

Short communication

Potential of Ni supported on KH zeolite catalysts for carbon dioxide reforming of methane

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Abstract

The catalytic activity of Ni on a series of catalysts supported on the synthesized KH zeolite for the CO₂ reforming of methane has been investigated. The KH zeolite supports were previously synthesized via silatrane and alumatrane precursors using the sol–gel process and hydrothermal microwave treatment. Eight percent Ni was impregnated onto the synthesized KH zeolites, which have different morphologies: called dog-bone, flower, and disordered shapes. The prepared Ni/KH zeolites were tested for their catalytic activity at 700 °C, at atmospheric pressure, and at a CH₄/CO₂ ratio of 1. The results showed that Ni supported on dog-bone and flower-shaped KH zeolites provided better activity than that of disordered KH zeolite due to higher CH₄ and CO₂ conversions, a higher H₂ production, and a smaller amount of coke formation on the catalyst surface. Furthermore, the stability of the Ni/KH zeolite was greatly superior to that of Ni supported on alumina and clinoptilolite catalysts after 65 h on stream.

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1. Introduction

The CO₂ reforming of methane (CH₄) is an attractive way to utilize CO₂ [1–4] since it offers several advantages over steam reforming and a partial oxidation of CH₄: (1) it forms a suitable H₂/CO product ratio (nearly 1/1); (2) it reduces CO₂ and CH₄ emissions contributing to the greenhouse effect; and, (3) it is better used in chemical energy transmission. Moreover, since natural gas can contain up to 20–30% CO₂, it can be used as an independent source for the production of synthesis gas on the condition that some amount of any oxidizing agent (carbon dioxide or oxygen/water) is added.

However, the major obstacle preventing commercialization of this process is that, due to the endothermic nature of the process, a high operating temperature is required to attain high conversions. This condition is conducive to carbon deposition or coking and catalyst deactivation [3,5,6]. For this reason, a number of studies have been focused on the development of a coke-resistant catalyst for the CO₂ reforming of CH₄.

CO₂ reforming was first studied by Fischer and Tropsch in 1928 [7], in which Ni or Co was used as a catalyst. Since then, CO₂ reforming using a metal in group VIII (such as Ru, Rh, Pt, Ir, and Pd) as a catalyst have been investigated [8–10]. It was found that these noble metals have higher activity and stability for this reaction than other metals because of less sensitivity to carbon deposition, whereas Ni, Co, and Pd are deactivated by coking. However, considering the high cost and limited availability of noble metals, Ni could be a good practical choice for industrial purposes due to its ubiquity and lower cost, in comparison with noble metals.

Besides the metal, the catalyst support is also an important parameter for CO₂ reforming. Several studies have shown that the nature of the support employed influences the catalytic activity. Amorphous solids (such as SiO₂ [8,11], MgO [12,13], α -Al₂O₃ [14], Perovskite [15], CeO₂ [16], La₂O₃ [17]) and crystalline solids (such as zeolites [10,18,19]) were examined as the catalyst supports. Although many amorphous solid supports have been investigated and Al₂O₃ exhibited the highest initial activities, it is highly sensitive to coke formation. Therefore, it is of interest to investigate the activity of Ni supported on zeolite for the development of a Ni-based catalyst for the industrial applications of CO₂ reforming of CH₄.

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Zeolites have many potential properties for being supports for Ni catalysts in reforming reactions, such as their micropore structure, high surface area, and high affinity for CO₂ as adsorbents [19]. There are some reports that studied the utilization of zeolite as a support for Ni catalyst in dry reforming, such as Chang et al. [10] and Iwamoto et al. [18]. They reported that higher activity can be attained when using zeolite as a support. In addition, zeolite supports have the potential to deliver very high metal dispersion that is stable, combined with a low potential for support metal interaction, and they show superior coke resistance in the CO₂ reforming of CH₄. In our group, we successfully synthesized KH zeolite [20] from alumatrane and silatrane as the starting materials for the sol–gel process and obtained a hierarchical structure which resembles flower petals. This coincided with our investigation using Ni/clinoptiolite catalysts for the dry reforming of CH₄ showing the potential of zeolite [21]; therefore, we decided to study the effect of the zeolite support. Following these ideas, we used the KH zeolite as the catalyst support due to its basic property, which reduces coke formation or improves the stability for dry reforming of CH₄.

In this work, catalysts using KH zeolite as a basic support for CH₄ reforming with CO₂ reaction were studied. Then, a Ni supported KH zeolite (Ni/KH zeolite) was prepared by the incipient wetness impregnation method. The properties of the prepared catalysts, in terms of activity, catalyst stability, and coking resistance, are reported and compared to Ni/alumina and Ni/clinoptiolite catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

The KH zeolite was prepared by the sol–gel process using fumed silica (SiO₂, 99.8% purity, surface area of 473.5 m² g⁻¹) and aluminium hydroxide hydrate (Al(OH)₃, surface area of 50.77 m² g⁻¹) according to a method previously described [18]. Gel formation was studied at a molar ratio of SiO₂:0.1Al₂O₃:3K₂O:410H₂O. The solution mixture was aged for 12 h before being transferred to a Teflon-lined vessel (100 ml). The Teflon vessel was sealed with a Teflon cap and placed in a microwave oven (model MSP1000, CEM Corporation) (Spec. 1000 W and 2450 MHz), for hydrothermal treatment. The mixture was heated at 150 °C for 5 h. The obtained white precipitates were washed with distilled water and dried overnight at 75 °C.

Ni supported KH zeolites were prepared by impregnating the above synthesized KH zeolite with an appropriate amount of aqueous solution of Ni(NO₃)₂·6H₂O as the metal precursors. Firstly, the synthesized KH zeolite was calcined in air at 500 °C for 5 h before being impregnated with Ni(NO₃)₂·6H₂O to get an 8 wt% Ni loading with respect to the weight of the support. The catalyst was dried at 110 °C for 24 h and then calcined in air at 500 °C for 5 h.

For comparison, Ni/Al₂O₃ and Ni/clinoptiolite catalysts were prepared by impregnating supports with an appropriate amount of an aqueous solution of Ni(NO₃)₂·6H₂O. After the excess water was evaporated at 110 °C for 24 h, the catalysts were cal-

culated using the method mentioned above. For all catalysts, the loaded amount of Ni on the support was around 8%.

The crystallinity of the KH zeolite was characterized using the Powder X-ray diffraction (XRD) instrument. XRD patterns were obtained by a Rigaku power diffractometer system equipped with a RINT 200 wide-angle goniometer using nickel-filtered Cu Kα radiation (30 mA tube current, 40 kV tube voltage). The morphology of the aluminosilicate products were observed by using a JEOL 5200-2AE scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was employed to estimate the amount of carbon deposition that generally occurs with the dry reforming reaction after the deactivation tests at 700 °C on the spent catalysts. The weight loss from the combustion of the deposited carbon was observed under flowing air (50 ml min⁻¹) using the Du Pont TGA 2950 Thermogravimetric Analyzer at a temperature range of 30–800 °C with a heating rate of 10 °C min⁻¹.

2.2. Catalytic activity

The prepared catalysts were placed in a fixed bed reactor for the CO₂ reforming of CH₄ to study the activity and stability of the catalysts. The reactor was made of a 7 mm i.d. quartz tube ($H = 350$ mm) imbedded in an insulated electric furnace, equipped with a temperature programmable controller. A K-type thermocouple was inserted into the catalyst bed to measure and control bed temperature. Before catalytic measurement, the sample of 0.2 g was reduced in flowing hydrogen (99.99% purity) at 50 ml min⁻¹ for 1 h at 600 °C and then was purged with flowing helium at 100 ml min⁻¹ for 30 min to remove adsorbed hydrogen from the catalyst surface. CH₄ and CO₂ at a molar ratio of CH₄:CO₂ = 1:1 were introduced into the reactor at 700 °C, atmospheric pressure, with a space velocity of total gas mixture (GHSV) of 30,000 h⁻¹. The concentration of input reactants and output products were analyzed using a Hewlett Packard 5890 Series II gas chromatograph. The column utilized in the chromatograph was a Carbosphere, 80/100 mesh, 10 ft × 1/8 in. stainless-steel packed column. The conversions of CH₄ and CO₂, selectivity of H₂ and CO are defined as follows:

$$X_{\text{CH}_4} = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100$$

$$X_{\text{CO}_2} = \frac{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100$$

$$S_{\text{H}_2} = \frac{1}{2} \frac{[\text{H}_2]_{\text{out}}}{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}} \times 100$$

$$S_{\text{CO}} = \frac{[\text{CO}]_{\text{out}}}{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}} + [\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}} \times 100$$

where [CH₄]_{in} and [CO₂]_{in} are the flow rates of the introduced reactants and [CH₄]_{out}, [CO₂]_{out}, [H₂]_{out}, and [CO]_{out} are the flow rates of the corresponding compositions in the effluents. No by-products were observed in this experiment.

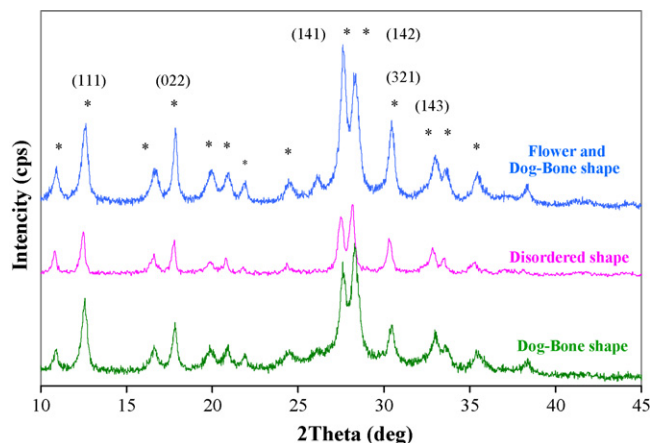


Fig. 1. XRD patterns of KH zeolites synthesized from $\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$ at 150°C and 5 h hydrothermal conditions.

3. Results and discussion

3.1. KH zeolite characterization

Fig. 1 shows the XRD patterns of the synthesized KH zeolite, which closely match that of KH zeolite reported in the literature [18]. It is apparent that the XRD pattern consists of 15 main reflections corresponding to (1 1 1), (0 2 2), (1 4 1), (1 4 2), (3 2 1), and (1 4 3) planes. The intensities of the XRD patterns characteristic of KH zeolite decrease significantly in the order of flower-shaped KH zeolite > dog-bone-shaped KH zeolite > disordered KH zeolite. The XRD result confirms that KH zeolite was successfully synthesized. The SEM micrographs shown in Fig. 2(a–c) indicate the morphology of disordered, dog-bone and flower shapes of the synthesized KH zeolites, respectively, with estimated diameters of $13\ \mu\text{m}$.

For the disordered KH zeolite (Fig. 2a), there could be the presence of some octahedral aluminum atoms causing defects in the framework and generating grains or a different orientation in the polycrystalline solid. During the zeolite framework formation, uniform needle-like single crystals are produced and dog-bone-shaped and flower-shaped polycrystals are eventually formed (Fig. 2b and c).

3.2. Effect of KH zeolite morphology on catalytic activity

Three different morphologies of synthesized KH zeolites were selected to study the effect of morphology on the catalytic activity for the CH_4 reforming with CO_2 reaction. Eight percent Ni was loaded onto disordered, dog-bone, and flower-shaped KH zeolites using the incipient wetness impregnation method. Activity testing was performed at 700°C for 5 h. The activity results of the three prepared samples are shown in Fig. 3.

As depicted in Fig. 3, the synthesized KH zeolites give very high activity on both CH_4 and CO_2 conversions of $\sim 85\text{--}95\%$ and $\sim 85\text{--}90\%$, respectively. No significant difference in CO_2 activity was observed for all of the Ni supported on the three different morphologies KH zeolite after long testing times. However, the CH_4 conversion of Ni supported on the disordered KH zeolite

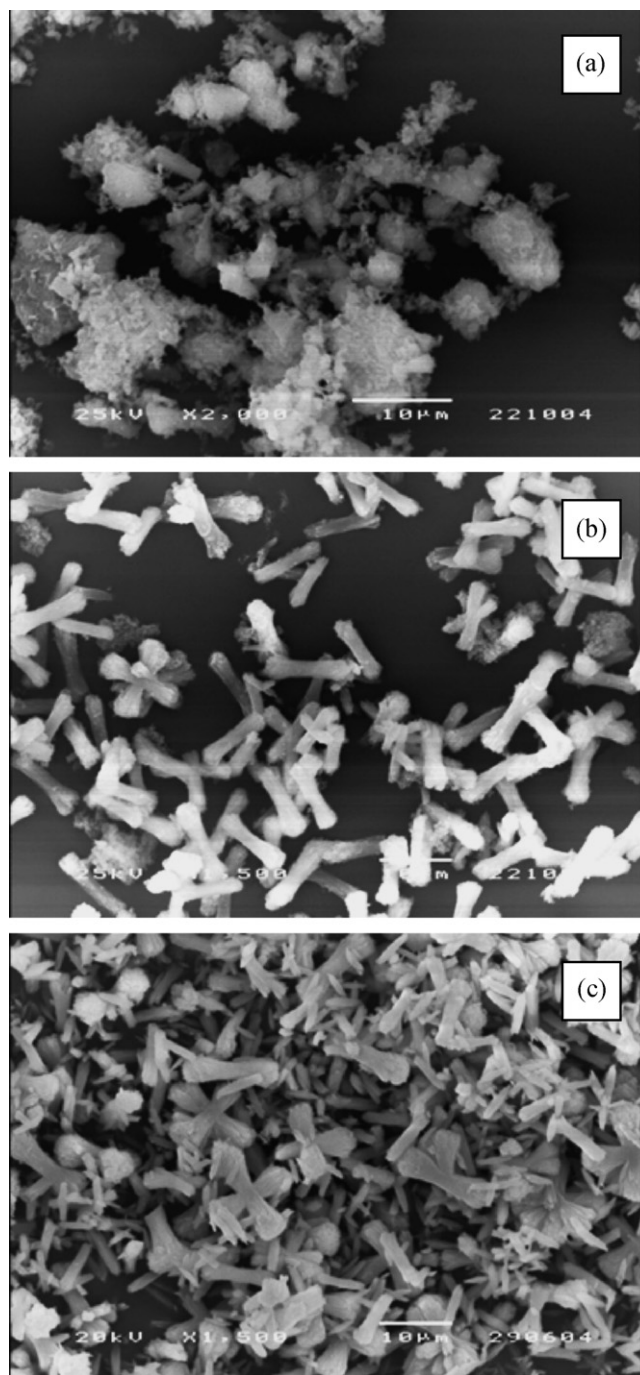


Fig. 2. SEM micrographs of KH zeolites at different morphologies synthesized from $\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$ at 150°C and 5 h hydrothermal conditions: (a) disordered, (b) dog-bone-shaped, (c) flower-shaped.

seemed to be lower than those of Ni supported on the other two KH zeolites. In other words, Ni/flower-shaped KH and Ni/dog-bone-shaped KH did not give much different activity to convert both CH_4 and CO_2 to CO and H_2 . This might result from the fact that the flower-shaped morphology was destroyed by the grinding force during catalyst preparation, and each petal of the flower became isolatable, presented as a dog-bone. Therefore, almost no difference in catalytic activity was observed, whether Ni was supported on flower-shaped or dog-bone-shaped KH zeolite.

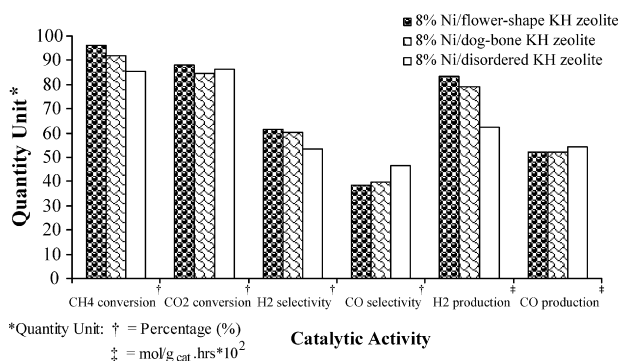


Fig. 3. Effect of KH zeolite morphology on the CO₂ reforming of CH₄ (reaction conditions: $T = 700\text{ }^{\circ}\text{C}$, $\text{CH}_4:\text{CO}_2 = 1:1$, GHSV $30,000\text{ h}^{-1}$ and reaction time = 5 h).

The results of H₂ selectivity and H₂ production also followed the trend of CH₄ conversion, since the majority of H₂ was produced by CH₄ dissociation. For CO selectivity, a higher percentage was observed for Ni/disordered KH zeolite; however, it provided lower H₂/CO ratio. Table 1 shows the comparison of H₂/CO ratio produced from the three Ni supported on different morphology KH zeolites. For Ni/flower-shaped and Ni/dog-bone-shaped KH zeolites, it is obvious that both catalysts can provide a higher ratio of H₂/CO than one with the same quantity. On the other hand, Ni/disordered KH zeolite gave a lower H₂/CO ratio, which means less profit on H₂ production. Therefore, it can be concluded that the morphology can affect CH₄ reforming activity; and the flower-shaped KH zeolite is suggested as the suitable support for this reaction, since it can give the highest CH₄ conversion, and H₂ production.

3.3. Effect of KH zeolite morphology on coke formation

Coke formation in the CO₂ reforming of CH₄ is generally known to cause catalyst deactivation. Thermogravimetric analysis (TGA) was employed to estimate the amount of carbon deposition. Fig. 4 shows the effect of KH zeolite morphology of spent catalysts on the coke formation. The results show that the carbon deposition on spent 8% Ni supported on flower-shaped and dog-bone-shaped KH zeolites was lower than that on the spent 8% Ni supported on disordered KH zeolite. Additionally, the coke deposition and CO₂ conversion clearly disclosed a similar trend. According to thermodynamics, carbon deposition originates mainly from the Boudouard reaction (Eq. (1))

Table 1
Comparison of H₂/CO ratios produced from the three Ni supported on different morphology KH zeolites and Ni/ γ -alumina (at $700\text{ }^{\circ}\text{C}$, $\text{CH}_4:\text{CO}_2 = 1:1$)

Catalyst	H ₂ /CO ratio
8% Ni/flower-shape KH zeolite	1.58
8% Ni/dog-bone KH zeolite	1.50
8% Ni/disordered KH zeolite	1.18
8% Ni/ γ -alumina	0.82

Note: Theoretical H₂/CO ratio calculated from CH₄ reforming with CO₂ = 1.

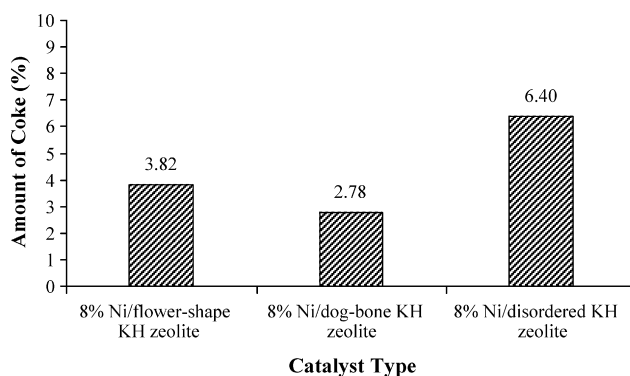
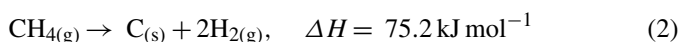


Fig. 4. The amount of coke formed of spent catalysts after catalytic testing for 5 h (reaction conditions: $T = 700\text{ }^{\circ}\text{C}$, $\text{CH}_4:\text{CO}_2 = 1:1$, GHSV $30,000\text{ h}^{-1}$).

and from methane decomposition (Eq. (2)) which are favorable under the conditions of CO₂/CH₄ reforming:



This can be explained in that the formation of coke may take place via the CO disproportionation (Boudouard reaction) instead of CH₄ decomposition because the coke deposition showed a different trend compared to CH₄ conversion.

The reaction mechanism might follow the mechanism proposed by Stagg et al. [22]; that is, CH₄ is initially decomposed into a carbon atom (C_(s)) and 2 mol of H₂. Subsequently, CO₂ in the feed reacts with C_(s) to produce 2 mol of CO, which further disproportionate to reproduce CO₂ and additional C_(s). If there is no further reaction involved in the mechanism, the CO₂ conversion should be low. The observed CO₂ conversion was, however, rather high (Fig. 3). Therefore, it is proposed that CO₂ is further reacted with H₂ to form CO and H₂O; the reversed water gas shift reaction. But, the H₂/CO ratio was greater than one (Table 1) which means that the water gas shift reaction only slightly takes place in the reaction.

In addition, our XRD patterns revealed that the high activity of Ni/KH zeolite catalysts were in the order of Ni/flower-shaped KH zeolite > Ni/dog-bone-shaped KH zeolite > Ni/disordered shaped KH zeolite. Generally, the deactivating coke was identified as a polymorphic form of graphite which develops as veils around the particles and tends to encapsulate them, therefore suppressing the access of reactants to the metal surface and the desorption of products. As seen in Figs. 2 and 4, we cannot speculate directly about the relationship between the morphology and coke since our results do not show sufficient detail. However, we noted that the SEM images show great differences in contrast among the large spherical and dog-bone and flower features, which means that the coke aggregated preferentially around the edges of the large particles; therefore, the disordered or different orientations in the polycrystalline solid of KH zeolite has the highest amount of coke while highly crystalline KH zeolite would hinder the formation of deactivating coke by limiting the carbon migration through the nickel particles. A possible explanation of this effect could be directly related to the catalyst

morphology, e.g. the influence of surface roughness, crystallinity or surface area related to the distribution of metal particles on the catalyst surface.

3.4. Comparison of KH zeolite with γ -alumina support

It has been generally observed that the nature of the support greatly affects catalytic performance in dry reforming [23]. In this work, we found that Ni/synthesized KH zeolite is active and stable for the dry reforming of CH_4 at elevated temperature; therefore, it was investigated and compared to Ni/ γ -alumina, which is a conventional catalyst. After loading with 8% Ni by incipient wetness impregnation on the support, both catalysts were tested for their activity and stability under the same conditions as previously mentioned.

Fig. 5 shows the activity results of KH zeolite and γ -alumina employed Ni supported catalysts under the studied conditions. It was found that Ni supported on synthesized KH zeolite provided excellent activity on CH_4 and CO_2 conversions. Moreover, its activity tended to be quite constant along the testing time (5 h). This indicated that the Ni particles being dispersed on the KH zeolite supports were very favorable for the improvement of the catalytic activity and stability, whereas Ni supported on the γ -alumina catalyst showed very poor activity and stability on both CH_4 and CO_2 conversions. It is suggested that rapid carbon for-

mation causes the deactivation of the catalyst since a higher coke deposition (4.48%) was obtained for 8%Ni/ γ -alumina compared to 3.82% for 8%Ni/KH zeolite (flower-shaped). Its initial activity was significantly lower than Ni supported on KH zeolite and it dramatically decreased as the time on stream increased.

In regards to the H_2 and CO selectivity, a comparison of H_2/CO ratios produced from the Ni/synthesized KH zeolite and Ni/ γ -alumina catalysts is shown in Table 1. All Ni/synthesized KH zeolite catalysts exhibited a H_2/CO ratio more than one, whereas the Ni/ γ -alumina catalyst initially provided a H_2 and CO selectivity around 50%, and its H_2 selectivity also dramatically decreased along time on stream. This result reveals that the Ni/ γ -alumina catalyst initially facilitated the reforming reaction and that deactivation occurs after the catalytic testing for 5 h, as clearly observed in Fig. 5.

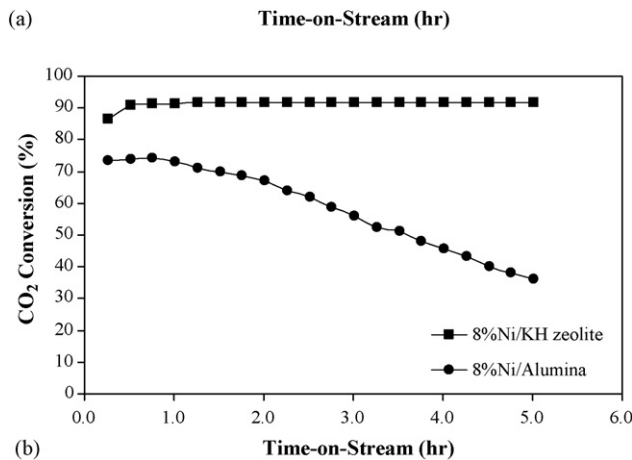
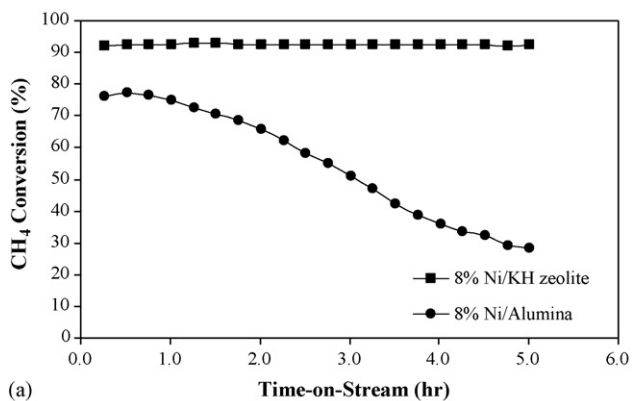


Fig. 5. Conversion of: (a) CH_4 and (b) CO_2 on 8% Ni/KH zeolite (flower-shaped) and 8% Ni/ γ -alumina (reaction conditions: $T = 700^\circ\text{C}$, $\text{CH}_4:\text{CO}_2 = 1:1$, GHSV $30,000\text{ h}^{-1}$ and reaction time = 5 h).

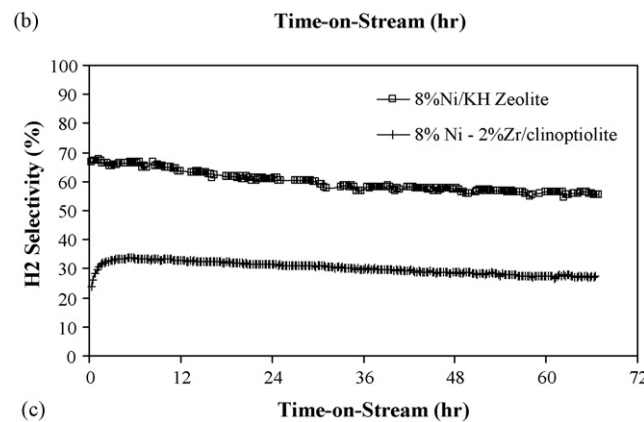
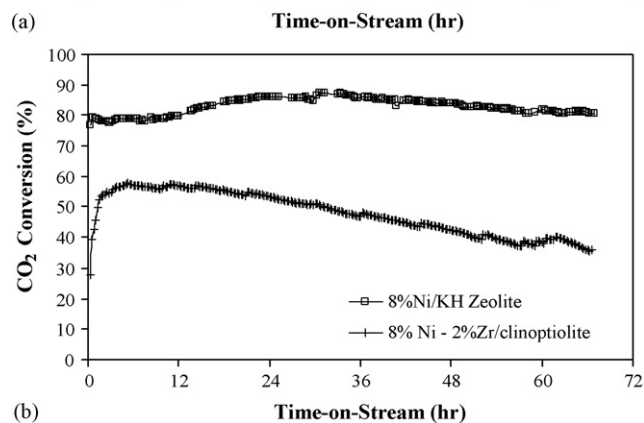
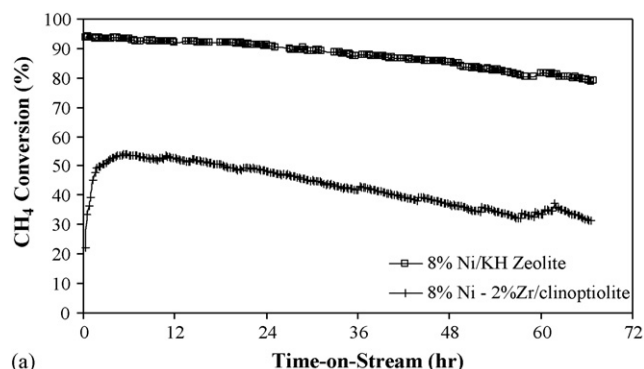


Fig. 6. Conversions of: (a) CH_4 , (b) CO_2 , and (c) H_2 selectivity of 8% Ni/KH zeolite (flower-shaped) and 8% Ni-2% Zr/clinoptiolite (reaction condition: $T = 700^\circ\text{C}$, $\text{CH}_4:\text{CO}_2 = 1:1$, GHSV $30,000\text{ h}^{-1}$ and reaction time = 65 h).

3.5. Stability of KH zeolite as compared to clinoptilolite

Thermal stability of the catalyst is the most important parameter for catalyst screening for appropriate applications or reactions. The carbon dioxide reforming of methane is a reaction that requires a high thermal stability catalyst for the prevention of carbon deposition. Therefore, the thermal stability of the Ni/KH zeolite catalyst should be compared to other supports such as clinoptilolite, which is a natural zeolite having a high affinity for carbon dioxide [21]. Eight percent Ni was loaded on both KH zeolite and clinoptilolite by using the incipient wetness impregnation method. The addition of a Zr promoter to 8% Ni/c clinoptilolite, in the method previously described, was employed to enhance the catalytic stability. The activity testing was performed at 700 °C for 65 h. A comparative study of 8% Ni/KH zeolite and 8% Ni-2% Zr/c clinoptilolite is shown in Fig. 6.

It is surprising that the 8% Ni/KH zeolite showed much higher outcomes than the 8% Ni-2% Zr/c clinoptilolite in terms of CH₄ and CO₂ conversions (Fig. 6a and b), and H₂ selectivity (Fig. 6c). All tendencies of the 8% Ni-2%Zr/c clinoptilolite and the 8% Ni/KH zeolite catalysts were quite constant with increasing time on stream; however, the 8% Ni/KH zeolite catalyst provided excellent H₂ production. Therefore, it is clear that the synthesized KH zeolite is a promising support for the CH₄ reforming with CO₂ since it gave much higher H₂ production and catalytic stability.

4. Conclusions

The morphology of KH zeolite affected the catalytic CO₂ reforming of CH₄; dog-bone and flower-shaped KH zeolites provided better activity than disordered KH zeolite in terms of CH₄ and CO₂ conversions, H₂ production, and coke formation. Furthermore, the Ni/synthesized KH zeolite catalyst provided the highest H₂/CO ratio compared to Ni/γ-alumina catalyst and Ni-2% Zr/c clinoptilolite. SEM and TGA analysis revealed that coke aggregates were clearly observed at surface defects, such as at the grain edges of the disordered KH zeolite, more than that of the dog-bone and flower-shaped KH zeolites. However, to correlate all the data obtained from the different morphologies and to understand the mechanism of coke formation, more detailed analysis is required.

It can therefore be concluded that the Ni/KH zeolite seems to be a promising catalyst to be used in fuel processors for fuel cell applications due to its hydrogen production and its high stability.

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