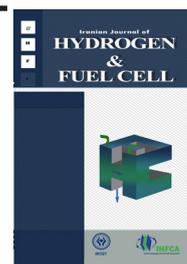


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Effect of K₂O on the catalytic performance of Ni catalysts supported on nanocrystalline Al₂O₃ in CO₂ reforming of methane

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Abstract

CO₂ reforming of methane (CRM) over unpromoted and potassium promoted Ni/Al₂O₃ catalysts was studied. The catalysts were prepared by the impregnation method and characterized by X-ray diffraction (XRD), N₂ adsorption (BET), temperature programmed reduction (TPR), temperature programmed oxidation (TPO) and scanning electron microscope (SEM) techniques. The obtained results showed that addition of K₂O to the Ni/Al₂O₃ catalyst increased surface area. Also, the addition of K₂O to this catalyst increased activity and decreased the amount of deposited carbon by enhancing the basic properties of the catalysts and CO₂ adsorption and preventing the Boudouard reaction. In addition, the effect of Ni and potassium loadings were investigated in Ni/K₂O-Al₂O₃ catalysts. It was observed that by increasing nickel content, the specific surface area decreased, but catalytic activity and coke formation increased. Also, catalytic tests showed that just a moderate amount of K could improve catalytic activity and decrease coke formation in the Ni/K₂O-Al₂O₃ catalyst in dry reforming of methane.

1. Introduction

In the last years, the CO₂ reforming of methane (1) has attracted increasing interest as it is a reaction that produces synthesis gas with a H₂/CO ratio close to unity, and contributes to the removal of methane and carbon dioxide, the two most important green-house gases [1-7].



However, deactivation of the catalyst creates difficulties for its application in the industrial level due to coke accumulation and sintering of both support and active metal particles [8-10]. Various catalysts have been developed for this reaction. Noble metals

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such as Pt, Rh, and Pd are reported to be active and fairly stable for the CO₂ reforming of CH₄. However, they are too expensive to utilize practically. Inexpensive transition metals such as Fe, Co, and Ni are also known to be active for the reaction to some extent, and among these Ni is the most favorable. The Ni-based catalysts have high activity and selectivity, but the major drawback of this reaction is the rapid deactivation of the catalysts as a result of carbon deposition. The origin of inactive carbon, C(s), during CO₂ reforming of methane may occur either via CH₄ decomposition (CH₄ → C + 2H₂) and/or the Boudouard reaction (2CO → C + CO₂) [8, 11-17].

The amount of deposited carbon can be affected by the nature of the support, the preparation method and the addition of promoters. Among the promoters, the alkali metal oxides (K₂O, Cs₂O, etc.) and alkaline earth metal oxides (MgO, CaO, BaO, etc.) are commonly chosen as support modifiers or promoters [16, 18-19]. The main objective of the present study was to investigate the effects of potassium oxide as a promoter for the Ni/Al₂O₃ catalyst in the dry reforming reaction. In addition, the effects of nickel and potassium contents were studied on the textural and catalytic performance.

2. Experimental

2.1. Catalyst preparation

The catalysts employed in the present work were prepared by the wet impregnation method. Nickel nitrate (NiN₂O₆·6H₂O) and KNO₃ were used as Ni and K precursors, respectively. γ-Al₂O₃, as catalyst support, was prepared by the sol-gel method. For this purpose, aluminum tri isopropylate (98% purity, Merck) was first hydrolyzed in distilled water by stirring for 1 hour at 80-85°C. Subsequently, HNO₃ was added dropwise with an HNO₃ to Al molar ratio of 1:1 and refluxed for 12h at 98°C. Then, the sol was kept for 2h at 98°C in air. After this step the sol became very viscous. The formed gel was dried overnight at 80°C and calcined at 600°C for 4h. Next, the prepared

γ-Al₂O₃ was impregnated with an aqueous solution of potassium salt with an appropriate concentration to obtain the desired content of potassium. After impregnation the promoted support was dried at 80°C overnight and calcined at 700°C for 4h. The promoted γ-Al₂O₃ was then impregnated with nickel nitrate with an appropriate concentration to get the desired content of nickel. Finally, the impregnated samples were dried at 80°C overnight and calcined at 500°C for 4h.

2.2. Characterization

The N₂ adsorption/desorption analysis was carried out at boiling temperature of nitrogen (-196°C) using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The samples were purged with nitrogen gas for 2h at 200°C using a VacPrep 061 degas system (Micromeritics). Temperature programmed reduction (TPR) analysis was used for evaluating the reduction properties of the prepared catalysts with Micromeritics chemisorb 2750 gas-adsorption equipment. In the TPR measurement, 200 mg of catalyst was subjected to a heat treatment (10°C/min) in a gas flow (30 ml/min) containing a mixture of H₂: Ar (10:90). Prior to the TPR experiment, the samples were heat treated under an inert atmosphere (Ar) at 200°C for 2h. The H₂ uptake amount during the reduction was measured using a thermal conductivity detector (TCD). Temperature-programmed oxidation (TPO) of the spent catalysts was carried out using a similar apparatus by introducing a gas flow (30 mL/min) containing a mixture of O₂: He (5:95) and the temperature was increased up to 800°C at a heating rate of 10°C/min. Scanning electron microscopy (SEM) analysis was performed with VEGA TESCAN operated at 30 kV.

2.3. Catalytic activity measurement

The catalytic activity measurements were carried out in a tubular fixed-bed continuous-flow reactor made of quartz (i.d. 8 mm) under atmospheric pressure. To control the catalyst bed temperature the thermocouple was introduced at the bottom of the catalyst bed.

The reactor was loaded with 200 mg of the prepared catalyst. Prior to the reaction, the catalysts were reduced in a H_2 gas flow of $20 \text{ mL}\cdot\text{min}^{-1}$ at 600°C for 2h. The reactant gas feed, consisting of CH_4 and CO_2 , was introduced into the reactor and the activity tests were performed at different temperatures, ranging from 550 to 700°C in steps of 50°C . The flow rates were controlled by Bronkhorst High-Tech mass flow meter/controllers EL-FLOW[®] Select Series. The loss in catalyst activity at 700°C was monitored up to a 5h time on stream. The gas composition of reactants and products were analyzed using a gas chromatograph (Varian 3400) equipped with a TCD and a Carboxen 1000 column.

3. Results and discussion

3.1. Structural properties of the catalysts

Physicochemical properties of the catalysts are summarized in Table 1. It is seen that all the samples possessed high specific surface areas up to $162 \text{ m}^2\cdot\text{g}^{-1}$. The average pore diameters of the samples were located in the range of 8.3 - 8.6 nm , which belong to mesoporous materials according to the definition of the IUPAC (2 - 50 nm) [5]. It is seen that the addition of a potassium promoter to the $5\%Ni/Al_2O_3$ catalysts decreased the S_{BET} and pore volume due to the blocking of some pores of support by potassium. Likewise, particle size increased with the addition of a potassium promoter.

Figures 1a and b show the nitrogen adsorption/desorption isotherms and pore size distributions of the prepared catalysts, respectively. For both samples, the isotherms can be classified as a type IV isotherm, typical of mesoporous materials. According to IUPAC

classification, the hysteresis loop is type H2. In this case pores can have non uniform size or shape [20]. As it is shown in Figure 1b, the pore size distributions of these catalysts are located between 5 - 17 nm . The XRD pattern of unpromoted $5\text{wt.}\% Ni/Al_2O_3$ catalysts is shown in Figure 2. As shown in this figure, the observed peaks at $2\theta = 37.2^\circ$ and 45.9° are assigned

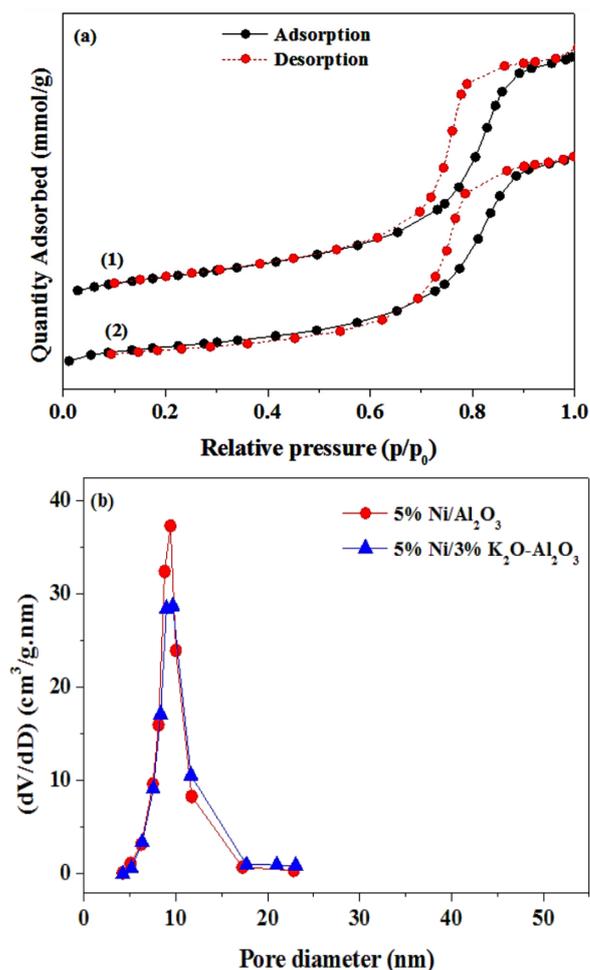


Fig. 1. (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of calcined catalysts.

to Al_2O_3 (JCPDS Card No. 01-1303). The peak at about $2\theta = 62^\circ$ is ascribed to the $NiAl_2O_4$ phase

Table 1. Structural properties of the catalysts

Catalyst	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Pore width (nm)	Particle Size ^a (nm)
$5\%Ni/Al_2O_3$	173	0.52	8.37	8.20
$5\%Ni/3\%K_2O-Al_2O_3$	162	0.46	8.62	8.86

^a calculated by $D=6000/(S_{BET}\cdot\text{density})$

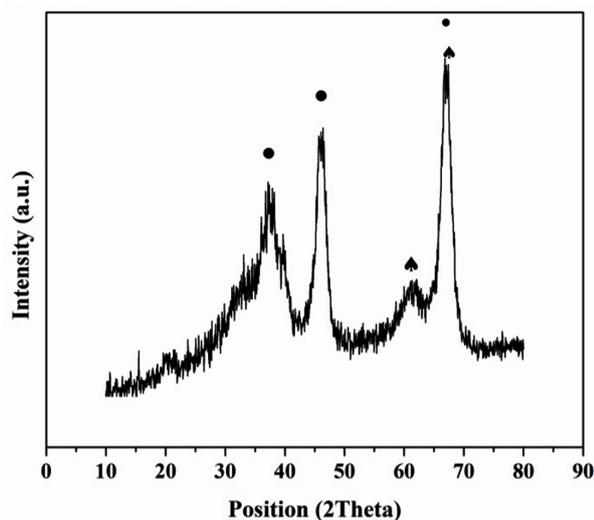


Fig. 2. The XRD pattern of 5wt.%Ni/Al₂O₃. (•) Al₂O₃, (▲) NiAl₂O₄.

(JCPDS Card No. 71-0963). The Al₂O₃ and NiAl₂O₄ phases are overlapped at $2\theta = 67^\circ$. Moreover, the diffraction peaks of the NiO phase were not detected in this catalyst due to the high dispersion of NiO on the support. For the promoted catalysts the diffraction peaks (not shown here) related to K₂O were probably not detected because of the low percentage of this promoter, which is in agreement with other published results [2, 21-22].

3.2. Temperature-programmed reduction (TPR)

TPR profiles of Ni/ γ -Al₂O₃ and K₂O promoted catalysts are displayed in Figure 3. The unpromoted catalyst showed two main reduction peaks in the TPR profile, while the K₂O promoted catalyst exhibited three main reduction peaks. The extra peak at 500°C in the promoted catalyst is attributed to NiO species with weak interaction with the catalyst support. In both catalysts, the first broad peak observed between 600-700°C can be ascribed to the reduction of NiO species with strong interaction with support. The second peak between 800-900°C is assigned to the reduction of NiAl₂O₄. This corresponds with other literature [19, 21-22]. It is obvious that by adding K₂O to the catalyst, the reduction temperature was shifted lower, which led to an improvement in catalyst reducibility.

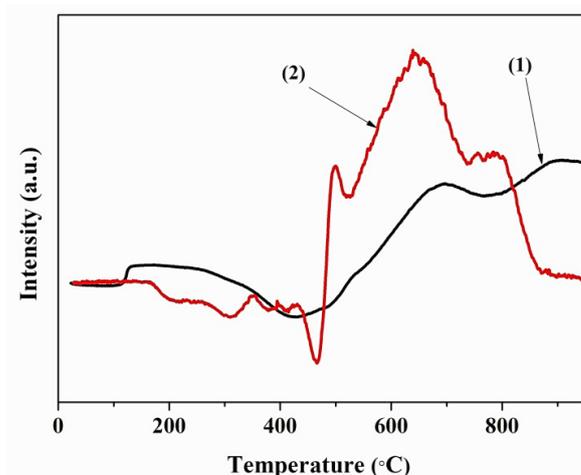


Fig. 3. TPR patterns of (1) 5%Ni/Al₂O₃, (2) 5%Ni/3%K₂O/Al₂O₃ catalysts.

3.3. Catalytic performance

The conversions of CH₄ and CO₂ are shown in Figure 4a and b, respectively. The results showed that with increasing reaction temperature, the conversions of CO₂ and CH₄ increased from 550-700°C due to the endothermic character of the CRM reaction. It is also obvious that the conversion of CO₂ is higher than that of CH₄ on the unpromoted and promoted catalysts due to the reverse water-gas shift reaction (CO₂ + H₂ ↔ CO + H₂O). As can be seen in Figure 4a and b, K₂O significantly improved the catalytic activity [23].

The H₂/CO molar ratios on both catalysts are displayed in Figure 4c. It is clear that the H₂/CO molar ratio for both catalysts is less than one because of the occurrence of the reverse water gas shift reaction. Meanwhile, by increasing the temperature, the endothermic dry reforming reaction proceeds better and hence the H₂/CO ratio increases.

A short time stability test was carried out at 700°C and the results showed that both the catalysts exhibited high stability during the test period of 300 min (Figure 5).

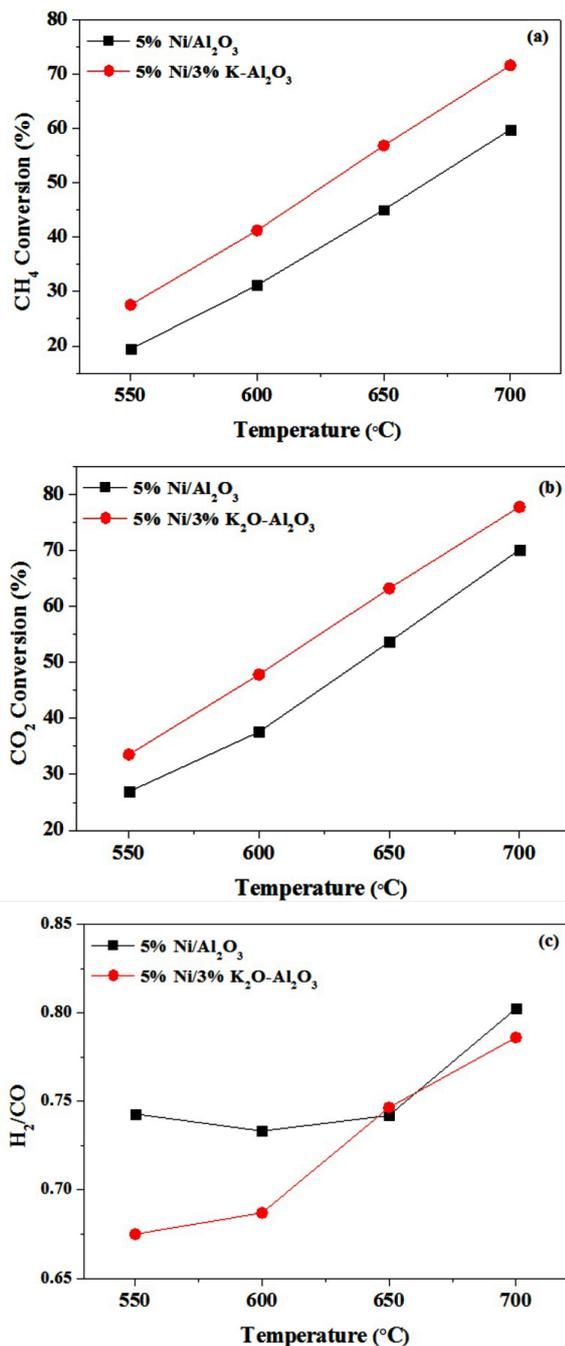


Fig. 4. (a) CH₄ conversion, (b) CO₂ conversion and (c) H₂/CO ratio. Reaction conditions: CH₄/CO₂=1/1, GHSV = 12000 (ml/h.g_{cat}).

3.4. Coke formation

3.4.1. Temperature-programmed oxidation (TPO)

Figure 6 shows the TPO profiles of the spent Ni/Al₂O₃

and Ni/K-Al₂O₃ catalysts. Three peaks appearing in the TPO profile of the unpromoted catalyst are attributed to different types of deposited carbon. They can be categorized as active carbon species or reaction intermediates that reacted with oxygen at low temperatures, amorphous and/or graphite forms of carbon and filamentous carbon, respectively. As can be seen, the addition of a potassium promoter to the Ni/Al₂O₃ catalyst decreased the amount of deposited carbon. The decrease in carbon formation is related to the enhancement of the basic properties of the catalysts and consequently increases the CO₂ adsorption capacity on the catalysts, which inhibits the CO decomposition reaction ($2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$) and suppresses the coke formation [14].

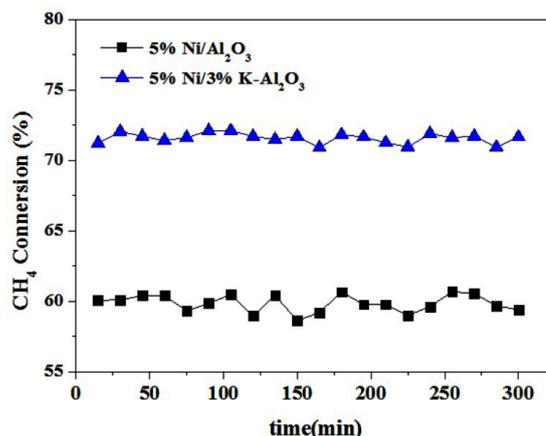


Fig. 5. Short time stability of the Ni/Al₂O₃, Ni/K-Al₂O₃ catalysts. Reaction condition: T = 700°C, CH₄:CO₂ = 1/1, GHSV = 12000 (ml/h.g_{cat}).

3.4.2. SEM analysis

Figure 7a and b shows the SEM images of the spent Ni/Al₂O₃ and promoted nickel catalysts, respectively. As can be seen, catalyst filamentous carbon was observed in the Ni/Al₂O₃, but no deposited carbon was observed in the potassium promoted catalyst. The SEM results showed that the addition of a K₂O promoter significantly decreased the amount of deposited carbon. These results are in agreement with those observed from the TPO analysis.

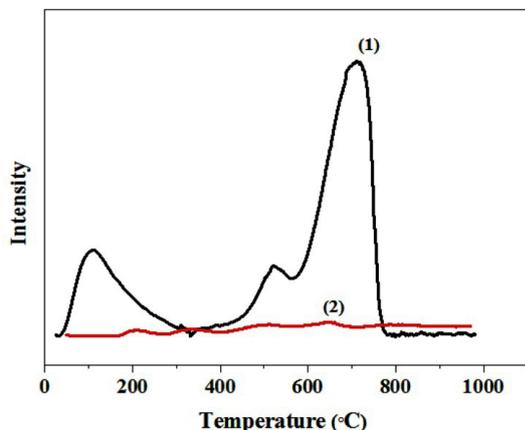


Fig. 6. TPO profiles of the spent (1) Ni/Al₂O₃ and (2) Ni/K-Al₂O₃ catalysts

3.5. Effect of nickel loading

3.5.1. Structural properties of the catalysts

The structural properties of the Ni/K₂O-Al₂O₃ catalysts with different Ni loadings are summarized in Table 2. As can be seen, when the Ni loading increased S_{BET} pore volume and pore diameter decreased but the particle size increased. Figure 8a displays the nitrogen adsorption/desorption isotherms of these catalysts. All the samples showed a IV type isotherm with a H2 shaped hysteresis loop, which indicated mesoporous features. The H2 shaped hysteresis loops also illuminated that all the mesopores were cylindrical-shaped channels with non-uniform pores [20]. The pore size distributions of these samples are presented in Figure 8b. It could be observed that the position of the peaks were located in the range of 5–17 nm.

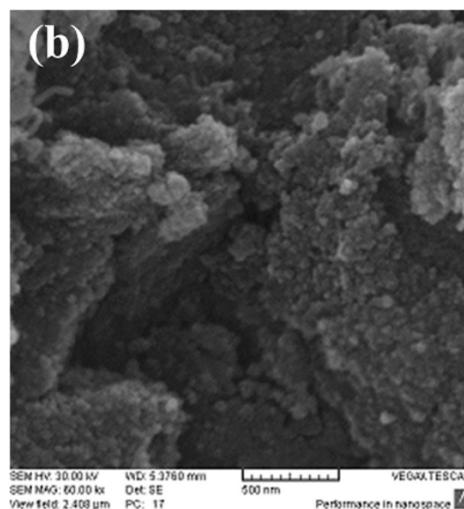
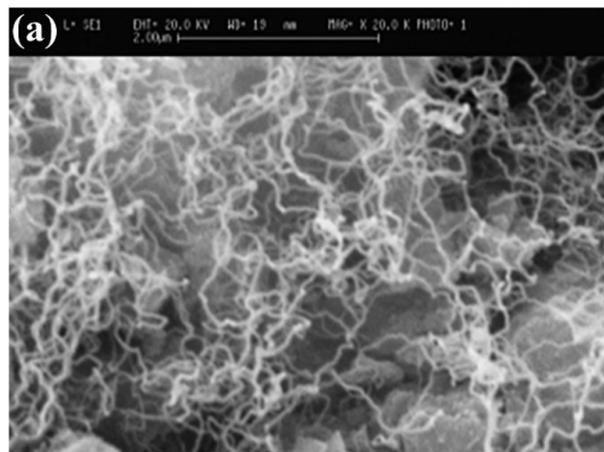


Fig. 7. SEM images of the spent (a) Ni/Al₂O₃, (b) Ni/K-Al₂O₃ catalysts. Reaction conditions: CH₄/CO₂=1, GHSV=12000 ml/g.h, time on the stream=300min.

3.5.2. Temperature- programmed reduction (TPR)

Figure 9 displays the TPR profiles of the fresh Ni/K₂O-Al₂O₃ catalysts with different nickel contents. Three reduction peaks were observed in the TPR profile

Table 2. Structural properties of the Ni/K₂O-Al₂O₃ catalysts with different nickel loadings

Catalyst	S_{BET} (m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹)	Pore width (nm)	Particle Size ^a (nm)
5%Ni/3%K ₂ O-Al ₂ O ₃	162	0.46	8.63	8.86
10%Ni/3%K ₂ O-Al ₂ O ₃	143	0.43	8.59	9.74
15%Ni/3%K ₂ O-Al ₂ O ₃	131	0.39	8.62	10.33
20%Ni/3%K ₂ O-Al ₂ O ₃	120	0.34	8.36	10.96

^a calculated by $D=6000/(S_{BET} \cdot \text{density})$.

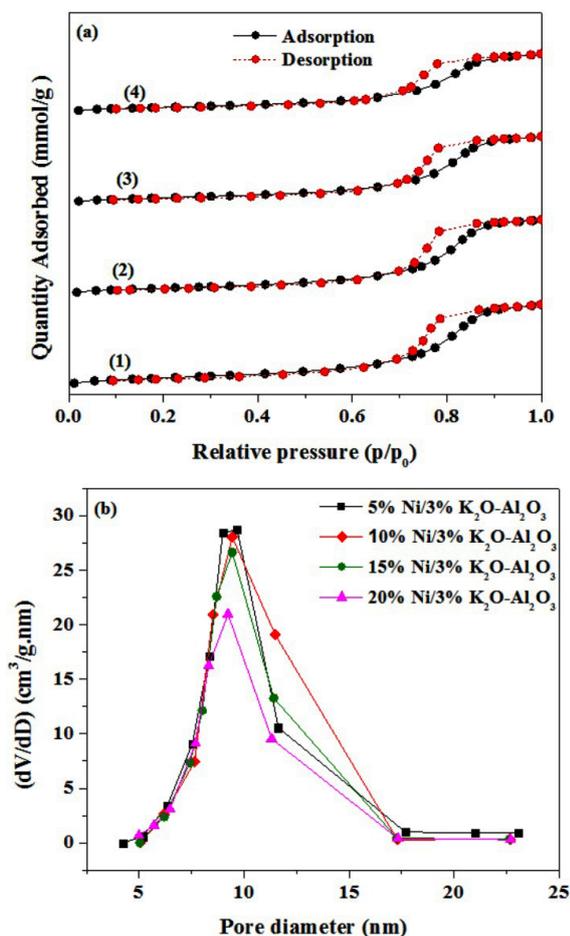


Fig. 8. (a) N_2 adsorption/desorption isotherms (b) and pore size distributions of the calcined catalysts.

of the catalysts with 5% and 10 wt% Ni. These peaks are assigned to NiO species with weak interaction with the support, NiO species with high interaction with the catalyst support and $NiAl_2O_4$ species, respectively. Four reduction peaks were detected in the catalysts with 15% and 20 wt% Ni. The first peak at 450-500°C is related to free NiO, the second one at 550-600°C is ascribed to NiO phases with weak interaction with the support, the third one at about 700°C is attributed to NiO species with high interaction with the catalyst support and the last low intensity peak is assigned to the reduction of $NiAl_2O_4$. As can be seen, as the Ni loading increased, the reduction temperature shifted to lower temperatures. It can be concluded that increases in Ni content increased the content of bulk NiO on the catalyst support and decreased the metal support interaction, which led

to an improvement in reducibility of the catalysts.

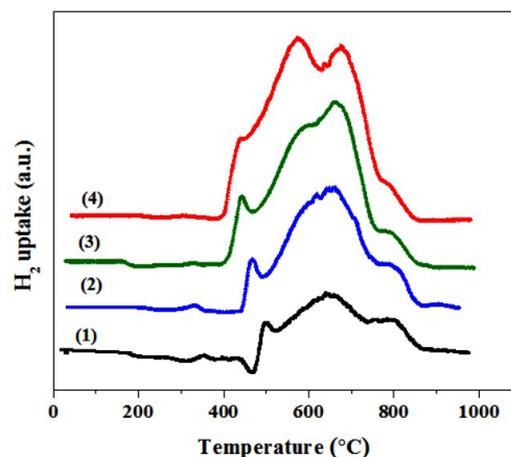


Fig. 9. TPR patterns of the Ni/ $K_2O-Al_2O_3$ catalysts with different Ni loadings. (1) 5%Ni/3% $K_2O-Al_2O_3$, (2) 10%Ni/3% $K_2O-Al_2O_3$, (3) 15%Ni/3% $K_2O-Al_2O_3$, (4) 20%Ni/3% $K_2O-Al_2O_3$.

3.5.3. Catalytic activity

The reactant conversion and H_2/CO ratio obtained for Ni/ $K-Al_2O_3$ catalysts with different Ni loadings are shown in Figure 10a and b. It is seen that increases in the reaction temperature increased the conversions of CO_2 and CH_4 due to the endothermic nature of the CRM reaction. It is also obvious that the conversion of CO_2 is higher than that of CH_4 due to the reverse water-gas shift reaction ($CO_2 + H_2 \leftrightarrow CO + H_2O$). It was found that the conversion of CH_4 and CO_2 increased as the Ni loading increased from 5% to 20 wt.%, suggesting that more active sites were provided with the increase in Ni loading.

3.5.4. Temperature programmed oxidation(TPO)

Figure 11 shows the temperature programmed oxidation of the spent Ni/ $K-Al_2O_3$ catalysts with different nickel loadings. It is seen that only one oxidation peak was detected for all the catalysts, corresponding to the filamentous carbon [24]. The obtained results showed that with an increase in Ni loading the intensity of the peak in these profiles increased because of an increase in the amount of deposited carbon. The highest amount of coke deposition was observed over the 20wt%Ni/3wt%K- Al_2O_3 catalyst. The increase in the

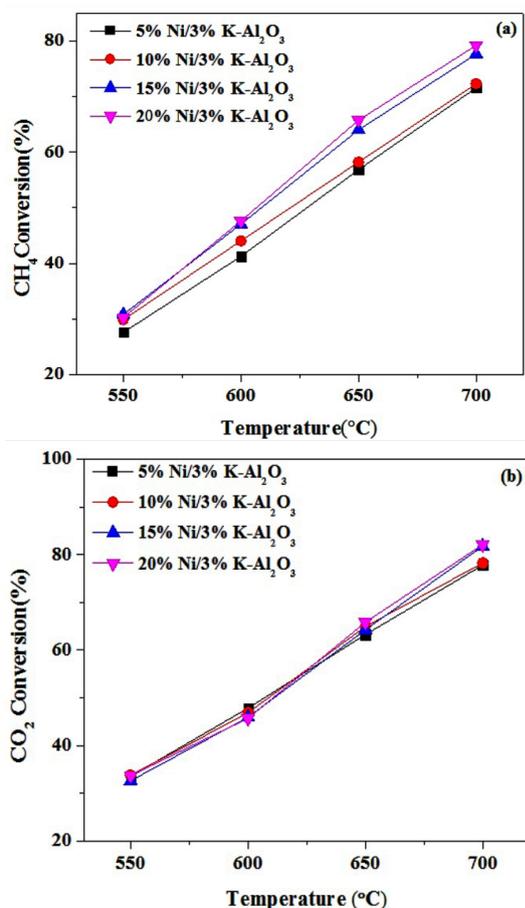


Fig. 10. (a) CH₄ conversion, (b) CO₂ conversion and (c) H₂/CO ratio. Reaction conditions: CH₄/CO₂=1:1, GHSV=12000 (ml/h.g_{cat}).

coke deposition on the catalysts with higher nickel loadings could be related to the larger particle size and lower Ni dispersion [25].

3.5.5. SEM analysis

The SEM images of the spent 5%Ni/3%K-Al₂O₃ and 15%Ni/3%K-Al₂O₃ catalysts are shown in Figure 12a and b, respectively. As can be seen, the filamentous carbon formation is increased when the Ni loading increased from 5 to 15 wt.% due to lower dispersion of nickel in 15%Ni/3%K-Al₂O₃ compared with 5%Ni/3%K-Al₂O₃ catalyst. This is in agreement with TPO results.

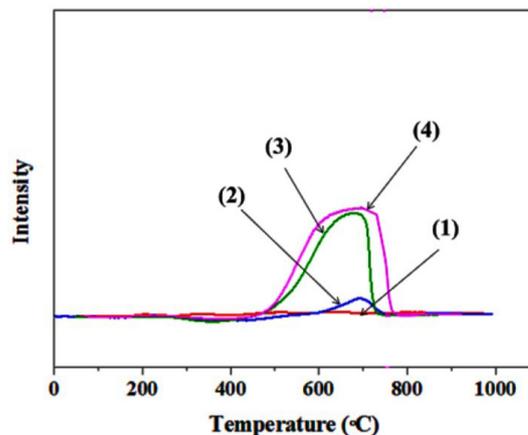


Fig. 11. TPO analysis of the Ni/K-Al₂O₃ with different Ni loadings. (1) 5%Ni/3%K-Al₂O₃, (2) 10%Ni/3%K-Al₂O₃, (3) 15%Ni/3%K-Al₂O₃, (4) 20%Ni/3%K-Al₂O₃.

3.6. Effect of potassium loading

3.6.1. Structural properties of the catalysts

The specific surface area (BET surface area), pore size and pore volume of the 15%Ni/K₂O-Al₂O₃ catalysts with different potassium loadings are listed in Table 3. It is obvious that the addition of 1.5 and 3 wt.% K₂O to the nickel catalyst does not have a significant effect on the BET surface area and pore volume. However, further increase in K₂O content decreased the BET area and pore volume due to pore filling with potassium. The same trend was also observed for the particle size as indicated in Table 3.

The N₂ adsorption/desorption isotherm of the prepared samples are shown in Figure 13a. All the prepared catalysts exhibited the IV type isotherm with a H2 shaped hysteresis loop, which are the significant features for mesoporous materials. Furthermore, the pore size distributions of these materials are shown in Figure 13b. The pore size distributions are located in the range of 5–20 nm.

3.6.2. Temperature- programmed reduction (TPR)

TPR profiles of the Ni/K₂O-Al₂O₃ catalysts with different potassium loadings are presented in

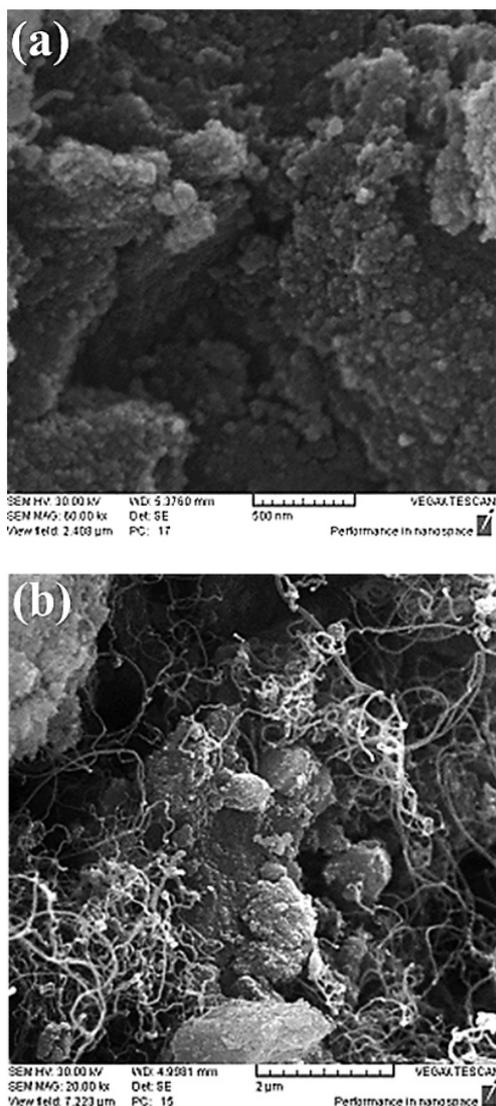


Fig. 12. SEM images of (a) 5%Ni/3%K-Al₂O₃ and (b) 15%Ni/3%K-Al₂O₃ catalysts. Reaction conditions: CH₄/CO₂=1, GHSV=12000 ml/g.h, time on the stream=300min.

Figure 14. It is seen that for all the samples four reduction peaks were detected. The first peak at about 400-450°C is attributed to the bulk NiO. The second peak located at 600°C is ascribed to the reduction of NiO species with weak interaction with the support. The third one is related to the NiO species with strong interaction with the catalyst support and the last small peak at about 850°C is assigned to the reduction of NiAl₂O₄. It is seen that the reduction temperature was shifted to higher temperatures by increasing potassium content. The results revealed that the

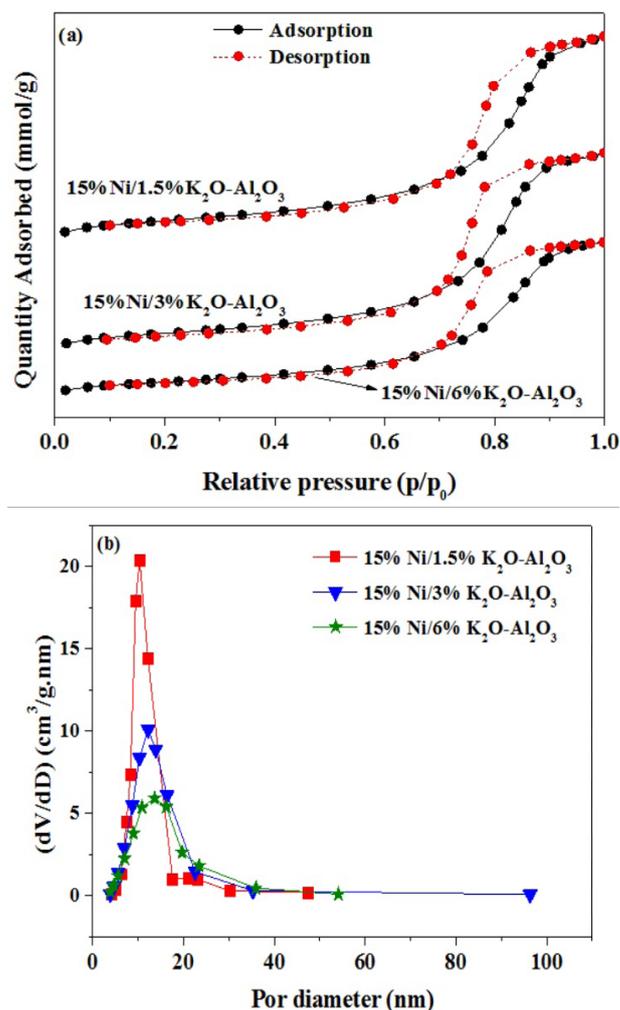


Fig. 13. (a) N₂ adsorption/desorption isotherms and (b) pore size distributions of the Ni/K₂O-Al₂O₃ catalysts with different potassium contents.

reducibility of the catalysts decreased with the increase in potassium content.

3.6.3. Catalytic performance

Figure 15 shows the catalytic performance of Ni/K-Al₂O₃ catalysts with different potassium loadings. As can be seen, CH₄ and CO₂ conversions increased when the reaction temperature increased from 550 to 700°C, due to the intensely endothermic character of the CRM reaction [5]. It is also obvious that CO₂ conversion is higher than CH₄ conversion due to the reverse water-gas shift reaction (CO₂ + H₂ ↔ CO + H₂O). It is found that by increasing

Table 3. Structural properties of the Ni/K₂O-Al₂O₃ catalysts with different potassium loadings

Catalyst	S _{BET} (m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹)	Pore width (nm)	Particle Size ^a (nm)
15%Ni/1.5%K ₂ O-Al ₂ O ₃	132	0.38	9.42	10.19
15%Ni/3%K ₂ O-Al ₂ O ₃	131	0.39	8.62	10.33
15%Ni/6%K ₂ O-Al ₂ O ₃	117	0.30	8.66	11.70

^a calculated by $D=6000/(S_{BET} \cdot \text{density})$

the potassium content from 1.5% to 3 wt.%, CH₄ and CO₂ conversions increased. However, further increase in potassium content to 6 %, decreased the catalytic activity. This confirms that there is an optimum for potassium content in which the catalyst showed the highest catalytic activity and the lowest carbon deposition. Although an increase in potassium content increased the basicity of the catalyst, which can improve the resistance of the catalyst against carbon formation, it can reduce the catalytic activity when the content of potassium increased above the optimum content. The addition of potassium above than the optimum content can reduce the BET surface area and nickel dispersion and consequently decrease the catalytic activity.

3.6.4. Temperature- programmed oxidation (TPO)

Temperature- programmed oxidation (TPO) analysis were carried out on the spent Ni/K-Al₂O₃ catalysts

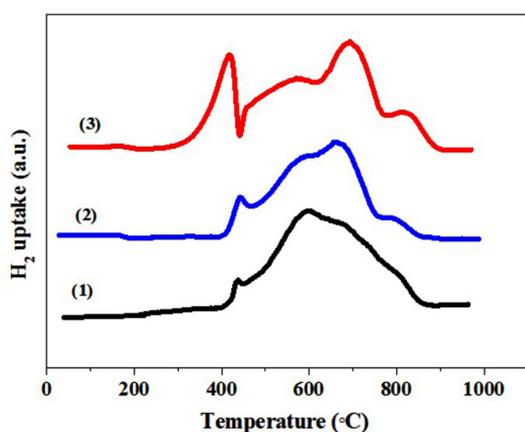


Fig. 14. TPR patterns of (1) 15%Ni/1.5%K₂O-Al₂O₃, (2) 15%Ni/3%K₂O-Al₂O₃, (3) 15%Ni/6%K₂O-Al₂O₃, catalysts.

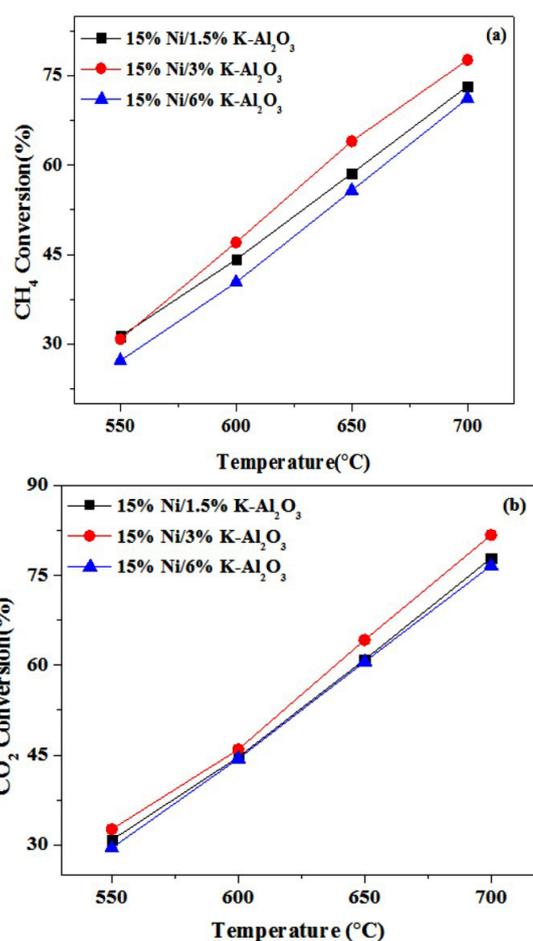


Fig. 15. (a) CH₄ conversion, (b) CO₂ conversion. Reaction conditions: CH₄/CO₂=1/1, GHSV=12000(ml/h.g_{cat}).

with different potassium loadings (Figure 16). The results showed just one peak, which is related to the whisker type carbon detected in all the samples. As can be seen, the highest and the lowest amount of deposited coke were detected in the catalysts with 3% and 6% potassium, respectively. It is worth noting that 15%Ni/3%K-Al₂O₃ and 15%Ni/1.5%K-Al₂O₃ catalysts exhibited the highest and the lowest catalytic

activity among the studied samples, respectively.

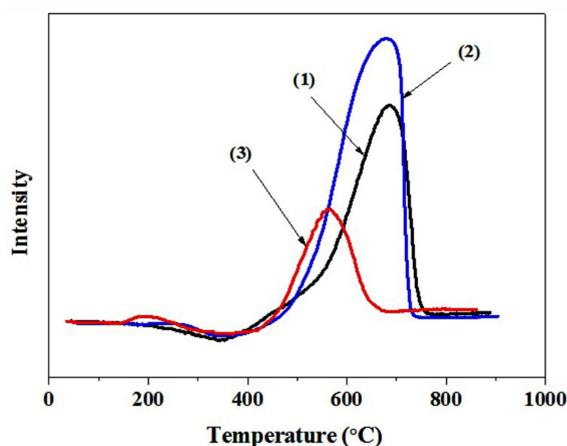


Fig. 16. TPO profiles of the spent catalysts with different potassium loadings (1) 15%Ni/1.5%K- Al_2O_3 , (2) 15%Ni/3%K- Al_2O_3 , (3) 15% Ni/6%K- Al_2O_3 catalysts.

4. Conclusions

The Ni/ Al_2O_3 and the K_2O promoted Ni/ Al_2O_3 catalysts were prepared and employed in CO_2 reforming of methane. The obtained results showed that the addition of potassium to the catalyst decreased the BET surface area and increased the pore diameter. The TPR results showed that the addition of a potassium promoter improved the catalyst reducibility. The catalytic activity increased dramatically and the coke formation decreased considerably by adding potassium to the catalyst during CRM. The textural properties of the Ni/K- Al_2O_3 catalysts with various Ni and K contents showed a decrease in specific surface area when K and Ni loadings were increased, due to partial blockage of the catalyst pores. The catalytic results demonstrated that the activity increased when the Ni loading increased because more accessible Ni active sites were provided for the reactants. The coke formation increased as the Ni content increased because of increases in catalyst particle size. The results showed that there is an optimum for potassium content where the catalyst showed the highest catalytic activity and the lowest carbon deposition.

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5. References

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