The influence of Ni loading on the activity and coke formation of ultrasound-assisted co-precipitated Ni-Al₂O₃ nanocatalyst in dry reforming of methane

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Abstract

Mesoporous nanocrystalline Ni-Al₂O₃ powders with different Ni loadings were synthesized via ultrasonic-assisted co-precipitation method and employed in methane dry reforming. The synthesized samples were investigated by BET, XRD, TPR, TPO and SEM analyses. The analyses showed that the increase in nickel loading from 15 wt.% to 25 wt.%, increased the surface area from 171.2 to 188 m²g⁻¹ and further increase in Ni loading has a negative influence on the surface area. It was seen that increasing in Ni loading from 15 wt.% to 33 wt.% decreased the crystallite size and also improved the reducibility of the catalyst. The TPO analysis exhibited that decreasing in Ni loading decreased the content of accumulated carbon. The catalytic results showed an improvement in catalytic activity by the increase in Ni loading. The activity measurements showed that the 25wt.%Ni-Al₂O₃ exhibited high catalytic performance in CH₄ dry reforming.

Keywords: Ni-Al₂O₃; Sonochemical synthesis; Nanopowder; Coke formation; Methane dry reforming

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1. Introduction

Production of hydrogen via dry reforming of methane ($\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$, $\Delta H^\circ = 247$ kJ/mol) received much attentions due to the lack of nonrenewable fuels and its environmental pollution. This process offers over steam reforming of methane due to the utilization of both CH_4 and CO_2 which are important greenhouses gasses and production of a lower H_2/CO ratio for use in Fischer-Tropsch process [1–6]. Methane dry reforming is a high endothermic reaction. So high energy input is required to take place. CO disproportionation which is named boudouard reaction and methane decomposition are side reactions in reforming which lead to the carbon deposition and catalyst deactivation. boudouard reaction (reaction (2)) is an exothermic reaction and is less favored at high temperature of methane dry reforming. Methane decomposition (reaction (1)) is an endothermic reaction and occurs on the nickel surface generating reactive carbon [7–9].

Numerous metals such as Ni, Co and noble metals (Rh, Ru, Pt and Ir) are active metals for methane reforming. Although noble metals are less sensitive to carbon deposition and displayed higher activity, high cost and their unavailability restrict their utilization in large scale and industry [10–12]. Nickel-based catalysts have been reported as an effective catalyst with low cost and desirable performance in methane dry reforming. The major drawback of the nickel-based catalyst is catalytic deactivation by carbon deposition on the catalyst or sintering of metal particles during reduction [13–23]. Consequently, preparation of a suitable catalyst with

desirable activity and high coke resistance capability is essential for methane dry reforming. For this respect selection of suitable supports can improve the catalytic performance because of their chemical properties and the interaction with active metal [24]. Most of the studies reported that the existence of strong metal-support interaction can suppress the sintering of nickel or carbon formation [25,26]. It has been reported that nickel supported on alumina with high surface area and usually proper pore sizes exhibited much better stability than the other supports [27,28]. Furthermore, it was indicated that small particle size in strong interaction with support had a critical influence on the resistance of carbon formation and sintering of active particles [29].

As it was mentioned, particle size plays an essential role in the catalytic activity and stability and the rate of carbon formation. Metal content is one of the various parameters which affects the particle size [30]. Tang et al. [31] reported that the critical size of nickel particles for preventing carbon formation was 10 nm. Kim et al. [32] synthesized nickel-alumina catalyst via a sol-gel method with different Ni/Al ratios (0.1-0.25). They reported that increasing in Ni loading increased the catalytic activity. Also, they reported that the critical particle size of nickel for the formation of filamentous carbon was 7nm. The catalyst with Ni/Al ratio of 0.1 with the smallest average particle size (6.3nm) exhibited the lowest rate of carbon formation. Zhang et al. [33] indicated that the lower Ni-Co content led to the production of smaller and highly dispersed particles. In addition, they reported that because of the absence of larger metal particles (>10nm) in the Ni-Co catalyst with lower metal content (0.04Ni-0.05Co and 0.02Ni-0.03Co), carbon deposition could be eliminated completely in methane dry reforming. Newnham et al. [34] reported that the catalyst with a moderate Ni loading (10 wt.%) exhibited the highest catalytic performance and high stability in dry reforming of methane, due to the inhabitation of active particle sintering which led to the decreasing of cluster size (less than 15 nm).

It has been reported that co-precipitation is a more desirable method for synthesis of nickel aluminate to optimize the reforming efficiency [35]. Growing of particles with no control in size and their tendency to aggregation are some disadvantages of co-precipitation method [36]. Hence, modifying conventional co-precipitation by ultrasonic irradiation would be able to improve its efficiency and produce particles in nano scale. Acoustic cavitation is a physical phenomenon caused by applying high intensity ultrasound irradiation to liquid in the sonochemical process. Ultrasound irradiations cause creation, grow and implosive of the bubble in the solution mixture. As the size of bubbles reaches a critical size in the micrometer range, the implosion of the bubbles causes exclusive conditions such as high temperatures and pressures (up to $\sim 5000^{\circ}\text{C}$ and $\sim 2000\text{atm}$) within the collapsing bubbles [37]. The formation of high-phase purity nanocrystals with uniform shape and narrow size distribution, reduction of particles growth, decreasing of phase transformation temperature, control in size and morphology and reduction of agglomeration of as-prepared nanoparticles are some advantages of ultrasound assisted co-precipitation method [38–40].

Previously we reported that the ultrasonic irradiation had a positive influence on the activity and stability of the prepared catalysts in methane dry reforming [41]. In this research paper, the influences of Ni content on the catalytic performance and coke formation of the ultrasonic assisted co-precipitated Ni-Al₂O₃ catalysts were investigated.

2. Experimental

2.1. Sample preparation

The Ni-Al₂O₃ catalysts with various nickel loadings (15, 20, 25 and 33 wt.%) were prepared via an ultrasonic-assisted co-precipitation (US) method. The effects of pH, the power of ultrasound irradiation, the time of aging and calcination temperature on the textural characteristics of the

samples were reported in our previous work [41]. In summary, desired contents of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98% purity, Merck) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98% purity, Merck) were dissolved in distilled water under vigorous stirring to form a transparent solution. After that, an aqueous solution of sodium hydroxide NaOH (1M) was added drop-wise at ambient temperature to the solution containing the Al and Ni precursor under constant ultrasound irradiation (70 W) to adjust the pH (pH=10). An ultrasonic device (QSONICA-Q700 Sonicator) with a 13mm diameter probe operating at 20 kHz with a maximum power output of 700W, which offers full amplitude control from 1-100% was applied for the ultrasonic irradiation. After completing the precipitation the slurry was filtered and washed for removal of free ions. Then the filter cake was dried at 80°C overnight and calcined at 700°C for 4 h.

2.2. Characterization

The temperature programmed reduction (TPR) analysis was done using a Micromeritics chemisorb 2750 instrument. In this analysis, a specific weight (0.1 g) of the degassed sample was heat treated in a reducing gas stream (H_2 : Ar=10:90, 30 ml/min) with a ramp rate of 10 °C/min. The details of the TPR analysis were described in our previous work [1]. Temperature-programmed oxidation (TPO) analysis was performed with the same instrument as described for TPR analysis. In this analysis, an oxidizing gas stream (O_2 : He=5:95, 30 ml/min) was employed and the details of the analysis were presented in our previous published papers [1,2]. The specific surface area and the pore characteristics of the samples were determined using a BELSORP mini II instrument. The scanning electron microscopy (SEM) analysis was done using a VEGA TESCAN microscope. X-Ray diffraction (XRD) data were obtained using a X-Ray diffractometer (PANalytical X'Pert-Pro) to investigate the crystallinity and crystalline size of the

samples. The crystallite sizes of the prepared catalysts were calculated using Debye-Scherrer equation:

$$d = \frac{0.9\lambda}{2\beta \cos \theta} \quad (3)$$

Where d is the crystallite size, λ is the X-Ray wavelength (1.5405nm), β is the peak width at the half maximum intensity and θ is the Bragg angle.

2.3. Catalytic evaluation

The catalytic performance of the calcined samples was evaluated by a quartz tubular fixed-bed continuous flow microreactor (i.d. 8 mm) at atmospheric pressure and different temperatures. The samples were pressed, crushed and sieved to 40-60 mesh particles. Typically, the microreactor was charged with a constant weight (0.2 g) of the catalyst granules. Before the catalytic reaction, the samples were reduced in pure H₂ flow (20 mL/min) at 600°C for 2h. Then, the reactor was cooled to 550°C and then a mixture of reactant feed was introduced to the microreactor. The activity evaluation was performed at various temperatures. The composition of the exit stream of the reactor was determined by a Varian 3400 gas chromatograph.

3. Results and discussion

3.1. XRD analysis

Fig. 1 illustrates the XRD patterns of Ni-Al₂O₃ with different Ni contents. The crystalline phases were identified using JCPDS files (Nickel aluminate/10-0339). Diffraction peaks assigned to nickel aluminate phase were observed at $2\theta = 19.6^\circ$, 31.7° , 37.5° , 45.3° , 60.2° and 66.1° [42–44]. Increasing in Ni loading decreased the intensity of NiAl₂O₄ at $2\theta = 19.6^\circ$, 31.7° and 60.2° which overlapped with Al₂O₃ phase. The absence of NiO peaks in the patterns

indicating the fact that the NiO was highly dispersed in the catalyst structure and the crystallite sizes were smaller than the detection limit of the instrument [45]. In the other word, the existence of a strong interaction between NiO and Al₂O₃ which leads to the high dispersion of NiO leading to the absence of NiO peaks in the XRD patterns [46,47]. The average crystallite size of nickel aluminate was calculated using Scherer equation. The increase in Ni loading reduced the NiAl₂O₄ crystal sizes (Table 1). It is noteworthy that the type of formed phases can be recognized by the color of the catalyst after calcination. The color of the catalysts with 15 and 20wt.% Ni loading was blue which is related to the formation of nickel aluminate phase. On the contrary, the color of the catalysts with 25 and 33wt.% Ni loading was dark and light green, respectively, which confirms the existence of NiO phase [42,45].

The formation of NiAl₂O₄ is due to the counter-diffusion of Ni²⁺ and Al³⁺ through aluminate structure. The following reactions describe the formation of nickel aluminate phase. The decomposition of Al₂O₃ to Al³⁺ and O₂ occurs at the interface of Al₂O₃ (reaction (4)). In addition, the movement of oxygen to the interface of NiO results in the occurrence of reaction with Al³⁺ to form NiAl₂O₄ spinel (reaction (5)) [48].

At Al₂O₃ interface:

At NiO interface:

3.2. Textural properties

The textural characteristics of the Ni-Al₂O₃ samples with various nickel contents are reported in Table 1. It is seen that by increasing the Ni loading from 15 wt.% to 25 wt.%, the surface area

increased from 171.2 to 188 m²g⁻¹ and further increase in Ni loading has a negative influence on the surface area.

Fig. 2a and 2b display the N₂ adsorption/desorption isotherms and pore size distributions of the samples prepared with different Ni loadings, respectively. The illustrated isotherms showed IV isotherm with H2 shape hysteresis loop attributed to the mesoporous powders [49]. The results showed that the amounts of N₂ adsorption increased by enhancing in Ni loading.

The pore size distributions of the synthesized samples (Fig. 2b) illustrated that all the samples have mesopore structure with the pore radius between 1.5–6 nm.

3.3. TPR analysis

The TPR profiles of the ultrasound-assisted co-precipitated Ni-Al₂O₃ with different Ni contents are depicted in Fig. 3. The reduction peaks with T_{max} at 766, 795, 716 and 782°C were observed for the catalysts with 15, 20, 25 and 33 wt.% Ni loadings, respectively. These peaks were related to the NiAl₂O₄ in which the nickel species were in strong interaction with the spinel. It is seen that no reduction peaks were observed at low temperatures. It means that there was not any free NiO in the samples prepared by ultrasonic assisted co-precipitation method. As can be seen, by decreasing in Ni content, the peak intensity decreased and the TPR peaks migrated towards higher temperatures, indicating that lower Ni content favored the formation of nickel species with stronger metal-support interaction which are less reducible. Whatever the nickel species are stable in the catalyst structure, the reduction temperature is high [43]. It is evidenced that the increase in Ni content improved the reducibility, due to the weaker interaction between Ni and catalyst carrier. This result is in good agreement with XRD pattern (Fig. 1), in which the intensity of NiAl₂O₄ peaks decreased with the increase of Ni content.

3.4. Catalytic activity

Fig. 4a, b and c show the CH₄ and CO₂ conversions and syngas molar ratio at different reaction temperatures, respectively. Both the CH₄ and CO₂ conversions improved by the increase in reaction temperature due to this fact that the dry reforming of methane is an endothermic reaction. The increase in the content of Ni from 15 to 25 wt.% enhanced the catalytic activity due to the existence of more active sites in the high Ni loading catalysts. In contrast, an additional increase in Ni content declined the CH₄ conversion due to the decrease of Ni dispersion. The catalysts with 15 wt.% and 20 wt.% Ni loading exhibited no activity at 550°C. According to the TPR Profiles, the reduction peaks of these catalysts are located around 750°C with lower intensity compared to the others. Consequently, these catalysts were not reduced completely at 600°C.

The H₂/CO molar ratios of the prepared catalyst are displayed in Fig. 4c. In the case of the 25%Ni-Al₂O₃ catalyst, initially, the H₂/CO ratio reached a maximum at 600°C by increasing in reaction temperature from 550 to 600°C, then reduced by increasing in temperature to 700°C (Fig. 4c). The Boudouard reaction is more possible than dry reforming of methane and reverse water gas shift reactions at low temperatures. In Boudouard reaction CO was decomposed to carbon and CO₂. The decomposition of CO led to the increase in the H₂/CO ratio. By enhancing the temperature up to 600°C, the Boudouard reaction was not possible to occur and dry reforming of methane and reverse water gas shift reactions ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$, $\Delta H^\circ = 41 \text{ kJ/mol}$) were occurred simultaneously. Reducing of the syngas ratio at high temperatures is attributed to reverse water gas shift reaction. It must be noticed that the reverse boudouard reaction is plausible at high temperatures [50]. It is seen that for the catalysts with 15, 20 and 33 wt.% the H₂/CO increased by increasing in reaction temperature from 550 to 700°C. The H₂/CO molar ratio was lower than one due to the occurrence of RWGS reaction.

Short time stability of the ultrasound-assisted co-precipitated catalysts with different Ni contents in DRM was carried out at 700°C for 5h. Fig. 5a, 5b and 5c illustrate the conversions of CH₄ and CO₂ and syngas molar ratio versus time on stream. It is clear that catalysts with 15 and 20wt.% Ni content showed more stable activity due to the existence of nickel aluminate species which leads to lower carbon formation. Also, in these catalysts formation of nickel aluminate phase results in increasing the nickel dispersion, which decreases the amount of carbon formation. It is noteworthy to mention that high dispersion of particles on the support leads to a decrease of carbon formation [29,51]. Sahli et al. [43] reported the existence of nickel in the structure of NiAl₂O₄ spinel results in a high dispersion and high stability for the active metal particles. Also, it was reported that the catalysts with a low weight content of the active metal are effective and coke resistance [52]. Consequently, the formation of nickel aluminate phase makes the catalyst more stable against carbon deposition. As can be seen in Fig. 5a and 5b, for the catalyst with 33wt.% Ni loading, the conversion of CH₄ was higher than the conversion of CO₂. According to the TPR profiles of this catalyst, the reduction peak was located at 782°C, while the catalyst was reduced at 600°C. So at the high reaction temperature, the reduction of nickel oxide is plausible to occur too. During the reduction of nickel oxide, dry reforming and RWGS reactions, NiO could be reduced to Ni by both of CO and H₂. The reaction (3) produces H₂O and causes the occurrence of WGS reaction (reaction (8)) which leads to CO₂ production. On the other hand, because of the existence of H₂O, reaction of steam reforming of methane (Equation (9)) is plausible to occur. So the CH₄ reacted with H₂O and converted to CO and H₂. Therefore because of producing CO₂, the conversion of CO₂ decreased and the conversion of CH₄ was higher than CO₂.

According to the TPR profiles in the case of catalysts with 15, 20 and 25 wt.% Ni content the nickel aluminate phase was formed completely and the intensity of their reduction peaks was lower compared to the catalyst with 33 wt.% Ni (Fig. 3). Consequently, these catalysts were not reduced at a high temperature of DRM reaction.

Fig. 6 shows the influence of the CO_2/CH_4 ratio on the catalytic performance of 25 wt.%Ni- Al_2O_3 catalyst. With an increase in CO_2/CH_4 ratio from 0.5 to 3, the CH_4 conversion increased whereas the CO_2 conversion and H_2/CO decreased by increasing the CO_2/CH_4 ratio. In methane dry reforming reaction, When the CO_2/CH_4 ratio is between 0.5-1, the CO_2 gas acts as limiting reactant and its conversion is high. in contrast, at CO_2/CH_4 higher than 1, the CH_4 gas acts as a limiting reactant and its conversion is higher than that obtained for CO_2 . Also, the increase in CO_2/CH_4 ratio reduced the H_2/CO ratio due to more occurrence of reverse water gas shift (RWGS) reaction.

Fig. 6c illustrates the effect of gas hourly space velocity (GHSV) over the catalyst with 25 wt.% Ni loading at constant feed ratio ($\text{CO}_2/\text{CH}_4=1$). It is evidenced that with an increase in GHSV both CO_2 and CH_4 conversions decreased due to the reduction of the residence time of the reactants on the catalyst surface and amount of adsorbed reactant.

3.5. TPO analysis

Fig. 7 illustrates the TPO profiles of the spent catalysts with different Ni contents. Carbon deposition blocks active sites and prevents methane adsorption and results in decreasing of the

catalytic activity. One oxidation peak was seen in the TPO profile of the catalysts. These peaks are located at a temperature above 450°C which are assigned to whisker carbon caused by diffusing of carbon through nickel particles and growth with nickel catalyst on the top. Breaking down of the catalyst via pore plugging caused by the formation of this type of carbon [53] . It is seen that, increasing in Ni content, increased the amount of carbon formation. As can be seen, in the case of catalyst with 15 wt.% Ni, no oxidation peak was observed in TPO profile due to the existence of high amounts of nickel aluminate phase (according to XRD pattern in Fig. 1) which leads to the increase of Ni dispersion. It has been reported that the coke inhibition could be improved by the formation of nickel aluminate phase [54]. Trimm et al. [55,56] reported that growing of whisker carbon is a result of carbon dissolution in nickel. Carbon formation continues when the metal crystal sizes are bigger than a critical size [57]. Liu et al. [54] reported that the catalyst coke inhibition can be improved by decreasing of catalyst particle size. Guohui li et al. [44] indicated that the spinel phase is less reducible than NiO phase. Therefore, during hydrogen reduction the nickel species which are strongly associated with the spinel can be reduced to the highly dispersed nanosized nickel particles [10,43]. It has been reported that high dispersed Ni particles exhibited good resistance against carbon formation because the ensemble size necessary for carbon formation is larger than that required for dry reforming of methane. Also, they reported that during the H₂ reduction and methane reforming with carbon dioxide, the Ni species with strong interaction with support can be reduced to nanosized Ni particles with high dispersion. [10]. Zhai et al. [29] reported that the small Ni particles in strong interaction with support result in high dispersion, having a slight tendency to carbon formation and sintering. So, the reason of less carbon formation is that the filamentous carbon species are not

deposited directly in a close contact with the highly dispersed Ni particles. CO₂ can remove this kind of carbon by the gasification of coke deposited and reverse of boudouard reactions [58].

3.6. SEM analysis

The SEM images of the fresh and spent 25%Ni-Al₂O₃ and 33%Ni-Al₂O₃ catalysts are shown in Fig. 8. It is observed that both the fresh catalysts have particles in nanometer scale with high dispersion. However, the 25%Ni-Al₂O₃ (Fig. 8a) has higher dispersion compared to the 33%Ni-Al₂O₃ (Fig. 8c). As can be seen, it is hard to recognize that which catalyst showed lower amount of deposited carbon due to the high Ni content in these two catalysts. However, as confirmed by the TPO analysis, the catalyst with higher nickel content exhibited a higher degree of carbon formation.

4. Conclusion

Ni-Al₂O₃ catalysts with different Ni loadings (15, 20, 25 and 33 wt.%) were synthesized via the ultrasound-assisted co-precipitated method and employed in dry reforming of methane. The results showed that the increase in nickel loading from 15 wt.% to 25 wt.%, increased the surface area from 171.2 to 188 m²g⁻¹ and further increase in Ni loading has a negative effect on the surface area. Also, It was seen that increasing in Ni loading from 15 wt.% to 33 wt.% reduced the crystallite size. According to the results increasing in Ni content up to 25 wt.% of Ni increased the catalytic activity due to the existence of more active sites in the high Ni loading catalysts. In contrast, an additional increase in Ni content has a negative influence on the catalytic performance due to the decrease of nickel dispersion. The catalysts with 15 and 20wt.% Ni content exhibited more stable activity due to the existence of nickel aluminate species which leads to lower carbon formation. Moreover, decreasing in Ni loadings made the catalysts less

reducible due to the increase of the interaction between Ni and the spinel in nickel aluminate species. In addition, the amount of coke deposition increased by increasing in Ni contents. In the catalyst with 15 wt.% Ni, no oxidation peak was observed in TPO profile due to the existence of high amounts of nickel aluminate phase.

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Figure caption

Fig. 1. XRD patterns of XNi-Al₂O₃ with different Ni contents

Fig. 2. a) N₂ adsorption/desorption isotherms and b) pore size distributions of XNi-Al₂O₃ with different Ni contents

Fig. 3. H₂ –TPR profiles of XNi-Al₂O₃ with different Ni contents

Fig. 4. a) Conversion of CH₄, b) conversion of CO₂ and c) the syngas molar ratio (reaction conditions: CH₄/CO₂ = 1/1, GHSV = 12,000(ml/h g_{cat}).)

Fig. 5. Short time stability of the catalysts. a) Conversion of CH₄, b) Conversion of CO₂ and c) the syngas molar ratio (Reaction conditions: CH₄/CO₂ = 1/1, GHSV = 12,000(ml/h g_{cat}).)

Fig. 6.s a) Effect of feed ratio on the catalytic activity over 25wt.%Ni-Al₂O₃ catalyst at 700°C and GHSV=12000(ml/h g_{cat})) b)Effect of feed ratio on the ratio of H₂/CO at 700°C and GHSV=12000(ml/h g_{cat}) c) Effect of GHSV on the catalytic performance of 25wt.% Ni at 700°C and CO₂/CH₄=1.

Fig. 7. TPO profiles of the spent catalysts (Reaction conditions: CH₄/CO₂ = 1/1, GHSV = 12,000(ml/h g_{cat})).

Fig. 8. SEM Images of the a) fresh and b) spent 25%Ni-Al₂O₃ catalyst and c) fresh and d) spent 33%Ni-Al₂O₃ catalyst [41]

Table 1. Structural properties of Ni-Al₂O₃ catalysts with different Ni loadings

Ni loading (wt. %)	S_{BET} (m² g⁻¹)	Total pore volume (cm³ g⁻¹)	Mean pore diameter (nm)	d_{XRD} (nm)
15	171.2	0.2	5.6	6.66
20	176.5	0.2	6.2	6.03
25	188.0	0.2	5.7	5.80
33	178.2	0.3	6.9	5.30

Fig. 2 . XRD patterns of XNi-Al₂O₃ with different Ni contents

Fig. 2. a) N_2 Adsorption/desorption isotherms and b) pore size distributions of $XNi-Al_2O_3$ with different Ni contents

Fig. 3. H_2 -TPR profiles of $XNi-Al_2O_3$ with different Ni contents

Fig. 4. a) Conversion of CH_4 , b) Conversion of CO_2 and c) the syngas molar ratio (Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1/1$, GHSV = 12,000(ml/h g_{cat}).)

Fig. 5. Short time stability of the catalysts in DRM. a) Conversion of CH_4 , b) Conversion of CO_2 and c) the syngas molar ratio versus time on stream (Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1/1$, GHSV = 12,000($\text{ml/h g}_{\text{cat}}$).)

Fig. 6 a) Effect of feed ratio on the catalytic activity over 25wt.%Ni-Al₂O₃ catalyst at 700°C and GHSV=12000(ml/h g_{cat})) b)Effect of feed ratio on the ratio of H₂/CO at 700°C and GHSV=12000(ml/h g_{cat}) c) Effect of GHSV on the catalytic performance of 25wt.% Ni at 700°C and CO₂/CH₄=1.

Fig. 7. TPO profiles of the spent catalysts (Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1/1$, GHSV = 12,000($\text{ml/h g}_{\text{cat}}$)).

Fig. 8. SEM Images of the a) fresh and b) spent 25%Ni-Al₂O₃ catalyst and c) fresh and d) spent 33%Ni-Al₂O₃ catalyst [41]

Graphical abstract

Ni-Al₂O₃ catalysts prepared by ultrasound assisted co-precipitation method

Ni-Al₂O₃ catalysts prepared by ultrasound assisted co-precipitation method exhibited high stability in dry reforming of methane. Increasing in Ni content increased the amount of deposited carbon on the catalyst surface.