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Research Article

Synthesis of Ash Derived Co/Zeolite Catalyst for Hydrogen Rich Syngas Production *via* Partial Oxidation of Methane

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Abstract

The objective of this study was to analyze the catalytic performance of series of cobalt-modified Zeolite-4A supported catalysts for the syngas (CO and H_2) production at 800 °C via the partial oxidation of methane (POM). The Co/Zeolite-4A catalyst was synthesized using a two-step hydrothermal method from coal fly ash. The synthesized catalysts were characterized by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX), and Thermogravimetric Analysis (TGA). The catalyst shows a crystalline structure with stability up to 900 °C. The catalytic performance analysis shows the CH_4 conversion increases from 29 to 68% for 0 and 10 wt% Co over Zeolite-4A, respectively. The H_2 selectivity was improved from 28–56%, while CO selectivity increased from 24–52 % making H_2/CO ratio > 1. The stability analysis shows the 10% Co/Zeolite-4A withstand for 24 h a time on stream (TOS). Finally, the spent catalyst analysis was carried out to check the carbon formation along with its structural analysis. The minimal carbon formation is analyzed in 24 h TOS for POM reaction.

Keywords: Partial oxidation of Methane (POM); Zeolite-4A; Hydrogen production; Syngas

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1. Introduction

Since the discovery of the ill effects of greenhouse gases (GHGs), the emphasis of the scientific community has been to mitigate those effects and transition towards zero emission fuels. Hydrogen, due to its high energy density and renewability, has been the major focus [1,2]. However, the renewable hydrogen production still needs to grow exponentially to meet the energy demands of the world. Therefore, there is a need of transition techniques to produce hydrogen from fossil fuels to consume them in an environ-

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mentally friendly way with minimum GHG emissions [3–6].

Obtaining valuable chemical products from CH_4 has been studied extensively [7–10]. Commonly, this is achieved by obtaining syngas from CH_4 [3,11,12]. The main component of natural gas is CH_4 which itself is a GHG but can be used in green energy applications which have been a focus of researchers owing to their high efficiency and low emissions [13–16]. The CH_4 is usually converted to syngas using steam methane reforming [17], dry reforming [18–20], and partial oxidation of methane (POM) [4,21–23]. Both the reforming processes are very endothermic, *i.e.* high temperature and/or high pressure of CH_4 is required, whereas none of these are required for POM to syngas as it is an exothermic process [4,24]. Moreover, POM yields a hydrogen to carbon monoxide ratio of >1 which is ideal for Fischer–Tropsch synthesis for liquid fuel production [9,22,25].

A vast number of catalysts have been studied and proposed for POM to syngas [3,4,21,24, 26–28]. Kobayashi *et al.* [27] used Rh/zeolite catalyst and were able to obtain conversion of 84% with a H_2/CO ratio of 2.0 at 600 °C and the catalytic performance further improved with the addition of cobalt [28]. Using of cobalt as catalyst with Co_3O_4 as the key active phase is usually considered a less expensive and practical substitute to costly noble-metal based catalysts which possess a higher activity [29]. Cobalt excellent catalytic activity is attributed to its good redox properties, especially, the ease with which cobalt ions can switch between their oxidation states of +2 and +3 allowing the lattice oxygen to move easily [2,30,31].

To enhance the catalytic activity of cobalt, the most used strategy is to disperse it over a porous support, increasing the available surface area for the reaction to take place [1,26,32]. Usually this results in Co_3O_4 having small crystallite size and high specific area, but it can result in strong cobalt-support interactions which can negatively affect the redox properties of cobalt [33,34]. This problem can be dealt with by using zeolite supports which has capability to improve the Co dispersion and provide more active sites [21]. Zeolite can be easily synthesized from a waste coal fly ash. Fly ash is another waste material which is difficult to handle in coal fired power plants [31].

In this study, zeolite-4A was synthesized from coal fly ash using two step hydrothermal reaction. The prepared zeolite was then impregnated with different Co loadings and was analyzed using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX), and Thermogravimetric Analysis (TGA). The catalytic activity tests of all the samples were performed. The stability test of the best performing catalyst was carried out for 24 h. The spent catalysts were analyzed using SEM and TGA analysis for carbon formation analysis.

2. Materials and Methods

2.1 Synthesis of Zeolite-4A from Coal Fly Ash

Coal fly ash which had been obtained from local coal plant is a waste and is very hazardous to environment, therefore, converting the fly ash into other useful products is very advantageous. Zeolite-4A preparation from fly ash is quite easy as the fly ash consists of compounds, which are main constituents of Z- 4A [35]. Zeolite-4A was prepared by 2 step hydrothermal treatment method [26]. First the collected fly ash was dried, crushed, and after sieving it from a screen of 0.2 mm, 30 g of fly ash was introduced into 5 M NaOH solution (ACS reagent) in 700 mL beaker. The temperature for the dissolution was kept at 100 °C for 2 h with nonstop stirring at 300 RPM using magnetic stirrer. Filtration process was then carried out to obtain a clear solution. The molar ratio of the synthesized mixture was adjusted as $SiO_2/Al_2O_3 \approx 1$, Na_2O/SiO_2 1–2, and $H_2O/Na_2O \approx 40$ for the synthesis of single phase and pure Z-4A [36]. A mixed solution was prepared to attain this ratio; therefore, 200 mL of aluminate solution (5 M NaOH solution and 3 g of Al powder) was added to clear filtrate Fly ash solution. Then this solution was stirred for 30 minutes at room temperature at 500 RPM. Primary gel was prepared by aging solution for 12 h overnight. After this the solution was filtered and filtrate were kept in Teflon autoclaves (heat resistant templates) and placed in oven for 1.5 hour for 90 °C and then for 2 h at 95 °C. After that solution was cooled for 12 h at room temperature and then it was again filtered. The obtained residue on filter paper was dried in oven as the dried product is Zeolite-4A. The dried sample was then calcined at 900 °C. After preparation, characterization, and analysis of its various properties, Zeolite-4A was incorporated as a catalyst support. Figure 1 shows the schematic route used for the synthesis of Zeolite-4A.

2.2 Synthesis of Co/Zeolite-4A Catalyst

The 5 wt% solution of cobalt was prepared by dissolving cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) (Sigma Aldrich, 99.99% pure) precursor salt in DI water. Then Zeolite-4A was added to the solution and stirred for 15 minutes at 60 °C. After stirring, the samples were washed with distilled water and were dried overnight at 110 °C in oven. Same process was repeated with 2.5, 7.5, and 10 weight percent cobalt loadings. Before usage of prepared catalyst for syngas production they were calcined at various temperature of 500, 600, 700, and 800 °C for 4 h. Figure 2 shows the synthesis route used for the preparation of Co/Zeolite-4A catalyst preparation.

2.3 Catalyst Characterization

The crystallinity and structure of the fresh catalyst was determined with X-Ray diffraction (XRD) using D-8 Advance (Bruker, Germany) with exciting wavelength of Cu-Kα radiation (λ = 0.15418 nm). The scan rate was set at 0.2 °s^{-1} for 2θ = 10° to 80°. JEOL scanning electron microscope (SEM) (Japan, JSM 6490-A) was used for surface morphological analysis of the prepared Zeolite-4A support and was also used for the determination of the surface morphology of

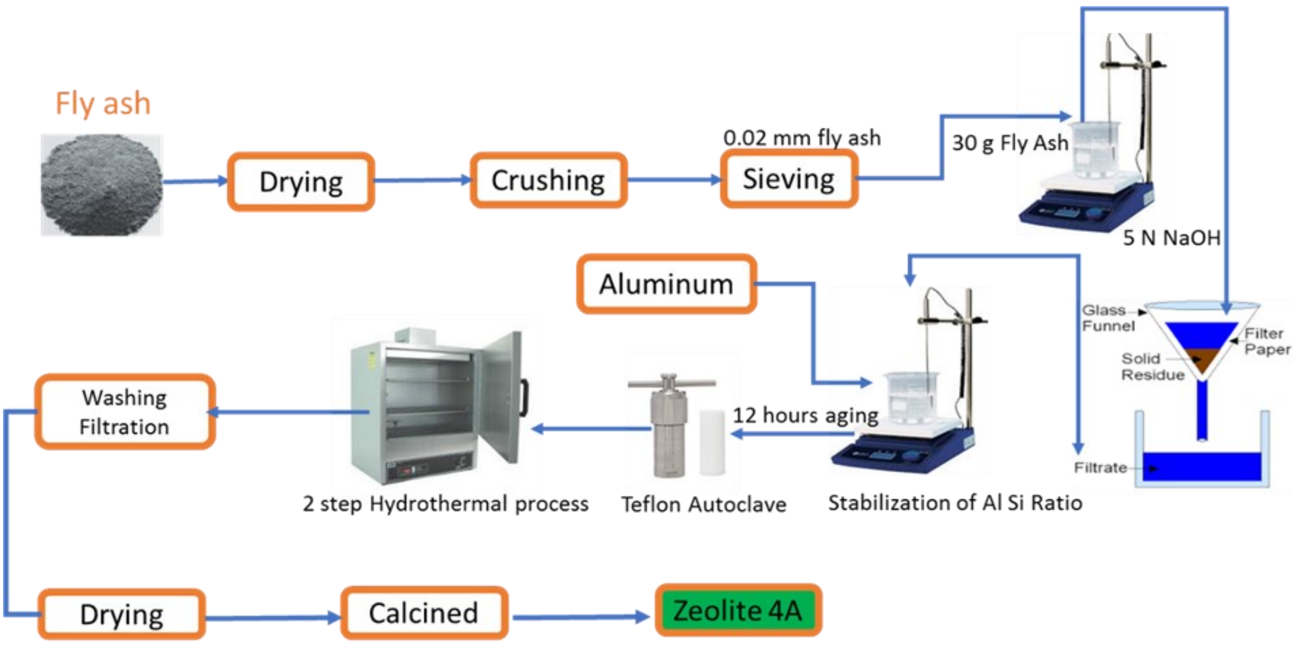

Figure 1. Schematic of Zeolite-4A synthesis via two step hydrothermal process from coal fly ash.

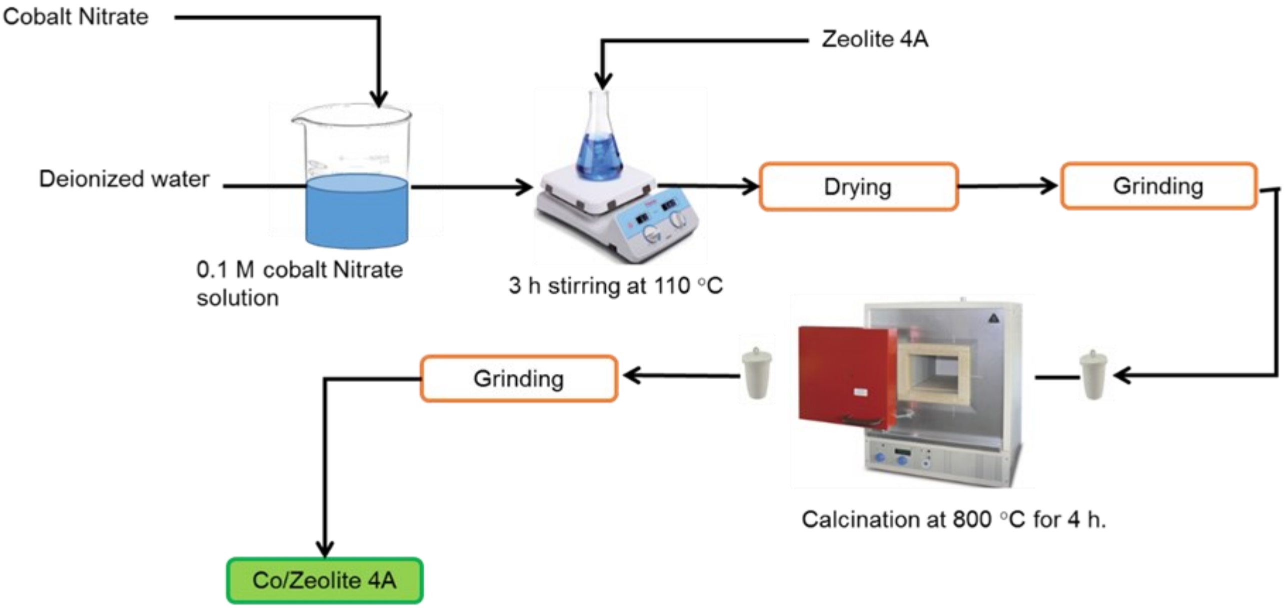

Figure 2. Synthesis of Co/Zeolite-4A.

the prepared Co based catalyst. The sample was gold coated before use for the analysis of SEM/EDX.

Thermal analysis was performed by (TA instruments USA) TGA Thermal Gravimetric analyzer. Samples were heated from 25 °C to 900 °C with a heating rate of 10 °C/min under N_2 flowrate of 50 mL.min^{-1} [37]. The product gases of POM were analyzed with Gas Chromatography (GC-2010 Pro, SHIMADZU Japan) equipped with a TCD column (RT-MS5A) capable of detecting H_2, CO, CO_2, and CH_4.

2.4 Experimental Setup for Partial Oxidation of Methane (POM)

Figure 3 shows the schematic of the experimental setup used to carry out POM reaction. The prepared cobalt loaded catalyst with varying amount of cobalt were mounted into, Parr Inc. (USA) fixed bed reactor. CH_4 and O_2 were introduced into the reactor with a ratio of 2:1. A thermocouple was associated with power controller to control the temperature of reactor. The rector was made of SS-316 having an inner diameter of ½ inch. The prepared catalysts were sandwiched between quartz wool and inserted into the center of the rector. The product were analyzed on Gas Chromatography (GC Shimadzu 2010) using TCD column [31].

2.5 Catalytic Activity Performance Calculations

The catalytic performance of Co/Zeolite-4A for POM was visualized by calculating CH_4 conversion, H_2 selectivity, CO selectivity, and H_2/CO ratio. CH_4 conversion, H_2 selectivity, CO selectivity, and H_2/CO ratio were calculated using Eqs. 1-4.

$$CH_4\ conversion\left(X_{CH_4}\right)\% = \frac{CH_{4,in} - CH_{4,out}}{CH_4} \times 100\% \quad (1)$$

$$H_2\ selectivity\left(S_{H_2}\right)\% = \frac{\left(nH_2\right)_{produced}}{\left(2 \times nCH_4\right)_{converted}} \times 100\% \quad (2)$$

$$CO\ Selectivity\left(S_{CO}\right)\% = \frac{\left(nCO\right)_{produced}}{\left(nCH_4\right)_{converted}} \times 100\% \quad (3)$$

$$H_2/CO\ ratio = \frac{\left(nH_2\right)_{produced}}{\left(nCO\right)_{produced}} \quad (4)$$

3. Results and Discussion

3.1 Physicochemical Properties of Catalyst

Figure 4 shows the XRD spectra obtained for Zeolite and Co/Zeolite-4A. Zeolite-4A was matched with JCPDS card #39−0222 while Co_2O_3 was matched with JCPDS card #42−1467. The cobalt oxide that formed as a result of impregnation was found to possess cu-

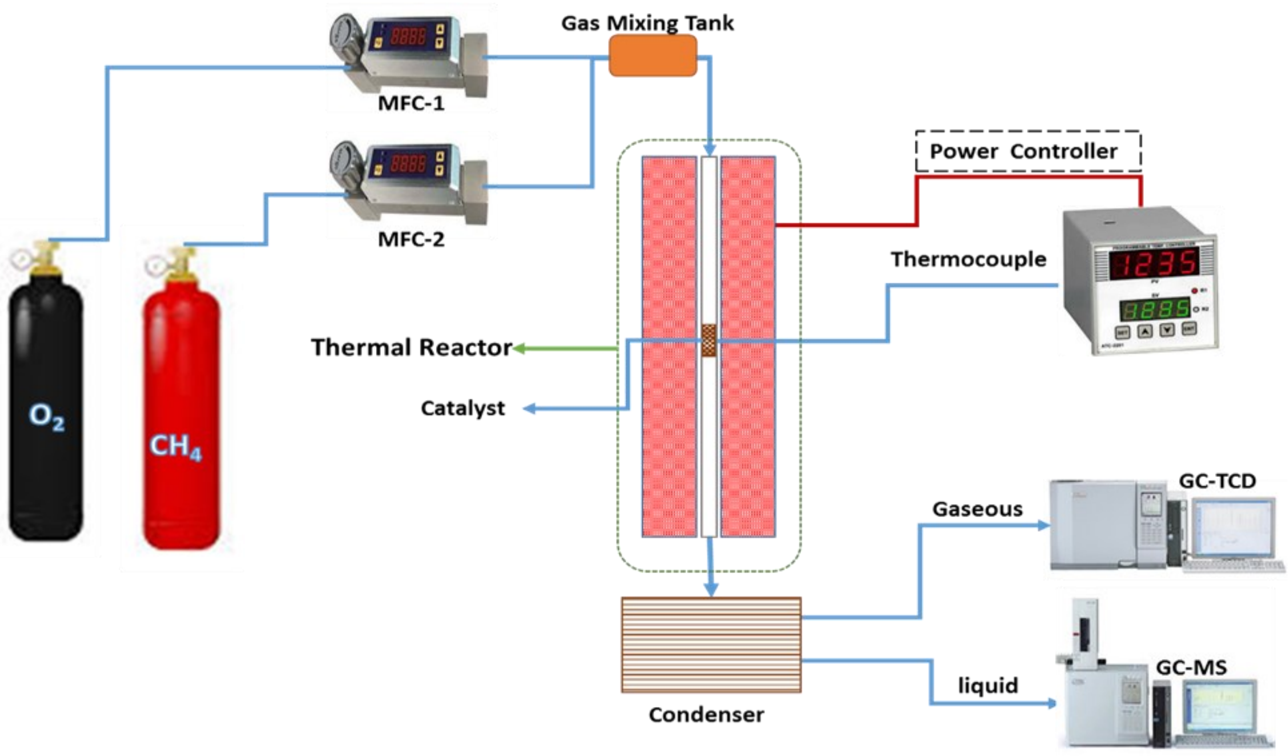

Figure 3. Experimental setup for catalytic partial oxidation of methane.

bic crystalline structure possessing the Fm3c space group. Figure 5 shows the SEM micrographs of Zeolite-4A and Co/Zeolite-4A at a magnification of 1 μm. It can be seen from the images that the zeolite itself possesses a flaky structure. Figure 5 (b) shows the SEM images of Zeolite-4A after impregnation with cobalt. The flake structure of Zeolite-4A can be seen and possibly the cobalt particles are dispersed over the surface. Figure 6 shows the EDX results of Co/Zeolite-4A. Since the precursor of Zeolite-4A, coal fly ash, consists of multiple metal oxides which got incorporated in the structure of Zeolite-4A, can be seen. The EDX results are in line with the XRD results and show that Co/Zeolite-4A was obtained, where we can see the presence of possible elements in the provided composition including cobalt.

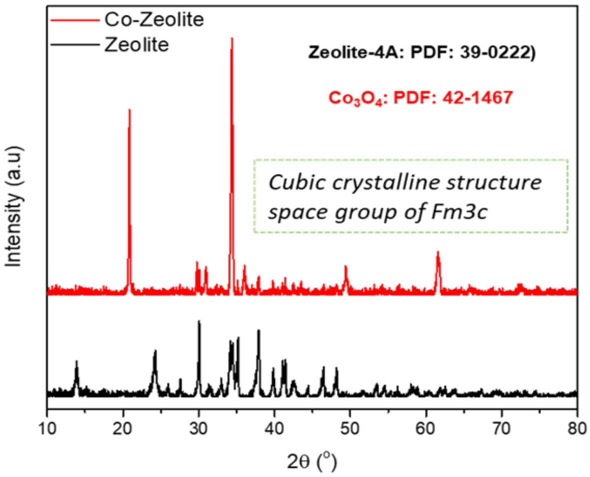

Figure 4. XRD analysis of Zeolite-4A and Co/Zeolite-4A.

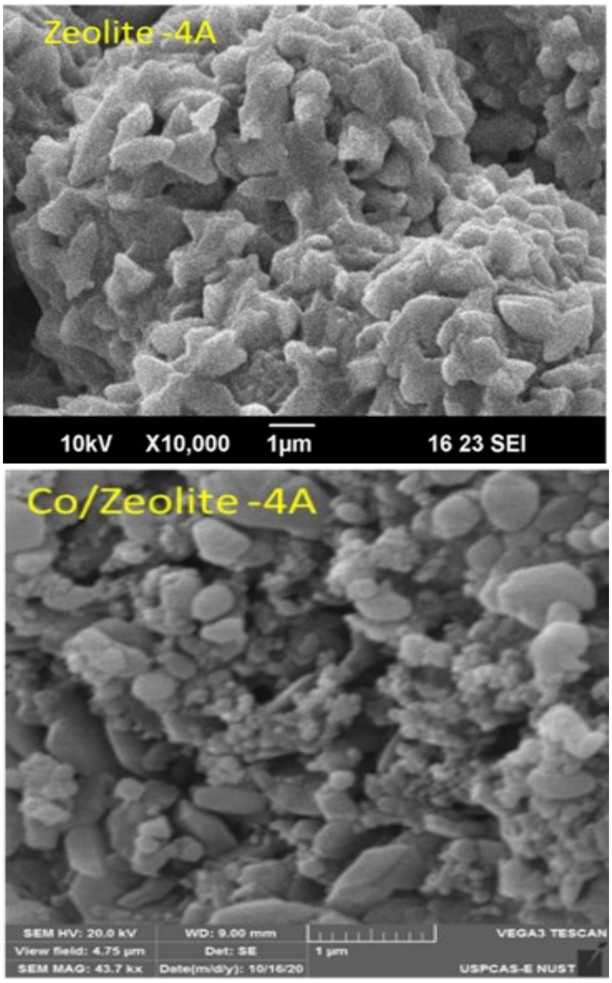

Figure 5. SEM Micrographs (a) Zeolite-4A (b) Co/Zeolite-4A.

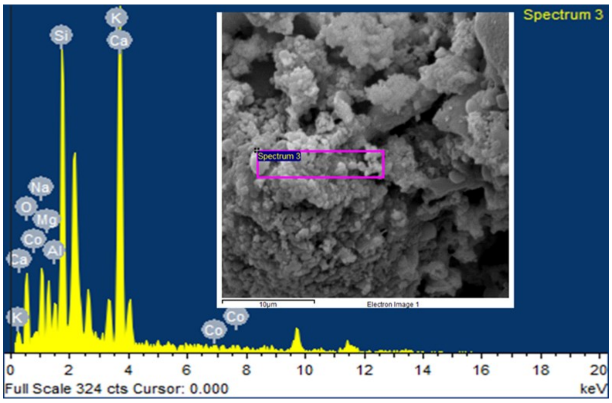

Figure 6. EDX analysis of Co/Zeolite-4A.

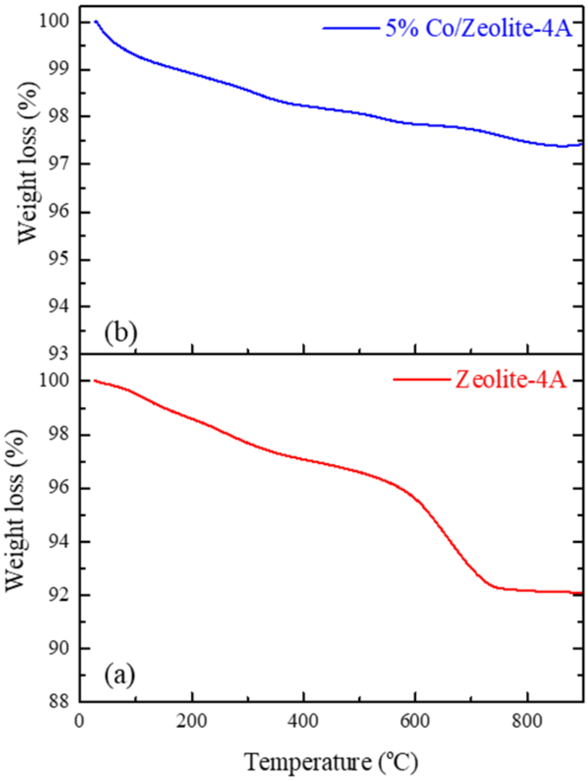

Figure 7. TGA analysis of fresh (a) Zeolite-4A before calcination (b) Co/Zeolite-4A after calcination.

Figure 7(a-b) shows the thermogravimetric analysis results of Zeolite-4A and Co/Zeolite-4A. As can be seen in the graph, the Zeolite-4A initially loses its moisture, ~3%, till 200 °C, the second weight loss between 200–600 °C can be attributed to the desorption of volatiles within the zeolite lattice and the third weight loss in the region of 600–750 °C can be attributed to the formation of stable and pure Zeolite-4A [36]. The TGA analysis shows the calcined Co/Zeolite-4A is highly stable at high temperatures. The weight loss of ~2.5% can be attributed to moisture loss absorbed and adsorbed in the Zeolite-4A framework. Once all the moisture is removed, no more weight loss is observed.

3.2 Catalyst Screening and Stability Analysis for POM

Figure 8 shows the results of catalytic screening test of Zeolite-4A, 2.5% Co/Zeolite-4A, 5% Co/Zeolite-4A, 7.5% Co/Zeolite-4A, and 10% Co/Zeolite-4A. As can be seen in Figure 8 (a), Zeolite-4A itself possesses moderate activity for POM as average CH_4 conversion is ~30% with H_2 and CO selectivity of ~28% and ~24%, respectively. However, as soon as the Zeolite-4A is impregnated with Co, the average CH_4 conversion increases significantly and achieves a maximum of ~68% for 10% Co/Zeolite-4A. Figure 8 (b,c) show that the average H_2 and CO selectivity follow a similar trend and reach ~56% and ~52%, respectively. Figure 8 (d) shows that the H_2 to CO ratio also stays >1 for all the compositions, indicating that Co/Zeolite-4A catalysts are very practical for industrial applications.

The catalyst stability test carried out for 10% Co/Zeolite-4A is presented in Figure 9. The catalyst was operated continuously for 24 h. The CH_4 conversion initially increases for 5 h. and stabilizes. The CH_4 conversion results than start declining gradually after 11 h and follows the declining trend until the end of the run. The H_2 and CO selectivity results follow a

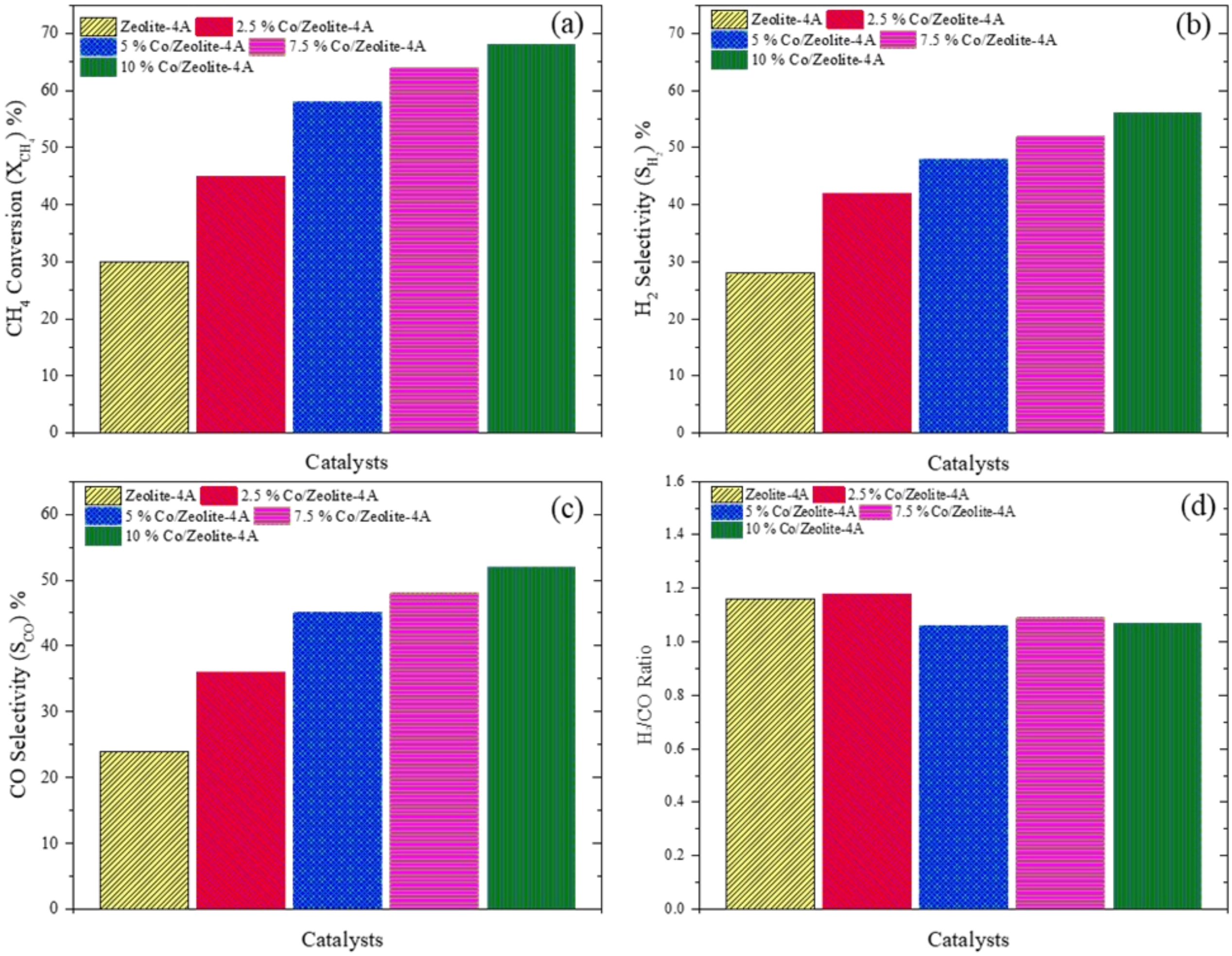

Figure 8. Catalyst screening (a) CH_4 conversion (b) H_2 selectivity (c) CO selectivity (d) H_2/Co ratio; flow rate 30 mL.min^{-1}, cat loading 0.25 g, reaction temperature 800 °C, $CH_4/O_2 = 2$.

similar trend. Moreover, The H_2 to CO ratio stays almost the same for 24 h and stays >1. The decrease in catalytic performance can be attributed to the formation of hot spots which result in the structural collapse and aggregation of the active phase [38,39].

3.3 Characterization of Spent Catalyst

Spent catalyst of 10 wt% Co/Zeolite-4A was analyzed using SEM and TGA. The analysis shows the change in surface morphologies and crystal structure. Figure 10 (a) depicts the weight loss trend of the spent catalyst. Two major weight losses can be seen in the graph. The first major weight loss is attributed to the oxidation volatile organics formed during the POM reaction and deposited on the surface of the catalyst, while the second weight loss, after 700 °C, can be attributed to the oxidation of graphitic carbon [4]. Figure 10 (b) presented the SEM micrograph obtained for the spent catalyst. The SEM image reveals that the surface morphology has changed considerably as majority of the surface is covered with deposited carbon. The deposited carbon can be seen to have granular structure. The coke formation can occur in catalytic partial oxidation of CH_4 due to the formation of hot spots on the catalytic surface due to the fact that Zeolite-4A has insulating properties and is unable to dissipate heat properly [40]. The catalytic stability test also see a decline in performance and are supported by the SEM images.

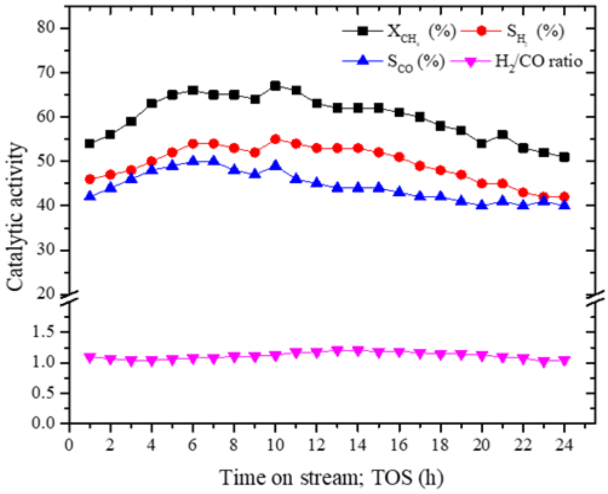

Figure 9. Effect of time on stream (TOS) on catalytic performance of 10 wt% Co/Zeolite-4A.

4. Conclusions

Cobalt loaded Zeolite-4A with different Co loadings were examined as catalyst for the POM with CH_4 to O_2 ratio = 2. The TGA of the prepared catalyst showed appreciable stability possessed by Co/Zeolite-4A. The SEM images showed that cobalt was successfully impregnated onto the Zeolite-4A framework. The catalytic activity test showed that Co/Zeolite-4A possess good catalytic activity for the POM achieving a maximum of ~68% average CH_4 conversion and a maximum of H_2 and CO selectivity average of ~56% and ~52%, respectively. The TOS test revealed that the catalyst possesses a good catalytic stability as CH_4 conversion of >50% can be seen even after 24 h. of continuous operation. Therefore, it can be concluded that Zeolite-4A framework can be used as po-

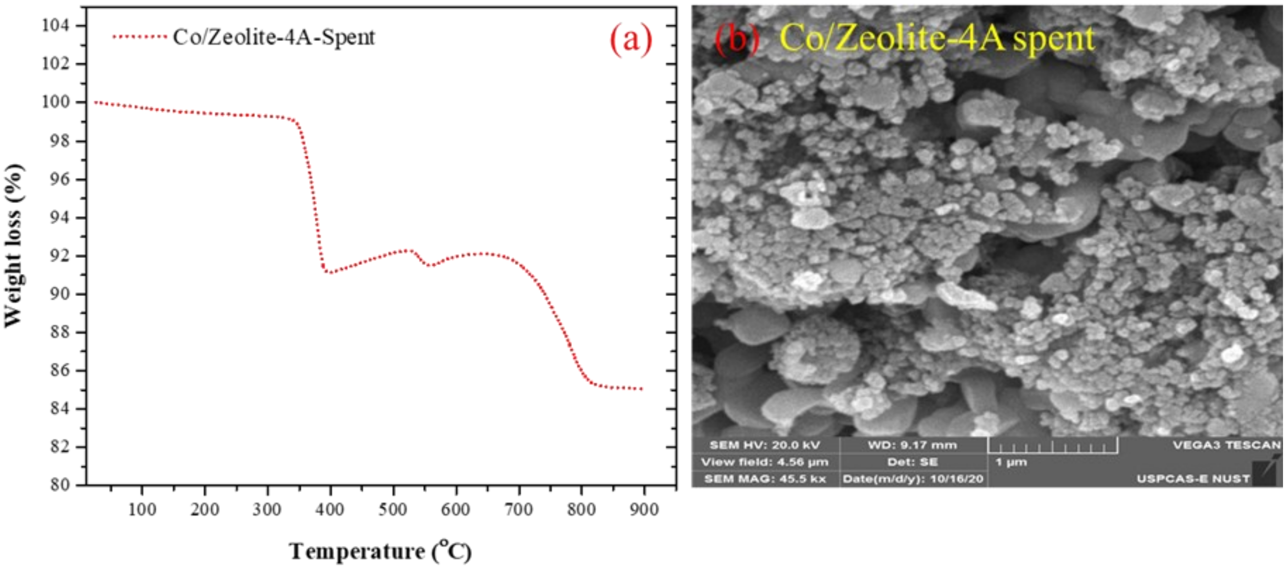

Figure 10. (a) TGA analysis of spent Co/Zeolite-4A (b) SEM analysis of spent Co/Zeolite-4A.

tential catalyst support for industrial applications specially in reforming techniques for H_2 production.

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