Ni–Zn–Al-Based Oxide/Spinel Nanostructures for High Performance, Methane-Selective CO₂ Hydrogenation Reactions

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Abstract
In the present study, NiO modified ZnAl₂O₄ and ZnO modified NiAl₂O₄ spinel along with pure Al₂O₃, ZnAl₂O₄ and NiAl₂O₄ for comparison in the CO₂ hydrogenation reaction have been investigated. It was found that NiAl₂O₄, NiO/ZnAl₂O₄ and ZnO/NiAl₂O₄ catalysts exhibited outstanding activity and selectivity towards methane even at high temperature compared to similar spinel structures reported in the literature. NiO/ZnAl₂O₄ catalyst showed CO₂ consumption rate of ~ 19 μmol/g·s at 600 °C and ~ 85% as well as ~ 50% of methane selectivity at 450 °C and 600 °C, respectively. The high activity and selectivity of methane can be attributed to the presence of metallic Ni and Ni/NiO/ZnAl₂O₄ interface under the reaction conditions as evidenced by the XRD results.

1 Introduction
The catalytic conversion of CO₂ is desirable strategy to not only reduce the CO₂ emission but also to produce useful chemicals/fuels [1, 2]. Depending upon the catalysts used, different kinds of products were obtained such as CO via reverse water gas shift (RWGS) reaction, methane (Sabatier reaction) and methanol [3–5]. The obtained CO in the RWGS reaction can be converted into value added chemicals through Fischer–Tropsch synthesis. RWGS is endothermic (CO₂ + H₂ ↔ CO + H₂O, ΔH_RWGS = +41 kJ/mol).
and thermodynamically favoured at high temperatures [6].

Cu [7], Pt [8] and Rh [9] on various supports have been reported as the most active catalysts for RWGS reaction. Methanation is exothermic \(\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \Delta H_{\text{ab}} = -165 \text{ kJ/mol}\) and thermodynamically favoured at low temperatures [10]. Ni [11], Ru [4] and Rh [12] are most widely used catalysts for CO\(_2\) methanation reaction. Cu [13] and Pd [14] are most widely used catalysts for the reduction of CO\(_2\) to methanol [15–17]. Nickel based catalysts have been widely investigated as catalyst in CO\(_2\) hydrogenation reactions owing to its superior catalytic activity and low cost [18, 19]. Recently, nickel based spinel catalysts have been widely used in CO\(_2\) hydrogenation reaction due to their low cost and superior catalytic activity [20–22]. Further, they were also used in other fields such as in adsorption [23], sensors [24] and as flexible materials [25]. They have also been used as catalyst support due to its low reactivity with the active phase and its high resistance to high temperatures and acidic or basic atmospheres [26]. Interestingly, NiAl\(_2\)O\(_4\) was found to minimize the coke formation in CO\(_2\) reforming of methane [27]. Besides nickel based spinels, zinc based spinels were also used in various fields such as in catalysis [15, 28–30], adsorption [31] and optics [32] due to their superior catalytic activity and high thermal stability [33]. However, the catalytic applications of these spinel materials for CO\(_2\) hydrogenation is not reported. In the present study, various Nickel–Zinc–Aluminum-based spinels as well as oxide/spinel catalysts were produced where the position of the nickel and zinc atoms or ions were changed. The catalysts were characterized by XRD, N\(_2\) physisorption, TEM, SEM–EDX and TGA. These catalysts were tested in CO\(_2\) hydrogenation reaction in the gas phase. It was found that NiAl\(_2\)O\(_4\), NiO/ZnAl\(_2\)O\(_4\) and ZnO/NiAl\(_2\)O\(_4\) catalysts during the reaction conditions exhibited outstanding activity and selectivity towards methane even at high temperature as these catalysts comprise metallic nanoparticles in their structure. Among these catalysts, NiO/ZnAl\(_2\)O\(_4\) catalyst showed CO\(_2\) consumption rate of \(\sim 19\, \mu\text{mol/g s}\) at 600 °C and \(\sim 85\%\) as well as \(\sim 50\%\) of methane selectivity at 450 °C and 600 °C, respectively.

2 Experimental details

2.1 Chemicals

Zn(NO\(_3\))\(_2\)·6H\(_2\)O (\(\geq 99\%\)) and Al(NO\(_3\))\(_3\)·9H\(_2\)O (\(\geq 98\%\)) were purchased from Sigma-Aldrich. Aqueous ammonia solution was added dropwise into the mixed solution at room temperature until pH value of about 7. The obtained precipitate was aged for 2 h at 70 °C. Then, the solid product was recovered by filtration, washing with deionized water and drying overnight at 100 °C. The ZnAl\(_2\)O\(_4\) was obtained after calcination in air at 500 °C for 5 h. The NiAl\(_2\)O\(_4\) was prepared by the same procedure using their corresponding metal nitrate precursors. In order to investigate the interphase effect of metal cations present in the ZnAl\(_2\)O\(_4\) and NiAl\(_2\)O\(_4\) spinels, we loaded exactly the amount of ZnO present in ZnAl\(_2\)O\(_4\) onto NiAl\(_2\)O\(_4\) and vice versa. Based on the calculation, we loaded 44wt% of ZnO on NiAl\(_2\)O\(_4\) and represented as ZnO/NiAl\(_2\)O\(_4\) and 42wt% of NiO on ZnAl\(_2\)O\(_4\) and represented as NiO/ZnAl\(_2\)O\(_4\).

2.2 Catalyst Preparation

The ZnAl\(_2\)O\(_4\) oxide was synthesized by a co-precipitation method in accordance with the procedure reported in the previous work [34]. Typically, appropriate amount of Zn(NO\(_3\))\(_2\)·6H\(_2\)O and Al(NO\(_3\))\(_3\)·9H\(_2\)O with a molar ratio of 1:2 were dissolved in 100 mL deionized water. Then, an aqueous ammonia solution was added dropwise into the mixed solution at room temperature until pH value of about 7. The obtained precipitate was aged for 2 h at 70 °C. Then, the solid product was recovered by filtration, washing with deionized water and drying overnight at 100 °C. The ZnAl\(_2\)O\(_4\) was obtained after calcination in air at 500 °C for 5 h. The NiAl\(_2\)O\(_4\) and pure Al\(_2\)O\(_3\) were prepared by the same procedure using their corresponding metal nitrate precursors. In order to investigate the interphase effect of metal cations present in the ZnAl\(_2\)O\(_4\) and NiAl\(_2\)O\(_4\) spinels, we loaded exactly the amount of ZnO present in ZnAl\(_2\)O\(_4\) onto NiAl\(_2\)O\(_4\) and vice versa. Based on the calculation, we loaded 44wt% of ZnO on NiAl\(_2\)O\(_4\) and represented as ZnO/NiAl\(_2\)O\(_4\) and 42wt% of NiO on ZnAl\(_2\)O\(_4\) and represented as NiO/ZnAl\(_2\)O\(_4\).

2.3 Catalyst Characterization

2.3.1 N\(_2\) Adsorption–Desorption Isotherm Measurements

The specific surface area (BET method), the pore size distribution and the total pore volume were determined by the BJH method using a QuantaChrome NOVA 2200 gas sorption analyzer by N\(_2\) gas adsorption/desorption at −196 °C. Before the measurements, the samples were pre-treated in a vacuum (< ~0.1 mbar) at 200 °C for 2 h.

2.3.2 Powder X-ray Diffraction (XRD)

XRD studies of all samples were performed on a Rigaku MiniFlex II instrument with a Ni-filtered CuK\(\alpha\) source in the range of 2\(\theta\) = 10–80°.

2.3.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was obtained using TAQ500 instruments under flow of air from room temperature to 800 °C at a heating rate of 10 °C min\(^{-1}\).
2.3.4 Scanning Electron Microscopy (SEM–EDX)

Scanning electron microscopy equipped with an energy dispersive X-ray spectroscopy (Hitachi S-4700) was applied at 20 kV on the samples.

2.3.5 Transmission Electron Microscopy (TEM)

Imaging of all the samples were carried out using an FEI TECNAI G2 20 X-Twin high-resolution transmission electron microscope (equipped with electron diffraction) operating at an accelerating voltage of 200 kV. The samples were drop-cast onto carbon film coated copper grids from ethanol suspension.

2.4 Catalytic Activity Studies

2.4.1 Hydrogenation of Carbon-dioxide in a Continuous Flow Reactor

Before the catalytic experiments, the as-received catalysts were oxidized in O2 atmosphere at 300 °C for 30 min and thereafter were reduced in H2 at 300 °C for 60 min. Catalytic reactions were carried out at atmospheric pressure in a fixed-bed continuous-flow reactor (200 mm long with 8 mm i.d.) which was heated externally. The dead volume of the reactor was filled with quartz beads. The operating temperature was controlled by a thermocouple placed inside the oven close to the reactor wall, to assure precise temperature measurement. For catalytic studies, small fragments (about 1 mm) of slightly compressed pellets were used. Typically, the reactor filling contained 150 mg of catalyst. In the reacting gas mixture, the CO2:H2 molar ratio was 1:4, if not denoted otherwise. The CO2:H2 mixture was fed with the help of mass flow controllers (Aalborg), the total flow rate was 50 ml/min. The reacting gas mixture flow entered and left the reactor through an externally heated tube in order to avoid condensation. The analysis of the products and reactants was performed with an Agilent 6890 N gas chromatograph using HP-PLOTQ column. The gases were detected simultaneously by thermal conductivity (TC) and flame ionization (FI) detectors. The CO2 was transformed by a methanizer to methane and it was also analysed by FID. CO2 conversion was calculated on a carbon atom basis, i.e.

\[
\text{CO}_2 \text{ conversion (\%)} = \frac{\text{CO}_2 \text{ inlet} - \text{CO}_2 \text{ outlet}}{\text{CO}_2 \text{ inlet}} \times 100\%
\]

where \(\text{CO}_2 \text{ inlet}\) and \(\text{CO}_2 \text{ outlet}\) represent the CO2 concentration in the feed and effluent, respectively, and \(\text{CH}_4 \text{ outlet}\) and \(\text{CO}_2 \text{ outlet}\) represent the concentration of \(\text{CH}_4\) and CO in the effluent, respectively.

3 Results and Discussion

3.1 X-ray Diffraction (XRD)

The crystal structure of catalysts was investigated by XRD. Figure 1 shows the XRD patterns of NiAl2O4, ZnAl2O4, NiO/ZnAl2O4, ZnO/NiAl2O4 and Al2O3. The peaks located at 2θ of 18.9°, 31.38°, 36.67°, 44.39° and 64.88° are assigned to the (111), (220), (311), (400) and (440) planes of the cubic spinel structure of NiAl2O4 respectively (JCPDS Card no. 73-0239) [35]. The peaks located at 2θ of 18.99°, 31.69°, 37.17°, 45.26°, 49.06°, 55.66°, 59.65°, 65.62°, 74.15° and 77.33° are assigned to the (111), (220), (311), (400), (331), (422), (511), (440), (620) and (536) planes of the cubic spinel structure of ZnAl2O4 respectively (JCPDS Card no. 05-0669) [29]. For NiO/ZnAl2O4 and ZnO/NiAl2O4 samples no peaks characteristics of ZnO and NiO are seen indicating fine dispersion of these species on the NiAl2O4 and ZnAl2O4 supports respectively or may be overlapped with the supports diffraction peaks. The peaks located at 2θ of 19.86°, 32.38°, 37.85°, 46.20°, 57.40°, 61.02° and 67.12°...
are assigned to (111), (220), (311), (400), (422), (511) and (440) planes of the cubic structure of \( \gamma \)-Al\(_2\)O\(_3\) [36].

### 3.2 N\(_2\) Adsorption–Desorption Isotherm

The specific surface area together with the pore volume and pore size was summarized in Table 1. The \( \text{N}_2 \) adsorption–desorption isotherms of ZnO/NiAl\(_2\)O\(_4\) exhibit type IV isotherm with a narrow hysteresis loop of type H3 associated with plate-like particles giving rise to slit-shaped pores [37]. However, Al\(_2\)O\(_3\), NiAl\(_2\)O\(_4\), ZnAl\(_2\)O\(_4\) and NiO/ZnAl\(_2\)O\(_4\) displays type IV isotherms with H2 hysteresis loop at \( P/P_0 = 0.4–1.0 \) associated with pores with narrow necks and wide bodies, referred to as ‘ink-bottle’ pores [37, 38]. The average pore size distribution is in the range of 2–25 nm indicating the presence of mesopores. After loading ZnO and NiO respectively on NiAl\(_2\)O\(_4\) and ZnAl\(_2\)O\(_4\), the resulting catalyst showed decreased surface area and pore volume.

### 3.3 TEM Analysis

The morphology and particle size of the catalysts were examined by TEM measurements and shown in Fig. 2. NiAl\(_2\)O\(_4\) shows spherical shaped morphology with the size of 10 to 20 nm. ZnAl\(_2\)O\(_4\) displays rod like particles. TEM images of the NiO/ZnAl\(_2\)O\(_4\) and ZnO/NiAl\(_2\)O\(_4\) catalysts show two separate phases of metal oxides and supports that are well mixed and dispersed which is similar to what have been reported in the literature for NiO/NiAl\(_2\)O\(_4\) catalyst [39].

### 3.4 SEM–EDX Analysis

Table 2 summarizes the atomic percentages of various elements obtained from the SEM–EDX analyses. SEM–EDX spectra of Al\(_2\)O\(_3\) revealed the presence of Al and O elements with the percentages of 24.21% and 75.79% respectively. All other catalysts also clearly indicates the presence of their corresponding elements.

#### Table 1 Textural parameters of the catalysts

| Samples       | BET surface area (m\(^2\)/g) | Pore volume (cm\(^3\)/g) | Average pore size (nm) |
|---------------|-------------------------------|--------------------------|------------------------|
| NiAl\(_2\)O\(_4\) | 226                           | 0.33                     | 2.29                   |
| ZnAl\(_2\)O\(_4\) | 175                           | 0.31                     | 1.80                   |
| NiO/ZnAl\(_2\)O\(_4\) | 120                           | 0.19                     | 1.80                   |
| ZnO/NiAl\(_2\)O\(_4\) | 94                            | 0.13                     | 1.80                   |
| Al\(_2\)O\(_3\) | 321                           | 0.42                     | 2.51                   |

#### Table 2 SEM–EDX analysis of the catalysts

| Catalyst       | Elements, at % |
|----------------|----------------|
|                | Al   | O    | Ni   | Zn   |
| NiAl\(_2\)O\(_4\) | 19.51 | 73.32 | 7.17 | –    |
| ZnAl\(_2\)O\(_4\) | 21.50 | 72.19 | –    | 6.31 |
| NiO/ZnAl\(_2\)O\(_4\) | 25.87 | 52.81 | 12.73 | 8.59 |
| ZnO/NiAl\(_2\)O\(_4\) | 15.48 | 73.60 | 5.11 | 5.81 |
| Al\(_2\)O\(_3\) | 24.21 | 75.79 | –    | –    |

#### Fig. 2 TEM images of a NiAl\(_2\)O\(_4\), b ZnAl\(_2\)O\(_4\), c NiO/ZnAl\(_2\)O\(_4\) and d ZnO/NiAl\(_2\)O\(_4\)

#### Fig. 3 CO\(_2\) conversion as a function of temperature over NiAl\(_2\)O\(_4\), ZnAl\(_2\)O\(_4\), NiO/ZnAl\(_2\)O\(_4\), ZnO/NiAl\(_2\)O\(_4\) and Al\(_2\)O\(_3\) catalysts
3.5 Catalytic Performances

To explore the catalytic performance, CO₂ hydrogenation was performed over the prepared catalysts. Figure 3 depicts the CO₂ conversion as a function of temperature over all the catalysts. CO₂ conversion and product selectivity are given in Table 3 over all the catalysts. In general, the activity of Ni containing catalysts are remarkably better than that of Zn containing catalysts and Al₂O₃ catalyst. NiAl₂O₄, NiO/ZnAl₂O₄ and ZnO/NiAl₂O₄ catalysts exhibit highest activity with CO₂ conversion of 65% at 600 °C, which is 2.8-fold superior in catalytic activity than that of Al₂O₃.

Table 3  Conversion and selectivity for CO₂ hydrogenation over various catalysts

| Catalysts      | CO₂ conversion (%) | Selectivity (%) |
|----------------|--------------------|-----------------|
|                |                    | CO   | CH₄  |
| NiAl₂O₄        | 65.57              | 49.60 | 50.40|
| ZnAl₂O₄        | 31.02              | 100   | 0    |
| NiO/ZnAl₂O₄    | 65.18              | 53.35 | 46.65|
| ZnO/NiAl₂O₄    | 65.71              | 59.83 | 40.17|
| Al₂O₃          | 22.91              | 100   | 0    |

*Reaction conditions: T = 600 °C, CO₂/H₂ = 1/4, catalyst weight = 0.15 g

![Graphs of CO₂ hydrogenation over various catalysts](image-url)
Table 4: The CO2 consumption rate (μmol/g.s) at 600 °C in CO2 hydrogenation reaction over NiAl2O4, ZnAl2O4, NiO/ZnAl2O4, ZnO/NiAl2O4 and Al2O3 catalysts

| Catalysts       | CO2 consumption rate (μmol/g.s) |
|-----------------|---------------------------------|
| NiAl2O4         | 17.30                           |
| ZnAl2O4         | 11.24                           |
| NiO/ZnAl2O4     | 19.74                           |
| ZnO/NiAl2O4     | 18.62                           |
| Al2O3           | 7.97                            |

Figure 5: CO2 consumption rate as a function of temperature over NiAl2O4, ZnAl2O4, NiO/ZnAl2O4, ZnO/NiAl2O4 and Al2O3 catalysts

(Conversion = 23%) and twofold superior in catalytic activity than that of ZnAl2O4 (Conversion = 31%).

Figure 4 depicts the selectivity as a function of temperature for all the studied catalysts. The CO selectivity increases with increasing temperature due to the endothermic RWGS reaction. Among the five systems (NiAl2O4, ZnAl2O4, NiO/

Table 5: Comparative table of CO2 consumption rate with the reported spinel catalyst for CO2 hydrogenation

| Catalysts       | CO2 conversion (%) | Catalyst weight (g) | Temperature (°C) | Flow rate of CO2 (ml/s) | CO2 consumption rate (μmol/g.s) | References |
|-----------------|--------------------|---------------------|------------------|-------------------------|---------------------------------|------------|
| NiO/ZnAl2O4     | 65                 | 0.15                | 450              | 0.17                    | 10.16                           | This work  |
| 0.08wt%NaZnFe2O4| 34                 | 1                   | 340              | 0.13                    | 1.807                           | [46]       |
| Co3O4 spinel    | 48                 | 1                   | 450              | 0.17                    | 3.355                           | [47]       |
| Fe(2+) [Fe(3+)0.5Al0.5]2O4 spinel | 40 | 1 | 320 | 0.12 | 1.962 | [48] |
| CuZn1/2Al2O4 spinel | 4   | 1 | 250 | 0.42 | 0.687 | [49] |
| ZnFeO2-nNa      | 39                 | 0.5                 | 320              | 0.28                    | 8.927                           | [22]       |
| Cu–Zn–Al/SAPO-34| 33                 | 0.5                 | 400              | 0.19                    | 5.126                           | [50]       |
| ZnGa2O4/SAPO-34 | 37                 | 0.5                 | 450              | 0.19                    | 5.747                           | [50]       |

Fig. 6: Catalytic stability test over NiAl2O4, ZnAl2O4, NiO/ZnAl2O4, ZnO/NiAl2O4 and Al2O3 catalysts at 600 °C

ZnAl2O4, ZnO/NiAl2O4 and Al2O3 considered in this study, the Ni containing catalysts such as NiAl2O4, NiO/ZnAl2O4 and ZnO/NiAl2O4 produced CH4 and CO as the product but the Zn containing catalysts such as ZnAl2O4 as well as Al2O3 produced CO as the only product. All the nickel-containing spinels and oxide/spinel structures showed a high selectivity towards methane even at high temperature. NiO/ZnAl2O4 system has a methane selectivity of ~85% as well as ~50% at 450 °C and 600 °C, respectively.

The CO2 conversion exhibit a decrease in the order: NiO/ZnAl2O4 < NiAl2O4 < ZnO/NiAl2O4 < ZnAl2O4 < Al2O3. This can be correlated with increasing Ni content. Given that an increase in Ni content can enhance CO2 hydrogenation activity [40]. The NiO/ZnAl2O4 exhibited 65% CO2 conversion at 600 °C with CH4 and CO as the products. All of the Ni containing catalysts produce CH4 as main products and CO as minor products while ZnO and other Zn containing catalysts as well as Al2O3 produce only CO.
In general, Ni based catalysts produce CH₄ through decomposition of formate species to CO and subsequent hydrogenation of adsorbed CO leads to the production of CH₄ [41] and ZnO is more active for the RWGS reaction [42]. Table 4 lists the CO₂ consumption rates of all the catalysts studied at 600 °C. Figure 5 depicts the CO₂ consumption rate as a function of temperature for all the studied catalysts. The CO₂ consumption rate is highest on NiO/ZnAl₂O₄, namely ca. 19.7 μmol h⁻¹ g⁻¹ at 600 °C which was 2.5 times higher than that of Al₂O₃ (ca. 7.9 μmol h⁻¹ g⁻¹ at 600 °C) catalyst. This catalyst also outperforms other reported spinel catalysts (Table 5) in the CO₂ hydrogenation reaction.

Although the surface area of Al₂O₃ was far higher than the NiO/ZnAl₂O₄, the CO₂ consumption rate was far higher on NiO/ZnAl₂O₄. This was due to presence of metallic Ni under reaction condition in NiO/ZnAl₂O₄ than in the other catalysts. Comparative table of CO₂ consumption rate of the catalyst in this study with the spinel catalyst reported in the literature for CO₂ hydrogenation is given in Table 5.

The effect of metal-support interaction was investigated over Ni/SiO₂ catalyst in the CO₂ hydrogenation reaction.
It was reported that the oxygen vacancy present in the support produces surface carbon species and Ni dissociates $H_2$ into atomic hydrogen [44]. In the present study, the high catalytic activity of NiO/ZnAl$_2$O$_4$ catalyst can be attributed to the strong interaction between the Ni and the ZnAl$_2$O$_4$ leading to the incorporation of Ni into the ZnAl$_2$O$_4$ lattice and subsequent formation of oxygen vacancies [45]. This oxygen vacancies produce surface carbon species and the Ni dissociates $H_2$ into atomic hydrogen and forms CO and CH$_4$ as the final products.

### 3.6 Stability of the Catalyst

Figure 6 shows the stability test of all catalysts for CO$_2$ hydrogenation. For all the catalysts, CO$_2$ consumption rate had no obvious decline with time. This suggested that all the catalysts are more stable during CO$_2$ hydrogenation reaction. The ZnO/NiAl$_2$O$_4$ catalyst showed excellent catalytic stability for CO$_2$ hydrogenation among all the catalysts studied.

### 3.7 Spent Catalysts Characterization

The spent catalysts were characterized by XRD, TGA and TEM.

#### 3.7.1 X-ray Diffraction

The spent catalysts were studied by XRD to elucidate the structural changes. The XRD of spent catalysts after catalytic test are displayed in Fig. 7. All Ni containing spent catalysts show peaks in addition to fresh ones at 20 = 45.39°, 52.62° and 77° corresponding to the (111), (200) and (220) planes attributed to the metallic nickel (JCPDS No. 04-0850) [51]. However Zn containing spinels and Al$_2$O$_3$ spent catalysts showed almost no changes in their crystalline phases indicating that their crystal structures are more stable during the reaction.

#### 3.7.2 TGA Analysis

TGA was employed to characterize the carbonaceous deposits on the spent catalysts. The TGA and DTG curves of all the spent catalysts were shown in Figs. 8 and 9 respectively. For all the spent catalysts, the weight loss below 200 °C is ascribed to desorption of adsorbed water. This weight loss is also depicted by peak starting at 50 °C and ending at 200 °C in the DTG curve as shown in Fig. 9. For Ni containing catalysts such as NiAl$_2$O$_4$, NiO/ZnAl$_2$O$_4$ and ZnO/NiAl$_2$O$_4$ both weight loss and weight gain were observed. The weight loss between 200 and 300 °C on NiAl$_2$O$_4$, NiO/ZnAl$_2$O$_4$ and ZnO/NiAl$_2$O$_4$ catalysts were 6.37%, 2.17% and 1.6% respectively. The weight gain above 300 °C on NiAl$_2$O$_4$, NiO/
effectively reduce carbon deposit. This is in line with their higher catalytic activity in CO$_2$ hydrogenation reaction (Table 4).

3.7.3 TEM Analysis

Figure 10 displays the TEM images of the spent NiAl$_2$O$_4$, ZnAl$_2$O$_4$, NiO/ZnAl$_2$O$_4$ and ZnO/NiAl$_2$O$_4$ catalysts. TEM images of spent catalysts reveal notable differences compared to the fresh catalysts. All the used catalysts exhibit more agglomerated particles compared to fresh catalysts. This indicates that all the catalysts were resistive towards carbon formation during the catalytic reaction.

4 Conclusion

CO$_2$ hydrogenation over NiAl$_2$O$_4$, ZnAl$_2$O$_4$, NiO/ZnAl$_2$O$_4$, ZnO/NiAl$_2$O$_4$ and Al$_2$O$_3$ catalysts have been investigated and it was found that NiAl$_2$O$_4$, NiO/ZnAl$_2$O$_4$ and ZnO/NiAl$_2$O$_4$ catalysts exhibit high activity with CO$_2$ conversion of 65% at 600 °C, which is several times more active compared to other catalysts reported in the literature. On the other hand, these catalysts showed a high methane selectivity even at high temperatures. The higher catalytic activity and CH$_4$ selectivity of NiAl$_2$O$_4$, NiO/ZnAl$_2$O$_4$ and ZnO/NiAl$_2$O$_4$ catalysts can be attributed to the presence of metallic Ni under the reaction conditions which can enhance the CO$_2$ hydrogenation activity.

Acknowledgements Open access funding provided by University of Szeged (SZTE). This paper was supported by the Hungarian Research Development and Innovation Office through grants NKFIH OTKA PD 120877 of AS. AK, and KZ is grateful for the fund of NKFIH (OTKA) K112531 & NN110676 and K120115, respectively. The financial support of the Hungarian National Research, Development and Innovation Office through the GINOP-2.3.2-15-2016-00013 project “Intelligent materials based on functional surfaces—from syntheses to applications” and the Ministry of Human Capacities through the EFOP-3.6.1-16-2016-00014 project and the, Grant 20391-3/2018/FEKUSTRAT is acknowledged.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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