

CO₂ reforming of methane over Ta-promoted Ni/ZSM-5 fibre-like catalyst: Insights on deactivation behavior and optimization using response surface methodology (RSM)

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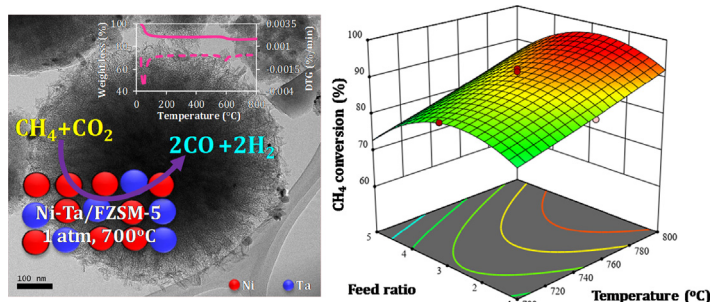
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HIGHLIGHTS

- Fibre-like Ni-Ta catalyst was prepared by microemulsion and impregnation method.
- Ta was evaluated as an effective promoter under different feeding compositions.
- Addition of Ta increases the rate of reactants dissociation and carbon gasification.
- Small-size and immobilized Ni sites led to strong catalytic stability.
- Optimum CH₄ conversion of 96.6% at T = 784.15 °C, CO₂:CH₄ ratio = 2.52 and GHSV = 33760 mL g⁻¹ h⁻¹.

GRAPHICAL ABSTRACT



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ABSTRACT

The catalytic performance of fibre-like Ta-promoted Ni/ZSM-5 in dry reforming of methane (DRM) was studied under different feeding compositions for obtaining a robust catalyst, which is important for large-scale production of syngas via DRM. The deactivation of unpromoted Ni/ZSM-5 was due to polymerization of carbon deposits which block the active sites and accelerate agglomeration. Introduction of Ta was shown to facilitate the rate of dissociation of reactants and carbon gasification due to increased Ni-support interaction and surface oxygen species. From ANOVA analysis, operating temperature was found to be the most significant operating parameter that influence CH₄ conversion. The optimum CH₄ conversion predicted from the response surface analysis is 96.6% at reaction temperature of 784.15 °C, CO₂:CH₄ feed ratio of 2.52, and GHSV of 33,760 mL g⁻¹ h⁻¹. The strong catalytic stability is a result of the small-size and immobilized Ni sites which is vital for efficient DRM catalyst development.

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1. Introduction

Carbon dioxide management in terms of capture and utilization has received attention in recent years (Abdulrasheed et al., 2018;

Sohaib et al., 2020). From an industrial standpoint, CO₂ is not only an effluent gas with detrimental environmental footprint, but also as an intriguing raw material (Li et al., 2020; Zhang et al., 2020a). Despite the potentials of carbon capture processes, utilization of hugely stored CO₂ has found limited application. The major alternative to address this problem is utilizing CO₂ as feedstock integrated with CH₄ conversion process to produce syngas used as

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platform chemical in the industries (Galadima and Muraza, 2019; Gambo et al., 2018). Dry reforming of methane (DRM) is an environmentally benign process for pure syngas (equimolar ratio of H_2 and CO) production appropriate for subsequent Fischer-Tropsch process (Hambali et al., 2020a; Siang et al., 2020). Despite its economic and environmental potentials, large-scale production of syngas via DRM is still in its infancy due to operational constraints exhibited by the several catalysts involved. As such, implementation is dependent on the successes attained in development of low cost and robust catalyst system that can withstand the harsh conditions of DRM process (Abdulrasheed et al., 2020; Chong et al., 2020a).

As we recently reviewed, catalyst component in terms of active metals, support and promoter is imperative for stable DRM performance (Abdulrasheed et al., 2019a). Ni-based catalysts are suitable for DRM due to their wide availability, moderate cost and high turnover frequency. Nevertheless, they are prone to fast deactivation due to formation of carbon species, usually of encapsulation and graphitic type. To produce a robust Ni catalyst, several factors have been explored. These factors include nature of active metal, type of support, metal dispersion, basic and acidic properties, particle size reduction, metal-support interaction, change in preparation and metal doping method (Abdulrasheed et al., 2019b; Aramouni et al., 2018). It has been substantiated in lots of researches that obtaining an anti-carbon and anti-sintering catalyst by tuning a single factor is difficult to achieve (Abdulrasheed et al., 2019a). Hence, collaborative association of various factors is prerequisite for stable and efficient catalyst development.

The development of structured support materials has been conceived to significantly hinder deactivation of Ni catalysts. Many findings attributed the remarkable performance of structured catalyst system to confinement of active metals in the support and enhanced metal-support interaction (Usman et al., 2015; Zhang et al., 2020b). Structured supports such as mesoporous silicalite-1 zeolite (Bawah et al., 2018), trimodal porous silica (Amin et al., 2017), core-shell Al_2O_3 (Jabbour et al., 2016) and core-shell SiO_2 (Abdulrasheed et al., 2019b; Sun et al., 2020) nickel catalysts with astonishing performance, have thus far been employed in DRM reaction. Fabricating structured materials was achieved via contemporary synthesis techniques, forming catalyst system with mesoporous architecture (Abdulrasheed et al., 2019a; Masudi et al., 2020a). Kobayashi et al. (Kobayashi et al., 2019) developed a high surface area ($S_{BET} = 487 \text{ m}^2/\text{g}$) birdcage-type zeolite support via microemulsion method. Likewise, one-pot micro-emulsion method was applied to fabricate yolk-shell SiO_2 support (Das et al., 2020). From our previous study, a bi-component Ni-Ta catalyst supported on fibrous ZSM-5 with surface area of $603 \text{ m}^2/\text{g}$ and pore sizes of 3–6 nm was for the first time reported in DRM process (Hambali et al., 2020b). The Ni-Ta catalyst showed low carbon deposition (4.2%) as a result of cooperative interaction between the catalyst components. Therefore, Ni-Ta/FZSM-5 was used in the current study in order to delve on the deactivation behavior under different feeding compositions.

Apart from tuning of the catalyst components, manipulating process parameters such as operating temperature, gas hourly space velocity (GHSV) and feed composition is an effective approach for ensuring optimal catalytic DRM performance (Alsaif et al., 2020; Chong et al., 2020b). Response surface methodology (RSM) is an analytical procedure for optimization via mathematical and statistical techniques towards designing, improving and optimizing complex processes (Masudi et al., 2020b; Zhalehrajabi et al., 2020). Essentially, optimization via RSM considers multi-variate designs in order to evaluate the interaction between input and output variables with the objective function of determining the optimum conditions. The central composite design (CCD) interface is commonly used to develop a

second-order model that predict responses. Hossain et al. (Hossain et al., 2019) applied statistical optimization via CCD to study the effect of feed ratio, reaction temperature and GHSV on reactant conversion over $Ni/CaFe_2O_4$ catalyst. The authors observed that effect of reaction temperature on the response variables is the most significant among the variables considered. This approach was recently used by Chong et al. (Chong et al., 2020b) and Izzah et al. (Izzah et al., 2020) for optimization of DRM process parameters.

In this work, catalytic stability of Ni-Ta/FZSM-5 under different feeding compositions was investigated to get insights on the anti-carbon deposition behavior. The catalytic stability was examined using reactant stream comprising of 20% CH_4 , 20% CO_2 and 60% N_2 for 30 h and then, the feed gas was switched to undiluted feed (50% CH_4 and 50% CO_2) with higher amount of reactant for another 30 h at 700 °C and atmospheric pressure. The structural changes after the stability tests were evaluated using combined techniques. Also, optimal operating conditions were determined using RSM. This research is an effort towards development of a robust catalyst for optimal production of syngas via DRM process. To the best of our knowledge, these researches have not been reported before for CO_2 reforming of methane.

2. Experimental section

2.1. Materials

Tetraethyl orthosilicate (TEOS), Cetyltrimethylammonium bromide (CTAB), 1-butanol (C_4H_9OH), ammonium nitrate (NH_4NO_3) and urea were purchased from MERCK Sdn. Bhd., Malaysia, respectively. The ZSM-5 seed ($Si/Al = 23$) was purchased from Zeolyst International. $Ni(NO_3)_2 \cdot 6H_2O$ and Ta_2O_5 were purchased from Sigma-Aldrich. The standard gases were purchased from Merck Industrial Company. All chemicals were applied as received without further purification.

2.2. Catalyst preparation

In this study, microemulsion coupled with zeolite seed crystallization technique was adopted to synthesize the fibrous ZSM-5 (FZSM-5) support according to the previous reported procedure (Hambali et al., 2019; Jalil et al., 2019; Teh et al., 2016). The metals were incorporated on FZSM-5 via incipient wetness impregnation method. Metal loading (5 wt%) was fixed for the monometallic samples, while the bimetallic sample comprise of Ni (5 wt%) and Ta (1 wt%). The impregnated samples were dried at 110 °C in drying oven overnight and calcined at 800 °C for 3 h. The samples were denoted as Ni/FZSM-5, Ta/FZSM-5 and Ni-Ta/FZSM-5.

2.3. Catalyst characterization

X-ray diffraction (XRD) analysis of the crystalline phases of the metal species on the synthesized catalysts were examined by Bruker Advance-D8 X-ray diffractometer. The phase description obtained were matched with JCPDS data. The amount of carbon deposition on spent catalysts surface was measured using Thermal Gravimetric Analysis (TGA) and derivative thermogravimetry (DTG) using Mettler Toledo (SDTA-851) TGA instrument. Typically, 10 mg of spent catalyst was heated in the TGA chamber at a temperature range 30–800 °C. The type of carbon deposits on the post reaction catalysts were examined via Raman spectroscopy, which was monitored on a Renishaw instrument. In a typical Raman measurement, excited laser beams ($\lambda = 512 \text{ nm}$) were focused on the glass slide containing the sample, and the Raman spectra were recorded over the region of $1200\text{--}1800 \text{ cm}^{-1}$.

Transmission electronic microscopy (TEM) was utilized to visualize the morphologies of carbon species on the spent catalysts. The TEM images were obtained using a microscope (JEOL JEM/2100F). Prior to the analysis, each sample was well dispersed via ultrasonication and dried on a copper grid. Temperature programmed oxidation (TPO) experiment with oxygen for the spent catalysts was carried out in a Chemisorption analyzer (Micromeritics Chemisorb-2720).

2.4. Catalytic stability test

The Ta-promoted Ni/FZSM-5 catalyst was chosen because it produced outstanding DRM performance using reactant gases with molar ratio of $\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:3$ (Hambali et al., 2020b). The stability tests under different feeding compositions were conducted in a reactor (fixed bed) with internal diameter of 8 mm, and the experimental setup is illustrated in Fig. 1. In a single run, 20 mg of catalyst in the form of pellets was loaded into the reactor. Prior to the commencement of the reaction, the catalyst was reduced at 700 °C for 3 h in the presence of $\text{H}_2/\text{N}_2 = 50\%$ under 100 mL min^{-1} flowrate. After activation treatment, the stability test of the catalysts was examined for 60 h at atmospheric pressure and operating temperature of 700 °C with gas space velocity of $30,000 \text{ mL g}^{-1} \text{ h}^{-1}$. The long-term stability test of the catalysts was examined using reactant stream comprising of 20% CH_4 , 20% CO_2 and 60% N_2 for 30 h and then, the feed gas was switched to undiluted feed ($\text{CH}_4/\text{CO}_2 = 50\%$) for another 30 h at the same operating conditions. The components of the off-gas were detected and analyzed via online Agilent gas chromatograph (GC-7820 N) coupled with carboxen 1010 column, and a thermal conductivity detector (TCD). The conversions and H_2/CO ratio were computed using Eq. ((1)–(3)). Thermodynamic values displayed in Fig. 2 (dashed-lines) were computed by HSC 6.0 Chemistry software.

$$\text{CH}_4 \text{ conversion} = \frac{n_{\text{CH}_4, \text{in}} - n_{\text{CH}_4, \text{out}}}{n_{\text{CH}_4, \text{in}}} \times 100 \quad (1)$$

$$\text{CO}_2 \text{ conversion} = \frac{n_{\text{CO}_2, \text{in}} - n_{\text{CO}_2, \text{out}}}{n_{\text{CO}_2, \text{in}}} \times 100 \quad (2)$$

$$\frac{\text{H}_2}{\text{CO}} = \frac{n_{\text{H}_2, \text{out}}}{n_{\text{CO}, \text{out}}} \times 100 \quad (3)$$

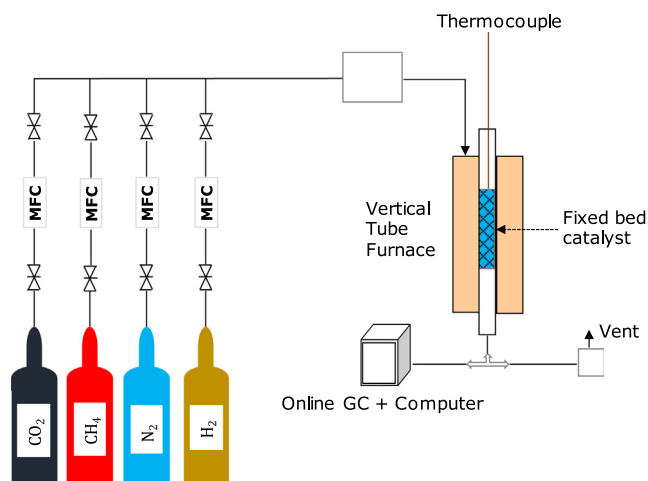


Fig. 1. Schematic diagram of reactor setup for dry reforming of methane reaction.

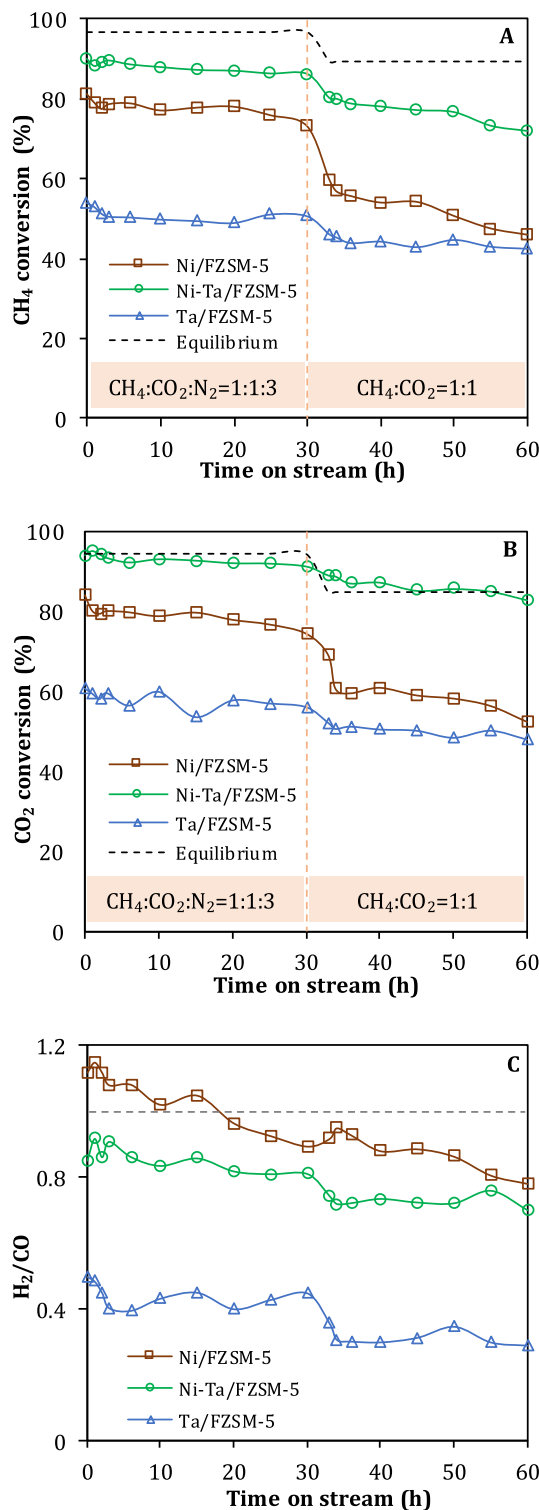


Fig. 2. Catalytic performance of the catalysts in DRM: (A) CH_4 conversion, (B) CO_2 conversion, and (C) H_2/CO ratio. (Reaction conditions: temperature = 700 °C and GHSV = $30,000 \text{ mL g}^{-1} \text{ h}^{-1}$).

2.5. Experimental design and optimization

To examine the impact of process parameters on Ta-modified Ni/FZSM-5 catalyzed CO_2 reforming of methane reaction, a statistical approach was employed to design the experiments using response surface methodology (RSM). The statistical experimental design and process parameter optimization was conducted on

Design Expert 11.0 software using a quadratic polynomial model as presented in Eq. (4).

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_a A^2 + \beta_b B^2 + \beta_c C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (4)$$

where Y denotes the predicted response, while A, B and C are the independent variables. The term β_0 represents constant coefficient, while the linear regression coefficients are denoted by β_1 , β_2 , while the β_a , β_b , β_c represent quadratic regression coefficients, and the interaction of regression coefficients are represented by β_{12} , β_{13} , β_{23} .

Three operating parameters, temperature, CO_2/CH_4 feed ratio and GHSV are chosen to evaluate their impact on catalytic performance. The selected range was temperature of 700–800 °C, 1–5 CO_2/CH_4 feed ratio and GHSV of 10,000–60,000 $\text{mL g}^{-1} \text{h}^{-1}$. The selected ranges were based on reported works (Alsaffar et al., 2020; Chong et al., 2020b). A total of sixteen runs of experiments were designed using a five-level-three-factor central composite design (CCD) to investigate the impact of the operating parameters on catalytic performance. CH_4 conversion, being the rate determining step for CO_2 reforming of methane on heterogeneous catalysts was selected as the response variable (Alsaffar et al., 2020; Sidik et al., 2016). The fit of model can be analysed via the analysis of variance (ANOVA). The correlation between the predicted and experimental values was derived to determine the coefficient of determination (R^2) value of the model (Eq. (5)).

$$R^2 = 1 - \frac{SS_{\text{Residual}}}{SS_{\text{Model}} + SS_{\text{Residual}}} \quad (5)$$

where SS represent sum of squares. The value of R^2 is a vital factor that access the variability in the experimental data. The Fischer variation ratio (F-value) and probability value (p-value) are important in determining the adequacy of the statistical model.

3. Results and discussion

3.1. Catalytic performance tests

The detailed characterization data of physicochemical properties of the fresh catalysts are available elsewhere (Hambali et al., 2020b). The catalytic performance test was carried out at reaction temperature of 700 °C, 1 atm and GHSV = 30,000 $\text{mL g}^{-1} \text{h}^{-1}$ for 60 h. The spent catalysts were tested for DRM under on-line feed changing conditions. Two types of feed were introduced into the reactor, a diluted feed comprising of 20% CH_4 , 20% CO_2 and 60% N_2 for 30 h and then, the feed gas was switched to undiluted feed ($\text{CH}_4/\text{CO}_2 = 50\%$) for another 30 h at the same operating conditions. The results of the catalytic performance are presented in Fig. 2. These results showed that all catalysts approximately retained their activity over 30 h of time on stream test with diluted feed ($\text{CH}_4/\text{CO}_2/\text{N}_2 = 1:1:3$). The drop in initial activity for CH_4 conversion (Fig. 2A) with diluted feed follows the order: Ni-Ta/FZSM-5 (3.9%) < Ta/FZSM-5 (6.3%) < Ni/FZSM-5 (9.8%). The decrease of initial activity of Ni/FZSM-5 was much higher than that of other catalysts. On the other hand, when the feed gas was switched to undiluted feed ($\text{CH}_4/\text{CO}_2 = 1:1$), the dynamics of the reaction slightly changed as a result of higher concentration of CH_4 and CO_2 in the reactant stream, which is expected to induce more coke formation (Aramouni et al., 2018; Usman et al., 2015). Ni/FZSM-5 catalyst displayed the highest drop in activity, while no substantial sign of deactivation in the case of the Ta-based catalysts. Similar catalytic behaviour was observed for CO_2 conversions as shown in Fig. 2B. For the 30 h of TOS study under diluted feed, Ni-Ta/FZSM-5 displayed the lowest drop in initial CO_2 activity. Furthermore, it showed no significant change in CO_2 conversion when the feed was switched to undiluted feed. However, Ta/FZSM-5 catalyst

showed a decline of 7.9% for the first 30 h on stream, with notable decrease when the type of feed gas was changed. The Ni/FZSM-5 catalyst was most affected with 42.3% loss in activity under undiluted feed atmosphere. Irrespective of the feed type, Ni-Ta/FZSM-5 displayed superior stability throughout the TOS. Ni/FZSM-5 catalyst performs inferiorly because activation of CH_4 and other reductive species occurred faster than carbon gasification, which led to rapid accumulation of coke.

The product H_2/CO ratio (Fig. 2C) on Ni/FZSM-5 was much higher than those of Ta-based catalysts. The higher H_2/CO ratio obtained by Ni/FZSM-5 suggests susceptibility to CH_4 decomposition side reaction, leading to more carbon deposition (Wittich et al., 2020). The addition of Ta species could amplify interaction of catalyst components and enhance surface basicity as reported in literatures (Guerrero-Pérez, 2019; Hambali et al., 2020b). The extra affinity for CO_2 chemisorption and activation offered by Ta facilitate more CO formation, thereby decreasing the product H_2/CO ratio to value near unity as depicted in Fig. 2C. Literatures (Aramouni et al., 2018; Usman et al., 2015) reported that increased CO_2 conversion result in more CO formation, which signifies less coke deposition as a result of accelerated gasification of surface coke. Overall, the difference between the catalysts in terms of deactivation behavior can be ascribed to differing properties of the Ni and Ta. The bi-component Ni-Ta/FZSM-5 gained the inherent activity of Ni while retaining the anti-sintering impact of Ta. This is in accordance with previous reports (Guerrero-Pérez, 2019; Li et al., 2019) on the stable performance of Ta promoted catalysts.

3.2. Catalyst characterization

The amount of carbon deposition on the spent catalysts after reaction at 700 °C for 60 h were measured using TGA/DTG. Fig. 3 shows the TGA/DTG plots of the spent catalysts examined in this study. According to literature, the weight loss in the temperature range 100–400 °C (zone I) can be attributed to thermal desorption of moisture, whereas weight-loss at 400–800 °C (zone II) are ascribed to oxidation of amorphous coke and carbon whiskers (Gao et al., 2020; Hussain et al., 2020). The overall rate is in the order of Ni-Ta/FZSM-5 (13.24%) < Ta/FZSM-5 (13.33%) < Ni/FZSM-5 (26.74%). For both Ta-based catalysts, there was negligible weight loss at high temperature signifying little carbon deposition. This is in accord with their stable performance throughout the sixty hours stability period (Fig. 2). The most obvious weight loss was observed on Ni/FZSM-5 catalyst. This indicates that large carbon deposits especially the inert carbon or whisker type are

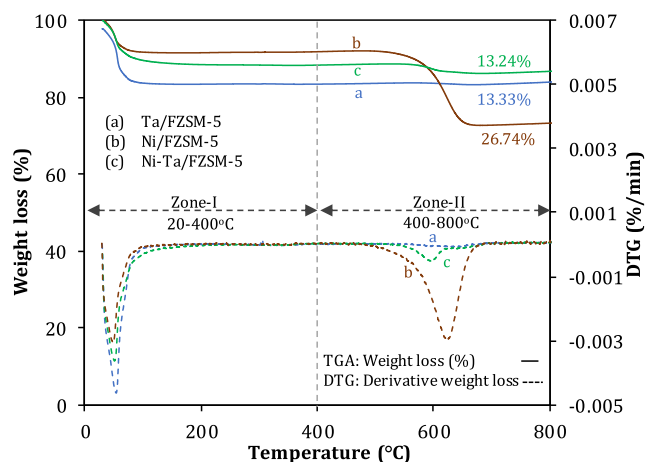


Fig. 3. Analysis of carbon deposition on spent catalysts by TGA/DTG profiles.

formed on the Ni/FZSM-5 catalyst. This form of carbon is difficult to burn off, which lead to blockage of active sites (Wei et al., 2020). It is evident that incorporation of Ta species to Ni catalyst could improve the coke-resistance performance. Odedairo et al. (Odedairo et al., 2016) attested that addition of Ta promoter to Ni/CeO₂ enhanced Ni-support interaction which hindered agglomeration of Ni particles. Zhu et al. (Zhu et al., 2015) observed that incorporation of Ta induced higher catalyst stability.

Raman spectroscopy was used to ascertain the nature of carbonaceous species on the catalysts after DRM reaction. As seen in Fig. 4, the Raman spectrum reveal the presence of G-band and D-band characteristic peaks located at 1580 cm⁻¹ and 1350 cm⁻¹, respectively. The G-band signify the presence of graphite carbon, whereas the D-band indicate the existence of disordered carbon structure (Abdulrasheed et al., 2019b). The relative intensity (I_G/I_D) shows the graphitization degree of carbon deposits. The computed I_G/I_D values were in the trend: Ni-Ta/FZSM-5 (0.85) < Ta/FZSM-5 (0.89) < Ni/FZSM-5 (0.92). This indicate that the carbon deposits on spent Ta-based catalysts possessed lower graphite degree than that on Ni/FZSM-5. Furthermore, the peak strength of Ta containing catalysts is lower compared to that of Ni catalyst, implying less carbon deposition. This agrees with the less amount of carbon deposits on Ta catalysts observed in the TGA/DTG analysis (Fig. 3). Thus, the higher I_G/I_D value for Ni/FZSM-5 led to the low performance observed throughout the stability test (Fig. 2). The graphitic carbon species seems to form readily on the Ni catalyst than on the Ta-based catalysts due to the d-electron transfer from Ta to Ni, which increased the 3d electron density around Ni. Similar observations were reported in literature (Guerrero-Pérez, 2019; Odedairo et al., 2016).

To investigate the amount and the reactivity of carbon deposit on the spent catalysts, O₂-TPO analyses was conducted (Fig. 5). All the spent catalysts displayed single peaks for O₂ consumption between 400 and 750 °C, signalling the oxidation of carbon species in the form of amorphous, whiskers, and carbon nanotubes (Singh et al., 2020). Spent Ni/FZSM-5 catalyst produced a broad peak at 650 °C indicating oxidation of amorphous and whisker carbons. The carbon on Ta/FZSM-5 and Ni-Ta/FZSM-5 were oxidized at lower temperature in contrast to Ni/FZSM-5, which indicates that the carbon species are predominantly of the amorphous type with less potential to cause catalyst deactivation (Al-Fatesh et al., 2020). This is also confirmative from their relatively stable performance throughout the 60 h on stream (Fig. 2). Intriguingly, addition of Ta was thus found to minimize carbon deposition and impede

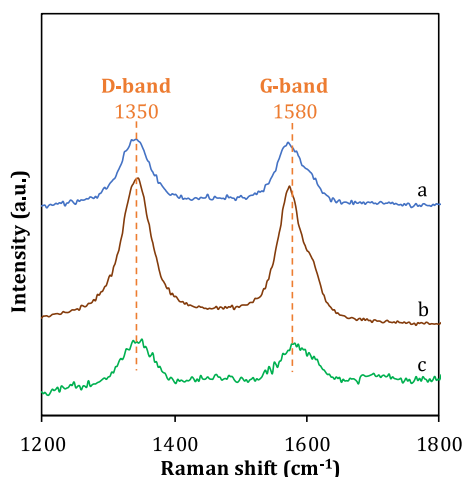


Fig. 4. (A) Raman profiles of spent catalysts (a) Ta/FZSM-5 (b) Ni/FZSM-5 (c) Ni-Ta/FZSM-5.

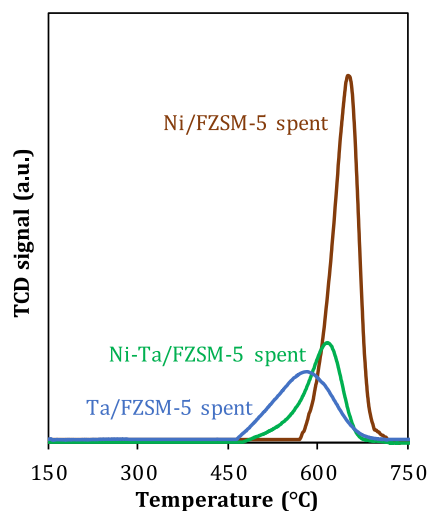


Fig. 5. O₂-TPO profiles of the spent catalysts.

the formation of stable carbon species, which, in turn, improved catalytic stability.

The plotted XRD patterns of the synthesized catalysts (Fig. 6) produced peaks in the range of 7–10° and 22–25° signalling the existence of ZSM-5 phase in the catalysts (Liu et al., 2020). Fig. 6A shows the presence of Ta₂O₅ characteristic peaks for the Ta-based catalysts (Zhu et al., 2015). Furthermore, NiO cubic phase were observed on the fresh Ni catalysts, while the NiO crystallite sizes are presented in Table 1 (Abdulrasheed et al., 2019b). The NiO crystallite size (Table 1) reduced from 14.65 nm to 12.08 nm on addition of Ta₂O₅. This is an indication of improvement in Ni particles dispersion in presence of Ta, which could expose more surface for reduction and reaction (Aramouni et al., 2018). It is well known that coking resistance is favored by small Ni particle size and optimal synergism of catalyst components (Abdulrasheed et al., 2019a). The fact that bimetallic Ni-Ta synergism impedes carbon deposition has been observed in our previous study (Hambali et al., 2020b), and in accordance with literature (Guerrero-Pérez, 2019; Odedairo et al., 2016). XRD patterns of the spent catalysts (Fig. 6B) reveals diffraction peaks at about 26°, which is ascribed to deposited carbon species (Bawah et al., 2018). Nevertheless, the intensity of the carbon peak is relatively lower in the XRD pattern of spent Ta-based catalysts suggesting low carbon graphitization level. This is consistent with the low carbon deposition on Ta promoted Ni/FZSM-5, which corroborates its stable catalytic activity as discussed earlier. The ZSM-5 peaks slightly decreased for monometallic Ni/FZSM-5 and Ta/FZSM-5 catalysts after the CO₂ reforming of methane reaction, which suggests that majority of the support structure was maintained during the long time on stream reaction. It is pertinent to note that the decay in activity was mainly caused by coke deposition rather than Ni sintering due to small Ni (111) peaks at 44.26° that was observed in the XRD patterns of Ni/FZSM-5 and Ni-Ta/FZSM-5. Hence, the absence of carbon whiskers on Ni-Ta/FZSM-5 as well as retained catalyst structure (Fig. 7) ruled out the possibility of pore shrinkage and fracture of the fibrous support (Abdulrasheed et al., 2019b; Das et al., 2020).

Aiming to shed light on the anti-coking behavior of Ni-Ta/FZSM-5, the morphologies of the spent catalysts were examined using TEM analysis (Fig. 7). The TEM images demonstrated the presence of fibrous morphology in the spent catalysts, which indicates a promising application of the spherical fibrous support in other high temperature catalysis. Fig. 7A&B showed the formation of carbon whiskers, located in the region around the Ni particles. Unlike

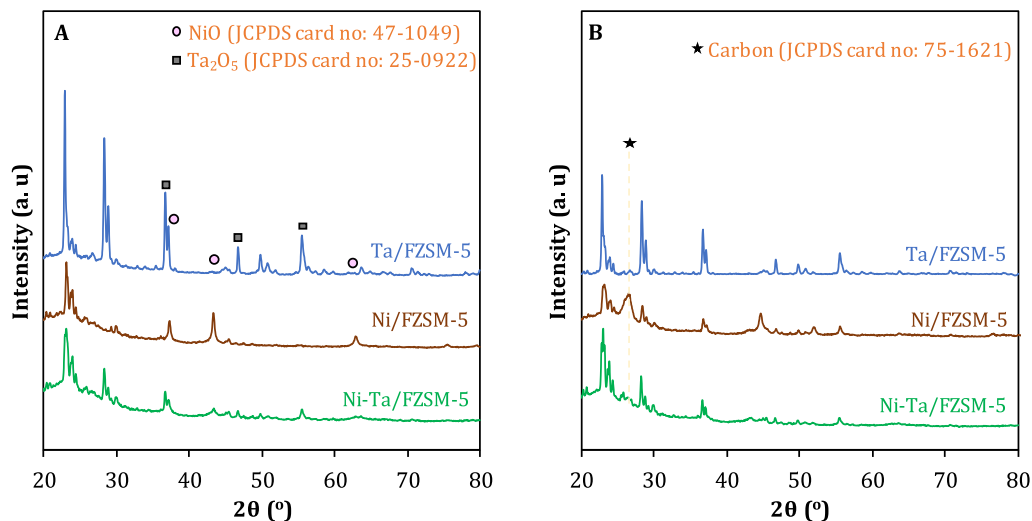


Fig. 6. X-ray diffraction pattern of (A) fresh and (B) spent catalysts.

Table 1
Physicochemical properties and catalytic stability of synthesized catalysts.

Catalysts	Metal Loadings, wt.%		NiO crystal size (nm)	Stability Index
	Ni	Ta		
Ni/FZSM-5	5.0	–	14.65	0.60
Ta/FZSM-5	–	5.0	–	0.81
Ni-Ta/FZSM-5	5.0	1.0	12.08	0.84

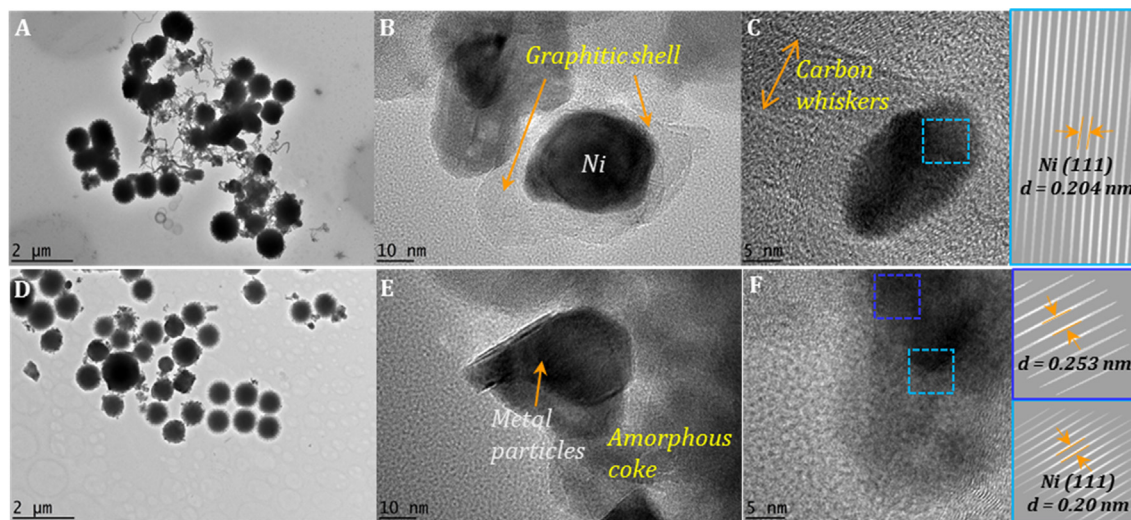


Fig. 7. TEM micrograph of spent Ni/FZSM-5 (A,B) with its lattice d-spacing (C), Ni-Ta/FZSM-5 (D,E) with d-spacing (F).

the situation with Ni/FZSM-5 catalyst which produced large amount of stable and inactive carbon species, the amorphous carbon was observed on spent Ni-Ta/FZSM-5 catalyst (Fig. 7D&E). The negligible visualization of whisker carbon on spent Ni-Ta/FZSM-5 was endowed by the impact of bimetallic Ni-Ta synergism and efficient carbon gasification (Al-Fatesh et al., 2020). This is in good agreement with the TGA/DTG, Raman, O₂-TPO and XRD results. The calculated interplanar distances of randomly selected particles of Ni/FZSM-5 and Ni-Ta/FZSM-5 in Fig. 7C and F are 0.204 nm and 0.20 nm, respectively. These values correspond to Ni (1 1 1) lattice

d-spacing (Abdulrasheed et al., 2019b). A different lattice spacing of 0.253 nm was obtained on Ni-Ta/FZSM-5 (Fig. 7F), which might be related to the texture of Ni-Ta structured particle (Komori et al., 1996; Odedairo et al., 2016). Formation of some bimetallic Ni-Ta alloyed surface should not be excluded, whose precise detection was difficult because of absence of high-resolution measurement. According to previous report, introduction of vanadium promoted coking resistance due to the increase in more reactive step sites on Ni interfacial regions (Valentini et al., 2003). Therefore, inclination of the fibre-like structure towards metal stabilization and the

inherent ability of Ta species to modify the Ni environment led to the anti-coking behavior of Ni-Ta/FZSM-5 catalyst (Guerrero-Pérez, 2019; Hambali et al., 2020b).

The catalytic performance of Ni-Ta/FZSM-5 was compared with literature data on zeolite Ni catalysts as presented in Table 2. The comparative studies (Table 2) reveal that fibre-like Ni/ZSM-5 catalyst exhibited superior stability over long time on stream in contrast to what is attainable by conventional zeolite supported Ni catalysts. This shows that bimetallic Ni-Ta synergism and confinement of metal particles on spherical structured support is a viable approach to enhance coking resistance. Conclusive reports affirmed that metal nanoparticles immobilization on core-shell SiO₂ (Das et al., 2020), KCC-1 (Abdulrasheed et al., 2019b), SBA-15 (Chong et al., 2020b), Al₂O₃ (Wei et al., 2017) and SiO₂-Al₂O₃ (Xiang et al., 2016) prevent catalyst deactivation during DRM. In this regard, fibre-like structured catalyst system seems imperative to the quest for an industrial and commercial DRM process.

3.3. Impact of Ta promoter on deactivation behavior

Carbon laydown is an inevitable accompaniment of syngas production via DRM, due to the harsh operating conditions that raises the molecular energy to cleave the C-H bonds (Abdulrasheed et al., 2019a). The carbonaceous deposit on all the catalysts after 60 h TOS study has been analyzed using TGA, DTG, Raman spectra, XRD, O₂-TPO and TEM. The difference in coking behavior of the catalysts was due to the type and amount of carbon present. Besides, the surface basicity-acidity, reducibility, Ni crystal size as well as metal support interaction controls the rate of carbon formation (Hambali et al., 2020b). Theoretical studies suggest that Ta species are energetically inclined to interact with support, thereby improving interaction of catalyst components (Guerrero-Pérez, 2019; Zhu et al., 2015). As schematically revealed in Fig. 8 and frequently reported by other researchers (Abdulrasheed et al., 2019a; Aramouni et al., 2018), the DRM reaction takes place via the following steps: decomposition of CH₄ on the Ni active sites producing H₂ and CH_x species, while O* species liberated by CO₂ activation then oxidize the CH_x species forming CO and H₂. The carbon species formed include adsorbed surface carbon (C_α), polymeric carbon (C_β) and ordered carbon (C_{whisker}). The C_{whisker} moieties were reported to cause catalyst deactivation by mechanically blocking the active sites (Abdulrasheed et al., 2019b). At high operating temperature, the main route of carbon formation is mostly via CH₄ decomposition. As the carbon build-up increases, the highly reactive carbon species (C_α or C_β) are transformed into carbon whiskers as a result of carbon atom diffusing C/Ni species interface (Aramouni et al., 2018). Ta may promote coke-tolerance by producing soft coke that are easily gasified. This speculation is sponsored by less amount of coke deposits and less refractory coke

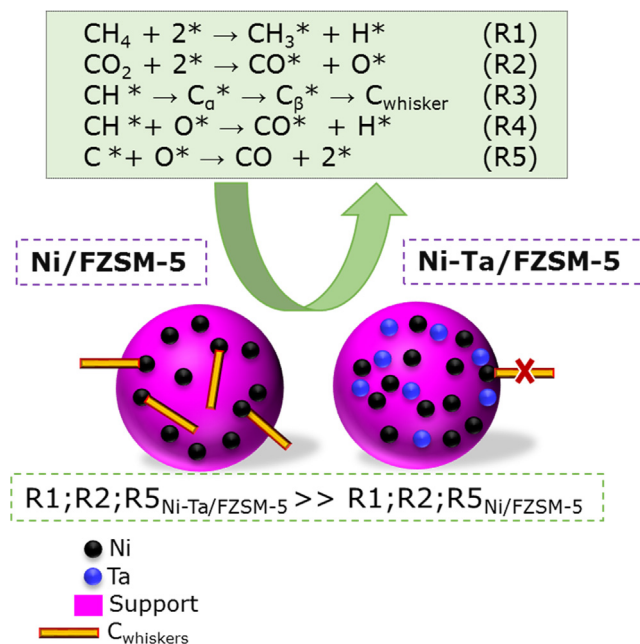


Fig. 8. Reaction scheme for the dry reforming of methane over Ni/FZSM-5 and Ni-Ta/FZSM-5.

observed on the spent Ta-promoted catalyst. The presence of Ta species induces abundant O* species, which readily oxidise and remove carbon formed on the surface of Ta-based catalysts (Chong et al., 2020a; Odedairo et al., 2016). In contrast, the rate of dissociation of reactants and carbon gasification is more rapid on Ta-promoted catalyst as compared to Ni/FZSM-5. The swift polymerization of carbon on Ni/FZSM-5 resulted in the growth of carbon whiskers which accelerated the driving force for agglomeration and coke formation. Furthermore, the stability index (Table 1), defined as the ratio of methane conversion at 3300 min to that at 60 min, increased from 0.60 to 0.84 during the 60 h time on stream when Ta was added. Therefore, it can be concluded that the presence of Ta led to a balance between deposition and removal of carbon species, thus, resulting in the outstanding performance of Ni-Ta/FZSM-5 catalyst.

3.4. RSM study for DRM process

3.4.1. Model analysis and regression equation

In order to study the effect of process parameters on the catalytic performance of Ni-Ta/FZSM-5, a statistical approach was employed to design the experiments using CCD interface of RSM.

Table 2

Comparison of catalytic performance of synthesized fibre-like Ni/ZSM-5 catalysts with selected zeolite based catalysts in DRM.

Catalysts	Catalyst morphology	Conditions	Deactivation degree ^b (%)		Amount of coke (wt.%)	Ref.
			CH ₄	CO ₂		
2Ni-1Co/ZSM-5	Cube-like	700 °C, 30 ^a , 12 h	20	15	25.6	(Estephane et al., 2015)
11Ni/MFI	Needle-like	750 °C, 150 ^a , 12 h	16	13	NR	(Drobná et al., 2017)
5Ni-1Ce/ZSM-5	Coffin-like	800 °C, 15 ^a , 24 h	12	21	NR	(Tang et al., 2014)
1.5Ni-0.5Pt@Hol S-1	Cube-like	800 °C, 72 ^a , 7 h	11.7	6.2	1.4	(Dai et al., 2015)
8Ni/ZSM-5	Plate-like	800 °C, 32 ^a , 9 h	24.2	NR	NR	(Sarkar et al., 2012)
5Ni/ZSM-5	Fibre-like	700 °C, 30 ^a , 60 h	44.3	37.9	26.7	This study
5Ni-1Ta/ZSM-5	Fibre-like	700 °C, 30 ^a , 60 h	20.1	10.3	13.2	This study

NR: Not Reported.

^a GHSV (Lg⁻¹h⁻¹).

^b Deactivation degree = ((Initial reactant conversion - Final reactant conversion)/ Initial reactant conversion).

Table 3

Central composite experimental design for the RSM optimization.

Run	Reaction temperature (°C)	CO ₂ :CH ₄ Feed ratio	GHSV (mL g ⁻¹ h ⁻¹)	CH ₄ Conversion (%)
1	700	1	60,000	75.3
2	750	3	10,000	89.6
3	700	1	10,000	80.21
4	750	3	35,000	91.7
5	700	5	60,000	69.7
6	800	5	10,000	86.8
7	800	1	60,000	87.9
8	700	3	35,000	84.4
9	800	3	35,000	95.2
10	750	3	35,000	92.5
11	800	5	60,000	82.8
12	750	1	35,000	85.2
13	750	5	35,000	78.3
14	750	3	60,000	84.8
15	800	1	10,000	92.6
16	700	5	10,000	71.63

The CCD was adopted to develop a model that predict the interaction between process parameters and the response (CH₄ conversion). The operating temperature (A), CO₂:CH₄ feed ratio (B) and GHSV (C) were chosen as process variables for DRM process. A series of experimental runs as presented in Table 3 was carried out to optimize the process parameters related to CO₂ reforming of methane. Based on the RSM analysis, a predictive model of the experimental design was determined by Eq. (6).

$$\begin{aligned} \%CH_4 \text{ Conversion} = & 56.02 - 0.06615A + 6.60779B \\ & + 0.00029C + 0.00013A^2 - 1.93397B^2 \\ & - 0.00000C^2 + 0.0041AB - 0.00000AC \\ & + 0.00001BC \end{aligned} \quad (6)$$

Statistical testing of the CCD model was performed by subjecting experimental CH₄ conversion data to ANOVA analysis (Table 4). The value of calculated probability (p-value) is a crucial parameter to ascertain the significance of each model terms. Based on the ANOVA results presented in Table 4, the model was statistically significant because of its low p-value of 0.0001 and high F-value of 37.89. Similarly, the process parameters selected were significant owing to the low p-value exhibited. Among the parameters considered, reaction temperature (A) was the most significant parameter in CH₄ conversion with the highest F-value (164.11) and low p-value (<0.0001). Another important parameter to determine the quality of a model is the coefficient of determination (R²) value. The obtained R² value of 0.9827 indicates 98.27% data variability, signalling the fitness and adequacy of the regression model.

Table 4Analysis of variance (ANOVA) for central composite design for CH₄ conversion.

Factors	SS	DF	MS	F-value	p-value
Model	852.73	9	94.75	37.89	0.0001
A	410.37	1	410.37	164.11	< 0.0001
B	102.27	1	102.27	40.9	0.0007
C	41.37	1	41.37	16.54	0.0066
AB	1.34	1	1.34	0.5378	0.491
AC	0.4325	1	0.4325	0.1729	0.692
BC	1.69	1	1.69	0.677	0.4421
A ²	0.2602	1	0.2602	0.104	0.758
B ²	157.77	1	157.77	63.09	0.0002
C ²	13.78	1	13.78	5.51	0.0573
Residual	15	6	2.5		
Total SS	867.74	15			

SS: sum of square; DF: degree of freedom; MS: mean square

3.4.2. Interactive effects of process parameters and optimization

Process optimization was accomplished using the CCD interface of the RSM. The optimization results were obtained from analysis of the surface response plots of interactive effects between process variable and CH₄ conversion. Fig. 9 shows the 3D response surface plot with semi-spherical shape revealing the effect of combined variables on CH₄ conversion.

The surface responses for CH₄ conversion (Y) as a function of two variables operating temperature (A) and CO₂:CH₄ feed ratio (B) are shown in Fig. 9A. The graphical representation illustrates that CH₄ conversion increases with increasing reaction temperature until it reaches its optimum value. This is ascribed to the endothermic nature of the reaction (Hambali et al., 2020a). Similarly, increasing the feed ratio result to increase in CH₄ conversion up to certain limit where further increment results in decline of CH₄ conversion. The obtained result indicates that CO₂ proportion in the feed serves as an active oxidant with positive effect on CH₄ activation (Alsaffar et al., 2020; Chong et al., 2020b).

The surface plot of the combined impact of GHSV and operating temperature on CH₄ conversion are shown in Fig. 9B, where the operating temperature displayed almost a linear relationship with the conversion. Based on the trend of results (Fig. 9B&C), CH₄ conversion gradually decrease with steady increase of GHSV. This shows that GHSV have an influence on activity, where steady drop in CH₄ conversion was observed on increasing GHSV. This is in accord with literature findings which indicated that the higher GHSV, the lesser the contact time for CH₄ molecules to interact with active sites for (Alsaffar et al., 2020; Sidik et al., 2016). The optimum conditions obtained from the RSM Analysis is 96.6% CH₄ conversion at operating temperature of 784.15 °C, 2.52 feed ratio and 33,760 mL g⁻¹ h⁻¹ GHSV. A complementary experiment was also performed to validate the regression model under the optimum predicted values. The CH₄ conversion obtained at optimum conditions was 95.8% and the difference between observed and predicted values is 0.8%. Table 5 summarized the optimization processes carried out using different catalyst configurations for DRM. CH₄ conversion is mostly selected as the appropriate response variable. This stems from the fact that activation of C-H bond is considered as the rate determining step for DRM on heterogeneous catalyst (Wittich et al., 2020).

Based on the above findings, fibre-like structured Ni-Ta/ZSM-5 catalyst possessed reduced ensemble size with abundant active centres for higher rate of dissociation of reactants under different feeding conditions. More so, the increased surface oxygen species accelerated gasification of surface carbon as schematized in Fig. 8 (and also reflected in the TGA/DTG, Raman spectroscopy, O₂-TPO, XRD and TEM properties). It has been substantiated in literatures that core-shell structuring of support material is beneficial to catalyst resistance (Abdulrasheed et al., 2019a; Das et al., 2020). We therefore highlight that even though our catalytic tests were conducted under a more stringent operating condition, a relatively stable DRM performance was recorded. The catalytic stability of the fibre-like Ni-Ta/ZSM-5 could be a key factor in the development of a potent catalyst for industrial production of syngas via CO₂ reforming of methane reaction.

4. Conclusion

High performance fibre-like Ni-Ta catalyst for DRM reaction was obtained by incorporation of Ta into Ni/FZSM-5. Thermal stability of Ta-based catalysts under different feeding compositions was better than the Ni catalyst. A detailed characterization of the spent catalysts revealed that Ta alters the amount and type of deposited carbon species from a graphitic type to a soft one, which enhanced coke-tolerance properties. The rapid polymerization of

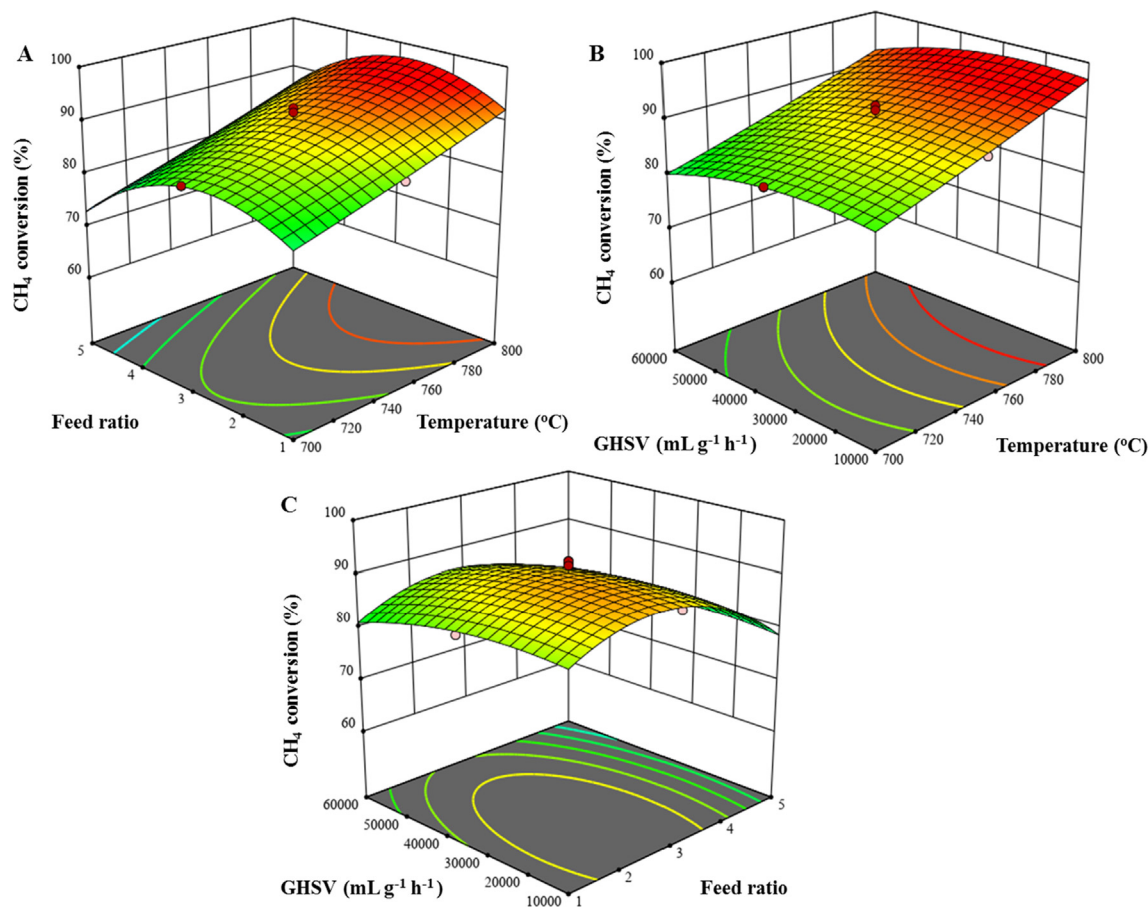


Fig. 9. Surface plot of interaction between the significant factors (A) feed ratio and reaction temperature at constant GHSV = 35,000 mL g⁻¹h⁻¹ (B) GHSV and reaction temperature at constant feed ratio of 3, and (C) feed ratio and GHSV at constant reaction temperature of 750 °C.

Table 5
Comparative studies on optimization of DRM process parameters.

Catalysts	Design	Optimal process performance		Ref.
		Input variables	Response	
Ni-Co/MgO-ZrO ₂	CCD	GHSV = 145,190 mL g ⁻¹ h ⁻¹ , CO ₂ :CH ₄ ratio = 3, O ₂ feed concentration = 7 mol%, T = 749 °C	X _{CH4} = 88%, Y _{H2} = 86%	(Fan et al., 2011)
10Ni/DFSAB-15	CCD	T = 794 °C, Feed ratio = 1.2, GHSV = 23,815 mL g ⁻¹ h ⁻¹	X _{CH4} = 93.48%, X _{CO2} = 95.67%, H ₂ /CO = 0.983	(Chong et al., 2020b)
Ni-Co/MSN	CCD	CO ₂ :CH ₄ ratio = 3.0, GHSV = 38,726 mL g ⁻¹ h ⁻¹ , T = 783 °C	X _{CH4} = 97%	(Sidik et al., 2016)
15Ni/CaFe ₂ O ₄	CCD	T = 832.45 °C, GHSV = 35,000 mL g ⁻¹ h ⁻¹ , Feed ratio = 0.96	X _{CH4} = 85%, X _{CO2} = 88%, Y _{CO} = 77.82%, Y _{H2} = 75.8%	(Hossain et al., 2019)
Ni/SiO ₂	CCD	T = 800 °C, CH ₄ /CO ₂ molar ratio = 2.125	X _{CH4} = 79.6%, X _{CO2} = 84.2%, H ₂ /CO = 0.4	(Braga et al., 2014)
Co/CeO ₂	BBD	Feed ratio = 0.6, P _{CH4} = 46.85 kPa, T = 728 °C	X _{CH4} = 74.84%, X _{CO2} = 76.49%	(Ayodele and Cheng, 2015)
Nano Ni powder	BBD	T = 900 °C, CH ₄ /CO ₂ ratio = 1.5, O ₂ /CH ₄ ratio = 0.10	X _{CH4} = 82.9%, X _{CO2} = 90.8%	(Rosha et al., 2018)
Ni-Ta/FZSM-5	CCD	T = 784.15 °C, Feed ratio = 2.52, GHSV of 33,76 mL g ⁻¹ h ⁻¹	X _{CH4} = 96.6%	This study

CCD: central composite design; BBD: Box-Behnken design; P: partial pressure; T: temperature, X: conversion; Y: yield; GHSV: gas hourly space velocity.

carbon on Ni/FZSM-5 resulted in the growth of carbon whiskers which accelerated the driving force for agglomeration and coke formation. However, Ta species on Ni-Ta/FZSM-5 accelerated the rate of dissociation of reactants and carbon gasification due to enhanced Ni-support interaction and abundant surface oxygen species. Furthermore, the effect of process parameters on CH₄ conversion was studied using CCD based RSM. From the results obtained from ANOVA analysis, operating temperature was found to be significant input variable in DRM. An optimum CH₄

conversion of 96.6% was achieved at the process conditions of 784.15 °C operating temperature, 2.52 CO₂:CH₄ ratio, and GHSV of 33,760 mL g⁻¹h⁻¹.

CRediT authorship contribution statement

H.U. Hambali: Conceptualization, Methodology, Data curation, Investigation, Writing - original draft. **A.A. Jalil:** Conceptualization, Supervision, Writing - review & editing. **A.A. Abdulrasheed:** Inves-

tigation, Writing - review & editing. **T.J. Siang**: Investigation, Writing - review & editing. **A.H.K. Owgi**: Data curation, Writing - review & editing. **F.F.A. Aziz**: Data curation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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