increased and finally it reaches the constant value of ca. 1.3×10^{-4} mol g⁻¹ s⁻¹ after an hour reaction. The increase in the CH₄ reaction rate can be due to the in situ regeneration of Ni–H in the fresh catalyst during the reforming reaction (curve h, Fig. 1), which maybe involves the surface reorganization [19]. Similar tendency of CH₄ rate (d and e in Fig. 4 CH₄) is obtained for the Ni/α-Al₂O₃ catalysts D and E without Ni–H corresponding to curves d and e in Fig. 1. The partial presence of Ni–H in the catalysts F and G, shown as curves f and g in Fig. 1, give the initial reaction rate of 0.72×10^{-4} mol g⁻¹ s⁻¹ and 1.16×10^{-4} mol g⁻¹ s⁻¹, respectively (f and g in Fig. 4 CH₄). And then the CH₄ conversion rate is again increased up to the constant value of 1.3×10^{-4} mol g⁻¹ s⁻¹ with the progress of the reaction.

These kinetic results clearly state that the initial CH₄ conversion rates much depend on the amount of Ni–H involved in Ni/α-Al₂O₃ catalysts. Similarly, the initial CO₂ conversion rates (Fig. 4 CO₂) are also increased with the amount of Ni–H in the catalysts and later reach a constant value of 1.47×10^{-4} mol g⁻¹ s⁻¹. The rates of CO formation on the above catalysts (Fig. 4 CO) are similar with those of CH₄ and CO₂. It can be concluded that the Ni–H indeed plays an important role in the improvement of CH₄/CO₂ reforming reaction, resulting in a higher initial reaction rates. The final constant reaction rates for the reforming reaction are due to that Ni–H can be in situ regenerated and reaches to a constant content during the reforming reaction.

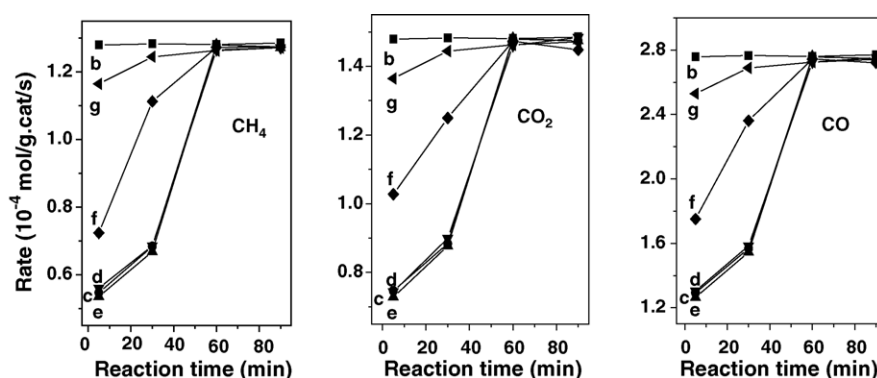


Fig. 4. The rates of CH₄, CO₂ and CO for the CH₄/CO₂ reforming reaction on the catalysts B–G with different amount of Ni–H.

3.3. The mechanism of Ni–H for the reforming reaction

In order to study how Ni–H in Ni/ α -Al₂O₃ affects the reaction performance, CH₄ and CO₂ pulse experiments were carried out on the catalysts with different amount of Ni–H. The catalysts **B**, **G** and **C** with the plentiful, some and no Ni–H were tested for the pulse experiments at 550 °C. Each of the three catalysts was pulsed by CH₄ followed by CO₂ and the conversions of CH₄ and CO₂ are listed in Table 1. The conversions of CH₄ are almost the same for the three catalysts (**B**: 22.4%, **G**: 21.5% and **C**: 23.1%). However, the succedent CO₂ pulse through the above CH₄-pulsed catalysts gives the completely different CO₂ conversions (**B**: 19.0%, **G**: 11.2% and **C**: 0.0%).

Another serial of pulse experiments were also carried out, in which the catalysts **B**, **G** and **C** were first pulsed by CO₂, followed by CH₄ then by CO₂ again and the pulse results are shown in Table 2. Almost the same conversions of CO₂ are achieved during the first pulse of CO₂ (**B**: 2.4%, **G**: 2.2% and **C**: 1.9%). The succedent CH₄ pulse through the above catalysts give the similar CH₄ conversions (**B**: 23.9%, **G**: 23.2% and **C**: 22.5%). When the above catalysts are exposed again to a CO₂ pulse, the large differences in the CO₂ conversions appear again (**B**: 21.7%, **G**: 14.5% and **C**: 1.2%, Table 2).

Both the pulse experiments show that Ni–H does not affect the pulse conversion of CO₂ or CH₄ alone, as well as the conversion of CH₄ after CO₂ pulse. But Ni–H greatly alters the conversions of CO₂ after CH₄ pulse. It has been reported that CH_{*x*} species are formed as the reaction active intermediate [5,20] over Ni/ α -Al₂O₃ during the CH₄ pulse. The different CO₂ conversion after CH₄ pulse can be due to the influence of Ni–H on the reaction between CO₂ and CH_{*x*} species. However, the almost same CH₄ conversions over the three catalysts mean the similar amount of CH_{*x*} species over each catalyst. The only reason for the different CO₂ conversions can be attributed to the different *x* value of the CH_{*x*} species on catalysts **B**, **G** and **C**. It has been reported that CH₄/CO₂ reforming activity is increased with increasing *x* value of CH_{*x*} intermediate [5,21]. Therefore, Ni–H must play a significant role in the formation of CH_{*x*} species with higher *x* value. It is different from the previous report that the spillover H on Ni-based catalysts improves reforming reaction by activating CO₂ [12].

The reforming mechanism is proposed as Eqs. (5)–(8). CH₄ is slowly dissociated to CH_{*x*} (Eq. (5)) [22]. The further dissociation of CH_{*x*} to CH_{*x*-1} is a quasi-equilibration reaction (Eq. (6)) [22]. Just as mentioned above, Ni/ α -Al₂O₃ without Ni–H is prone to sorb H till saturation in reforming reaction. In the pulse experiments, catalyst **C** without Ni–H will sorb H, just shown as the proposed Eqs. (7) and (8), resulting in CH_{*x*} species with smaller *x* value, while catalyst **B** with plentiful Ni–H will keep higher *x* value. Therefore, the presence of Ni–H on the Ni/ α -Al₂O₃ will offer CH_{*x*} species with higher *x* value, which leads to a higher activity for the reforming reaction. While the absence of Ni–H in catalyst presents the CH_{*x*} species with lower *x* value, resulting in a lower initial reaction activity. And the Ni–H will be in situ formed during the reforming reaction, accompanying

the increase in the reaction activity.



3.4. Ni–H reduces the *E_a*

In order to further quantitatively identify what extent Ni–H affects CO₂ reforming reaction, the reaction rates of CO₂ with adsorbed CH_{*x*} species were calculated by pulsing CO₂ after CH₄ pulse from 550 °C to 625 °C. The catalyst **B** with plentiful Ni–H and catalyst **C** without Ni–H were selected. The catalyst **B** results in CH_{*x*} species with higher *x* values, while catalyst **C** produces the CH_{*x*} species with lower *x* values. We can see from Fig. 5 that the rates of CO₂ obtained for the catalyst **B** are all much higher than those for the catalyst **C** in the range of 550 °C to 625 °C. The formation of CH_{*x*} species with higher *x* values greatly improves the reaction rate of CO₂ reforming reaction.

CH_{*x*} species have been adsorbed on the exposed Ni sites and CO₂ reacts with them in the following CO₂ pulse. The function of the Ni–H species is to increase *x* value of the CH_{*x*} species and to improve the reaction rate. The rate expression of CO₂ is shown as Eq. (1), in which *A* is the pre-exponential factor for the reaction and *n* is the reaction order of CO₂. *A*, *E_a* and *n* are considered unchanged with the reaction temperature during the reaction. The *P*_{CO₂} is also constant because of the same volume of CO₂ for every pulse. The concentration of CH_{*x*} on the Ni surface can be expressed as Eqs. (2) and (3), where the mol amount of CH₄ used for every pulse and the mol mono-layer area of metal Ni are constant for every pulse. The conversions of CH₄ and the mol amount of H₂ chemisorption can be determined, respectively. Then the Eqs. (1)–(3) can be summarized as Eq. (4). The apparent activation energies (*E_a*) over the both catalysts **B** and **C** can be obtained by plotting the ln(CO₂ rates × H₂ chemisorption amount/CH₄ conversion) versus the reciprocal of

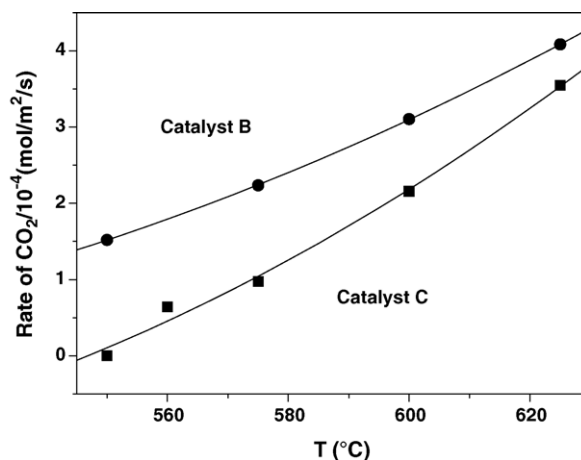


Fig. 5. The pulse reaction rates of CO₂ for the pulse of CO₂ with CH_{*x*} adsorbed on catalysts **B** with Ni–H (●) and **C** without Ni–H (■).

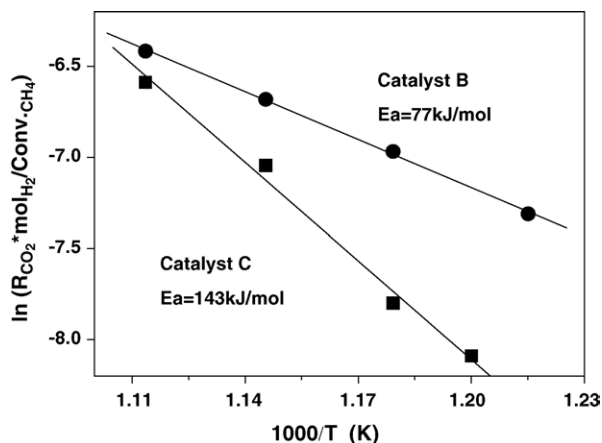


Fig. 6. The activation energy for the pulse reaction of CO₂ with CH_x adsorbed on catalysts **B** with Ni–H (●) and **C** without Ni–H (■).

the pulse temperature (Fig. 6). The E_a for the CO₂ pulse reaction with the adsorbed CH_x species can be estimated as 77 kJ/mol for catalyst **B** with Ni–H and 143 kJ/mol for catalyst **C** without Ni–H. It quantitatively shows that the catalyst with Ni–H can more effectively catalyze the reforming reaction of CO₂/CH₄ than that of without Ni–H.

4. Conclusions

The Ni–H can be formed in Ni/α-Al₂O₃ either by hydrogen reduction above 500 °C or during the in situ CH₄/CO₂ reforming reaction and it can also be eliminated by the treatment above 900 °C. The activity of the reforming reaction is initially increased with the amount of Ni–H in Ni/α-Al₂O₃ and finally it reaches one constant value due to the in situ regeneration of Ni–H. Ni–H greatly improves the reforming activity by increasing x value of CH_x species, which have higher activity for the reaction with CO₂. The catalysts with plentiful Ni–H show higher reaction rate and lower apparent activation energy than those of the catalyst without Ni–H for the pulse of CO₂ after CH₄. The formation of Ni–H in Ni/α-Al₂O₃ bridges the storage hydrogen of metal and catalytic activity of CH₄/CO₂ reforming reaction. The investigation on Ni–H in Ni-based catalysts

will open up new ways for a better understanding of reaction mechanism and catalyst design for the CH₄/CO₂ reforming reaction.

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