



Effect of Ni-Ta ratio on the catalytic selectivity of fibrous Ni-Ta/ZSM-5 for dry reforming of methane

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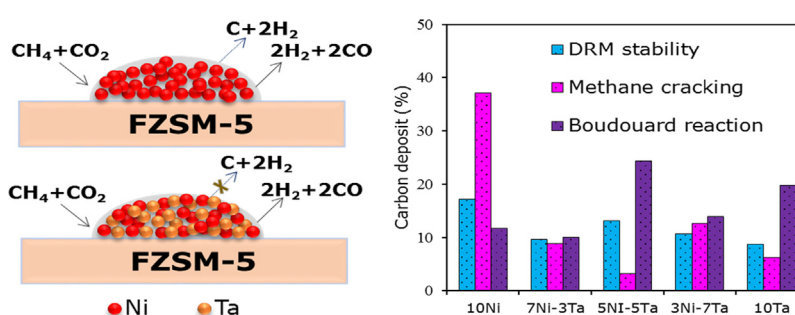
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HIGHLIGHTS

- Dry reforming of methane was carried out over Ni-Ta/FZSM-5 catalysts.
- The increased surface basicity lowered the reactants activation energies.
- Ni catalyst exhibited high inclination towards methane cracking side reaction.
- Incorporation of small amount of Ta to Ni lowered coke deposition by 60%.
- 7Ni-3Ta showed high CO₂ and CH₄ conversions of 95% and 93% over 100 h.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of Ni-Ta catalysts supported on fibrous ZSM-5 were synthesized by microemulsion and impregnation method. Catalytic activity and selectivity were influenced by incorporation of Ta into Ni catalyst. The side reaction (Boudouard, methane cracking, and reverse water gas shift reaction) tests gave more insights on source of coking, where 10Ni catalyst was more inclined towards methane cracking. The 7Ni-3Ta catalyst showed the best performance (CO₂ and CH₄ conversions of 95% and 93%, respectively) due to the inherent activity of Ni, and anti-sintering impact of Ta as affirmed by TEM and Raman spectra. Its TGA analysis revealed 9.8% carbon content after 100 h. Furthermore, activation energy of CO₂ and CH₄ conversions were reduced by 15% and 10% respectively. Thus, addition of small amount of Ta to Ni catalyst was able to dilute Ni surface and limit the degree of graphitization of carbon which is prerequisite for stable performance in DRM.

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1. Introduction

The persistent increase in CO₂ emission and diminution of crude oil reserves have triggered unprecedented research on potential technologies for the conversion of CO₂ into more valuable products

(Abdulrasheed et al., 2018; Gambo et al., 2018; Shen et al., 2020). Dry reforming of methane (DRM) (Eq. (1)) is a promising technology in the production of synthesis gas (syngas) with a low H₂:CO ratio by the utilization of greenhouse gases (CH₄ and CO₂). Syngas is known as an important platform chemical for the synthesis of liquid energy carriers and valuable chemicals (Galadima and Muraza, 2019; Shen et al., 2020). The catalyst component, in terms of support, active metals, promoter and binders employed for DRM is imperative for a stable performance (Abdulrasheed et al., 2019a). Ni-based catalysts are suitable for DRM due to their wide

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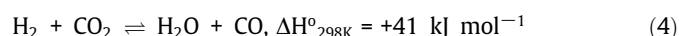
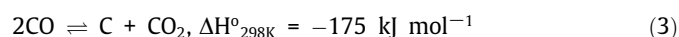
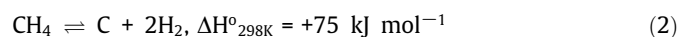
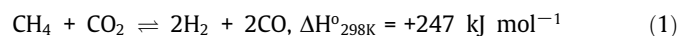
availability, moderate cost and high turnover frequency. Nevertheless, they are prone to fast deactivation due to the formation of carbonaceous deposits, usually of the encapsulation and graphitic type. Attempts to address these setbacks have been made via contemporary experimental and theoretical simulations (Abdulrasheed et al., 2020; Siang et al., 2020; Wittich et al., 2020). These efforts are aimed at enhancing metal dispersion, reducing metal particle size, immobilizing the active metals to the framework of the carrier material and thus hindering carbon formation, deposition and evolution.

Several studies have demonstrated the role of structured supports in keeping metal particles well dispersed and thermally stable at high temperatures (Abdulrasheed et al., 2019a, 2019b). Structured supports such as core-shell SiO_2 (Chong et al., 2020; Das et al., 2018; Abdulrasheed et al., 2019b), hierarchical silicate-1 (Bawah et al., 2018), birdcage-type zeolite (Kobayashi et al., 2019), and hollow sphere ZrO_2 have been investigated in DRM. From our previous study, we have shown that fibrous zeolite supported Ni catalyst exhibit superior coking resistance as compared to conventional zeolite Ni-based catalysts (Hambali et al., 2020a). A Ni-based catalyst supported on fibrous mesoporous MFI zeolite with a unique structure was studied for the first time in the DRM process. The remarkable performance was attributed to increased basicity and stabilization of Ni particles by the fibrous support framework.

It has been reported that adding a promoting metal influences the performance of Ni catalysts in DRM reactions (Abdulrasheed et al., 2020; Chong et al., 2020; Zhang et al., 2020). Catalyst promoters are categorized into either passivating or gasification generic types. Passivating promoters (Sn, Au, K, Ag) are typically introduced to block the under-coordinated sites which hinder the nucleation of carbon on Ni sites and decrease the Ni particle ensemble size, resulting in rapid gasification of surface carbon (Fukuhara et al., 2020; Stroud et al., 2018; Usman et al., 2015). Gasification promoters (Ca, Co, Ce, La) however accelerate oxidation of formed carbon deposits or enhance oxygenates coverage (Abdulrasheed et al., 2020; Sidik et al., 2016). Nevertheless, for cost effective catalyst fabrication, noble metal-based catalysts are rarely considered as the second metal in bicomponent Ni catalyst systems. Transition metals such as Co (Sidik et al., 2016), W (Vroulias et al., 2019), Fe (Zhang et al., 2020) and Y (Taherian et al., 2017) were recently used in alloy formation with Ni. The alloying of Ni with second metal finely tune the Ni surface structure, thus inhibiting coke formation and thermal sintering.

Congruently, many studies have shown that group five elements influence the catalytic properties of active Ni sites (Taherian et al., 2017; Usman et al., 2015; Valentini et al., 2003). We recently reported that Ta additive enhanced the performance of Ni/ZSM-5 catalyst (Hambali et al., 2020b). Nevertheless, the promoting effect of transition metal is dependent on the metal-promoter ratio (Guerrero-Pérez, 2019; Turap et al., 2020; Usman et al., 2015). For instance, the catalytic behavior of Ni/ Al_2O_3 was modified by low amount of vanadium doping. It was observed that increasing vanadium loading increases the propensity of carbon deposition (Valentini et al., 2003). Similarly, Zhang et al. (2020) have shown that Ni-Fe ratio in MgO supported catalyst play an integral role in DRM performance. Likewise, Shah et al. (2019) reported that doping of Al_2O_3 with 25% Ti/Al ratio induced a balance between the redox property and metal support interaction which resulted in improved catalytic performance. More recently, Vroulias et al. (Vroulias et al., 2019) investigated the effect of W loading on Ni/ Al_2O_3 . It was observed that lower reactants conversion was attained with increasing W loading. Modification with 11.9 wt% W loading resulted in suppression of carbonaceous deposits. Thus, an appropriate metal-promoter ratio seems decisive in improving the DRM performance of bimetallic catalysts.

In a typical DRM process, propagation of competing side reactions increases the propensity of coke deposition (Abdulrasheed et al., 2019a; Pakhare and Spivey, 2014; Usman et al., 2015). These side reactions are methane cracking (MC) (Eq. (2)) and the Boudouard (BD) reaction (Eq. (3)). In addition, the occurrence of reverse water gas shift (RWGS) reaction (Eq. (4)) was reported to affect the purity of syngas produced during DRM. However, selectivity of these side reactions during DRM are mostly measured by carbon formation and deviation of the H_2/CO ratio from the ideal stoichiometry. Nonetheless, these factors only give a rough estimate of catalyst selectivity and occurrence of these side reactions. Therefore, examining the independent roles of these side reactions (Eqs. (2)–(4)) will give better insights on the source of coking during the DRM reaction.



To the best of our knowledge, this is the first report on the effect of Ni-Ta ratio on DRM and selectivity of the individual side reactions that readily occur during DRM reaction. The goals of the present work are: (i) preparing a series of xNi-yTa/FZSM-5 catalysts, (ii) evaluating the effect of Ni-Ta ratio on catalytic performance, and (iii) examining the source of coking during DRM with respect to the independent roles of the competing side reactions over the xNi-yTa/FZSM-5 catalysts.

2. Experimental

2.1. Materials

Zeolite seed (CBV 2314) was purchased from Zeolyst International. Cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), n-butanol ($\text{C}_4\text{H}_9\text{OH}$) and urea ($\text{CO}(\text{NH}_2)_2$) were purchased from MERCK (Sdn. Bhd.) and were used to fabricate the fibrous ZSM-5 support. Metal precursors were all purchased from Sigma-Aldrich. Reaction gases (CH_4 and CO_2), carrier gas (N_2), and reducing gas (H_2) were all obtained and applied as received without any purification for catalytic tests.

2.2. Preparation of catalysts

Fibrous ZSM-5 support was fabricated according to the method reported in our previous work (Hambali et al., 2019). The mono and bimetallic catalysts were prepared by the wetness impregnation method. Appropriate amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Ta_2O_5 aqueous solution were used to provide Ni and Ta, respectively. The salt solutions were each poured into the fibrous ZSM-5 suspension and gently agitated for 30 min. The resultant powder was oven dried (at 110 °C for 12 h) and then calcined (at 800 °C for 3 h). For each catalyst, the total metal loading was 10 wt%. For clarity purposes, the fibrous ZSM-5 supported catalysts were written as xNi-yTa for a specific discussion. In total, 5 catalysts were prepared and are listed in Table 1, where the metal loadings and NiO particle sizes are shown.

2.3. Characterization

The field emission scanning electron microscopy (FESEM) characterization was performed on an X-ray analyzer (Zeiss Supra-VP35). Mapping of metal spots using FESEM image was carried

Table 1

Summary of physicochemical properties and catalytic activity of synthesized catalysts.

Catalysts	Metal loadings (wt.%)		NiO crystal size (nm) ^a	CH ₄ conversion (%) ^b		Deactivation degree (%)	Activation energies (E _a , kJ/mol) ^c CH ₄ CO ₂
	Ni	Ta		Initial	Final		
10Ni	10.0	–	15.45	71.1	43.0	39.6	34.2 33.1
7Ni-3Ta	7.0	3.0	11.07	80.1	74.4	7.1	30.8 29.0
5Ni-5Ta	5.0	5.0	13.65	75.8	62.0	18.2	38.9 34.3
3Ni-7Ta	3.0	7.0	12.32	74.6	66.0	11.5	41.5 40.9
10Ta	–	10.0	–	56.3	39.2	30.3	48.1 52.6

^a Calculated by Scherrer equation from XRD.^b Reaction conditions: 700 °C, GHSV = 30 L g⁻¹ h⁻¹, CH₄/CO₂/N₂ = 1/1/3, TOS = 100 h; initial: at 1.5 h TOS, final: at 100 h TOS.^c Computed from slopes of Arrhenius plot.

out. Morphology of the support was further examined using transmission electron microscopy (TEM) (JEOL-JEM-2100F), situated in the Ibnu-Sina Institute for Scientific and Industrial Research. Powder X-ray diffraction analysis was carried out to ascertain the crystalline phases in the catalysts using a Bruker Advance-D8 diffractometer. The mean nickel crystalline sizes were estimated using the Scherrer equation. The reducibility of the synthesized catalysts was conducted on a Micromeritics Chemisorb analyzer (2720), equipped with a cold trap and TCD instrument. CO₂-TPD was performed using the same apparatus to quantify the basic sites on the catalyst surface. In situ IR- lutidine analysis was conducted to investigate the presence of acid sites on the catalysts using an Agilent FTIR Spectrometer (Cary 640). Thermogravimetric analysis (TGA) for post reaction catalysts was performed with a TGA instrument (Mettler Toledo, 851E), while Raman spectroscopy (Renishaw in Via spectrometer) was used to evaluate the type of carbon deposits.

2.4. Catalytic activity tests

Analysis of the catalytic performance for DRM and the competing side reactions was conducted separately in a fixed bed reactor (internal diameter = 8 mm) under atmospheric pressure. For each test, 0.2 g of fresh catalyst diluted with quartz particles (20–40 mesh) was loaded into the reactor. Prior to commencement of the reaction, the catalyst was reduced at 700 °C for 4 h with a H₂/N₂ mixture (50%, 100 mL min⁻¹). Thereafter, the reduced catalyst was purged with a N₂ flow for 45 min to remove H₂ in the reactor. Reactant gas mixture consisting of CH₄/CO₂/N₂ = 1:1:3, with a total flow of 100 mL min⁻¹ (GHSV of 30 L g⁻¹ h⁻¹) was fed into the reactor for the DRM (Eq. (1)) activity tests. Blank test (no catalysts loaded) using same feed composition and reaction conditions was conducted. The flow of gases was controlled by flow meters (SEC-400 MK2, Stec Ltd). The DRM stability tests were performed at 700 °C for 1800 min. The same reactant gas composition and flow-rate used for the DRM activity test was maintained. To investigate the selectivity of the DRM side reactions, different reactant gas compositions were used, while the reaction temperature and flow-rate was consistent with the DRM stability tests.

A reactant gas ratio of CH₄:N₂ = 1:2 was used in the MC reaction for 60 min. For BD reaction, the test was conducted for 150 min with a reactant ratio of CO:N₂ = 1:2. The RWGS reaction used reactant gases composed of CO₂:H₂:N₂ = 1:1:4, and the reaction was tested for 750 min. The composition of product gases was analyzed by online gas chromatograph (Agilent Technologies, 7820 N). The reactant conversions and selectivity of the products were evaluated by Eqs. (5)–(9).

$$CH_4 conversion = \frac{F_{CH_4, in} - F_{CH_4, out}}{F_{CH_4, in}} \times 100 \quad (5)$$

$$CO_2 conversion = \frac{F_{CO_2, in} - F_{CO_2, out}}{F_{CO_2, in}} \times 100 \quad (6)$$

$$H_2 selectivity = \frac{F_{H_2, out}}{2[F_{CH_4, in} - F_{CH_4, out}]} \times 100 \quad (7)$$

$$CO selectivity = \frac{F_{CO, out}}{2[F_{CH_4, in} - F_{CH_4, out}] + [F_{CO_2, in} - F_{CH_4, out}]} \times 100 \quad (8)$$

$$\frac{H_2}{CO} = \frac{F_{H_2, out}}{F_{CO, out}} \times 100 \quad (9)$$

$$Deactivation degree = \frac{X_{CH_4, initial} - X_{CH_4, final}}{X_{CH_4, initial}} \times 100 \quad (10)$$

3. Results and discussion

3.1. Morphology and phase composition

Fig. 1a reveals the formation of anticipated core shell architecture typical of the fibrous ZSM-5 structure, with uniform size of 600 nm (Hambali et al., 2019). The TEM image (Fig. 1b) confirms the presence of dendrimers coating the core with large inter dendrimer distance (Teh et al., 2016). It was reported that core-shell structured support enhances catalytic performance, in line with our previous studies (Abdulrasheed et al., 2019b; Hambali et al., 2020a; Kobayashi et al., 2019). Thus, the fibrous structured catalyst could to some extent protect the active metal phase from coke deposition due to its inclination for confinement of the metal surface within its framework. The powder XRD (Fig. 1c) revealed characteristic peaks of the ZSM-5 structure in the 2θ range of 5–10° and 20–26° (Hambali et al., 2020a; Teh et al., 2016). Diffraction peaks at 36.5°, 46.7°, and 55.3° in the pattern of Ta-promoted catalysts indicates the presence of Ta₂O₅, which increases upon increasing Ta wt. % (Zhu et al., 2015). In addition, reflections were observed at 37.3°, 43.2°, 62.9°, 75.3°, and 79.4° assigned to the NiO crystal phase (Javan et al., 2020). Generally, the broader the full width at half maximum (FWHM) of NiO, the smaller the NiO crystallite sizes. Indeed, with the use of Scherrer's equation, 7Ni-3Ta had the smallest NiO crystallite sizes (Table 1). This is an indication of improvement in Ni dispersion in presence of low Ta content. However, there is no immediately recognizable pattern linking Ni-Ta ratio in the bimetallic catalysts to dispersion of NiO particles.

3.2. Reducibility

Fig. 2 exhibits the H₂-TPR results of the mono and bimetallic catalysts. The magnitude of the H₂-TPR peak indicates the amount

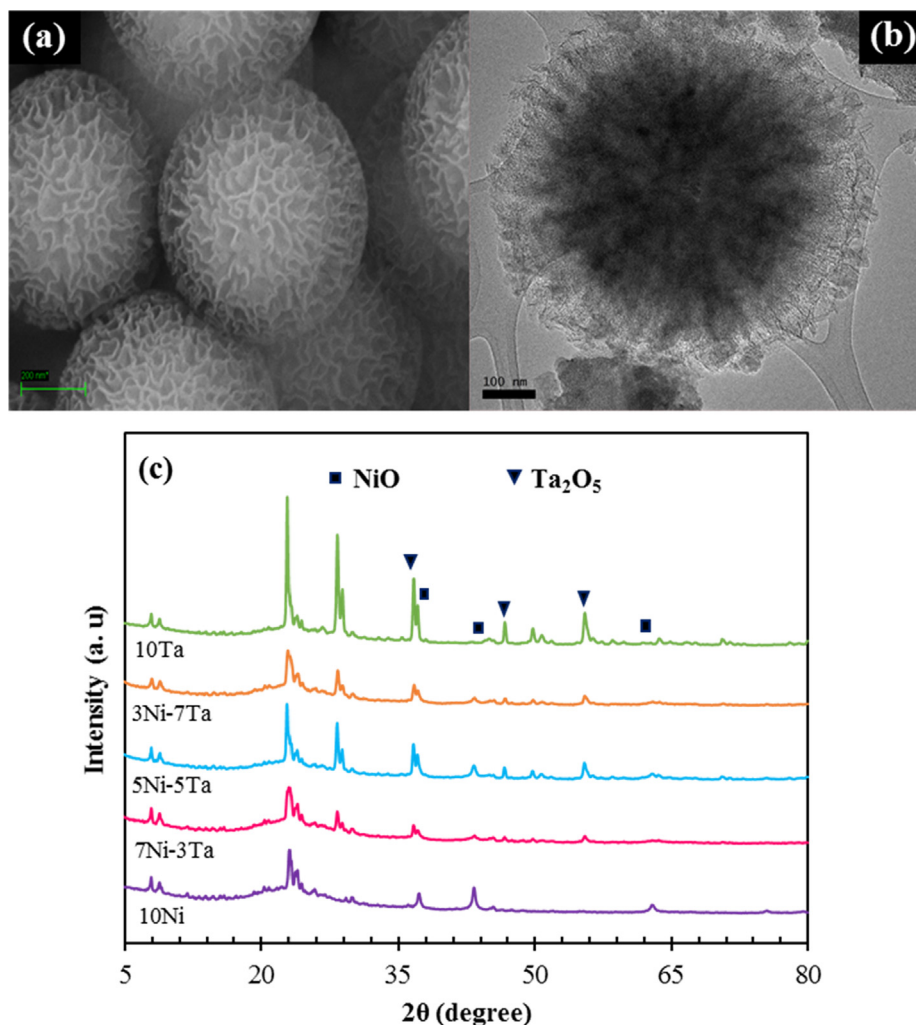


Fig. 1. (a) FESEM image of FZSM-5; (b) TEM image of FZSM-5 and (c) XRD pattern of synthesized catalysts.

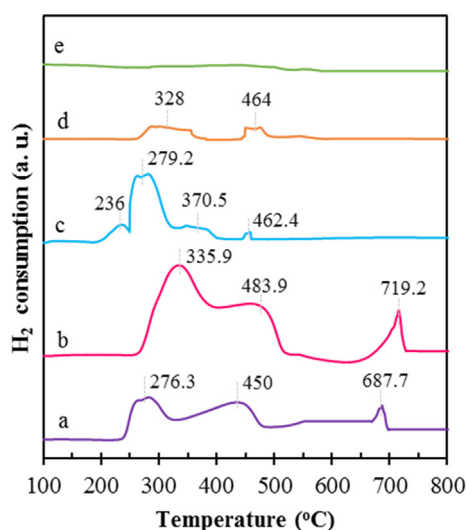


Fig. 2. H_2 -TPR profiles for the catalysts (a) 10Ni, (b) 7Ni-3Ta, (c) 5Ni-5Ta, (d) 3Ni-7Ta and (e) 10Ta.

of H_2 uptake by the Ni atoms on the catalyst surface. For monometallic 10Ta, no peak was observed signifying the reduction of Ta_2O_5 . This suggests that Ta_2O_5 is non-reducible under the con-

ditions used in the TPR measurement, which is in accordance with a similar investigation by Peddakasu et al. (2019). However, the 10Ni catalyst produced peaks at temperatures of 276.3 °C and 450 °C, which correspond to NiO species reduction to its metallic state (Ni°). Furthermore, a small peak appeared at 687.7 °C, which is derived from the reduction of NiO species having strong interaction with the support (Abdulrasheed et al., 2020). The broader peaks produced for 7Ni-3Ta shifted towards higher temperature, suggesting more reducibility as a result of enhanced metal-support interaction (Wu et al., 2020). It was reported that a small amount of Ta enhances the interaction of catalyst components, which induces increase in NiO reduction temperature (Zhu et al., 2015). In the case of 5Ni-5Ta and 3Ni-7Ta, peaks around 200–460 °C were observed, which are related to the reduction NiO particles. Overall, the introduction of Ta greatly influenced the redox property of the bimetallic catalysts. Addition of low amounts of Ta significantly favored the reduction of NiO on the 7Ni-3Ta catalyst, probably due to its smaller NiO particles sizes which exposes more of the NiO species to reduction under an H_2 atmosphere. On the contrary, 3Ni-7Ta with high Ta loading negatively influenced reducibility of Ni species. It was concluded that the promoting effect of transition elements is lost at high promoter concentrations as a result of saturation of Ni lattice sites (Guerrero-Pérez, 2019). Hence, reducibility of the Ni species on the bimetallic catalysts is hinged on the appropriate metal-promoter ratio, which seems to be highest on the 7Ni-3Ta catalyst.

3.3. Surface basicity/acidity

The surface basicity of xNi-yTa catalysts was characterized by CO₂-TPD as displayed in Fig. 3. The quantity of basic sites was evaluated based on the peak area of surface adsorbed CO₂ (inset Fig. 3). The basicity was found in the order: 3Ni-7Ta < 10Ta < 5Ni-5Ta < 10Ni < 7Ni-3Ta which indicates that, CO₂ interaction with the basic sites varied depending on the metal-promoter ratio. Essentially, high amount of basic sites result in more O₂ species on the catalyst surface, which facilitates the gasification of carbon deposited during dehydrogenation of CH₄ molecules, thus supporting coke free DRM (Abdulrasheed et al., 2020; Das et al., 2018). Besides the surface basicity, the amount of acid sites could have an impact on catalytic performance. In order to examine this possibility, in situ FTIR–lutidine was performed (Fig. 4). The bands around 1700 cm⁻¹ is ascribed to the adsorbed lutidine on Brønsted acid sites (BAS), whereas the bands at 1585 and 1613 cm⁻¹ represents adsorbed lutidine on the Lewis acid sites (LAS) (Ghani et al., 2019). However, the amount of BAS (inset Fig. 4) was highest for the 10Ni catalyst. The poor dispersion of Ni particles could be the reason for the presence of the large fraction of BAS on the 10Ni catalyst. The amount of LAS follows the trend 7Ni-3Ta > 3Ni-7Ta > 10Ta > 5Ni-5Ta > 10Ni. Several literatures reported that dispersion of Ni particles on catalyst support is dependent on the amount of LAS (Ni et al., 2016; Zhou et al., 2018). As we recently reported, activation of reactants on a zeolite supported Ni catalyst is hinged on surface acidity, where moderate acidity hindered the propagation of side reactions with inferior stability (Hambali et al., 2020a). Hence, the acid/basic properties of the 7Ni-3Ta catalyst could be advantageous in hindering coking via side reactions during the reforming reaction.

3.4. Catalytic test of xNi-yTa catalysts for DRM

The DRM catalytic activity of mono and bimetallic catalysts are shown in Fig. 5. As observed in Fig. 5, CO₂ conversion was higher than that of methane due to the high C–H bond activation energy as compared to the C–O bond (Pakhare and Spivey, 2014). Another explanation is the possible occurrence of RWGS side reaction. Among all catalysts tested, 7Ni-3Ta produced the highest CH₄ and CO₂ conversions (Fig. 5a and b). The activity of monometallic 10Ni catalysts was increased by the presence of the Ta promoter. On the contrary, a high content of Ta had a negative impact,

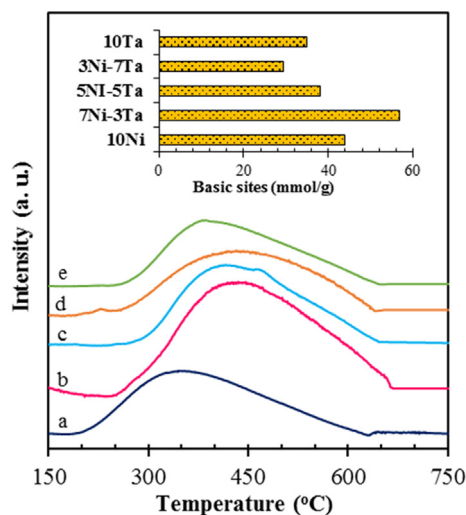


Fig. 3. CO₂-TPD profile and amount of basic sites (insert) for the catalysts (a) 10Ni, (b) 7Ni-3Ta, (c) 5Ni-5Ta, (d) 3Ni-7Ta and (e) 10Ta.

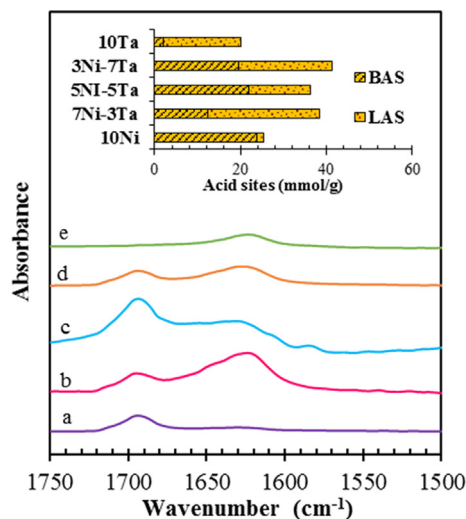


Fig. 4. Lutidine-FTIR profile and amount of acid sites (insert) for the catalysts (a) 10Ni, (b) 7Ni-3Ta, (c) 5Ni-5Ta, (d) 3Ni-7Ta and (e) 10Ta.

slightly decreasing the activity for 5Ni-5Ta and 3Ni-7Ta catalysts. The blank test results (Fig. S1) revealed very negligible catalytic activity. The quantity of carbon deposited was evaluated by TGA, as shown in Fig. S2 and summarized in Fig. 6. The results revealed that the amount of carbon deposits increased when the Ni content increased. Fig. 7 displays the effect of the Ni-Ta ratio on the initial methane conversion and carbon deposition. Therefore, carbon formation occurred mainly at the initial stage of the reaction and is relatively dependent on the Ta content. Other literatures concerning Ni-based DRM catalysts supports this finding (Valentini et al., 2003; Wu et al., 2019). In addition, the H₂/CO ratio of the product gas was studied as a function of reaction temperature (Fig. 5c). The H₂/CO ratio obtained shows a dependence on Ta loading. All catalysts studied showed a H₂/CO ratio above the expected thermodynamic ratio of 1, signaling occurrence of MC and/or BD reactions. The improved CO₂ conversion led to an increment in CO selectivity over H₂ for 7Ni-3Ta as shown in Fig. S3, which implies less carbon formation due to CO₂ gasification of surface carbon further producing CO. (Abdulrasheed et al., 2019b).

Stability of xNi-yTa catalysts were examined at 700 °C over 100 h TOS for DRM, as shown in Fig. 8. The lower CH₄ and CO₂ conversions on 10Ni was brought about by high surface acidity which impeded CO₂ chemisorption (Fig. 8a and b). Previous studies demonstrated that a high concentration of acid sites on ZSM-5 supported Ni catalysts was responsible for rapid catalyst deactivation (Estephane et al., 2015; Tang et al., 2014). The stability of bimetallic catalysts depended on the Ni-Ta ratio, as an increase in Ni-Ta ratio result in a subsequent decrease in CH₄ and CO₂ conversion. From the results in Fig. 8c, 5Ni-5Ta and 3Ni-7Ta catalysts suffered a slight decline in both reactant conversions over the 100 h TOS. The 7Ni-3Ta catalyst had the lowest degree of deactivation at the end of 100 h, as presented in Table 1. Fig. S4 shows that the deactivation degree is dependent on the amount of LAS. In previous studies, the stabilization effect of active metals on LAS was also observed (Hambali et al., 2020b; Ni et al., 2016). It seems that the abundant LAS on the 7Ni-3Ta catalyst serve as anchoring Ni sites, which has a positive influence on the observed stable performance (Fig. 8). Additionally, the superior performance of 7Ni-3Ta is ascribed to the availability of more exposed Ni species due to improved NiO reducibility (Fig. 2). Similar findings in literature showed that the performance of a vanadium promoted Ni/Al₂O₃ catalyst is hinged on the appropriate content of the vanadium promoter (Valentini et al., 2003).

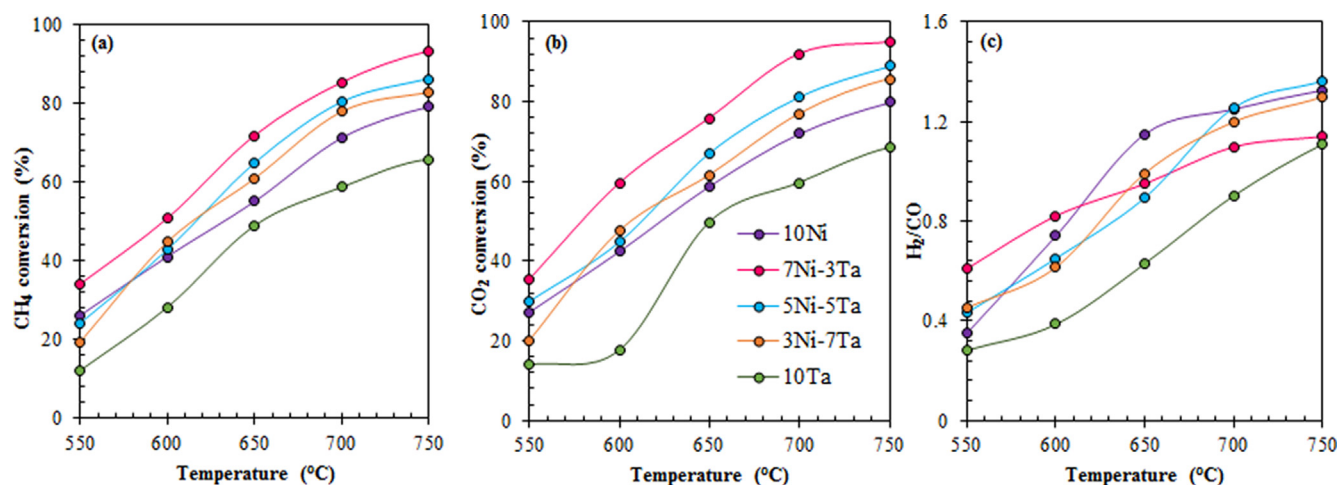


Fig. 5. Dry reforming of methane activity over the synthesized catalysts (a) CH₄ conversion; (b) CO₂ conversion; and (c) H₂/CO ratio, Reaction conditions: GHSV = 30 L g⁻¹ h⁻¹, CH₄/CO₂/N₂ = 1/1/3.

In order to further investigate the effect of the Ni-Ta ratio on DRM, kinetic analysis was carried out for the synthesized catalysts. The apparent activation energies were determined by recording

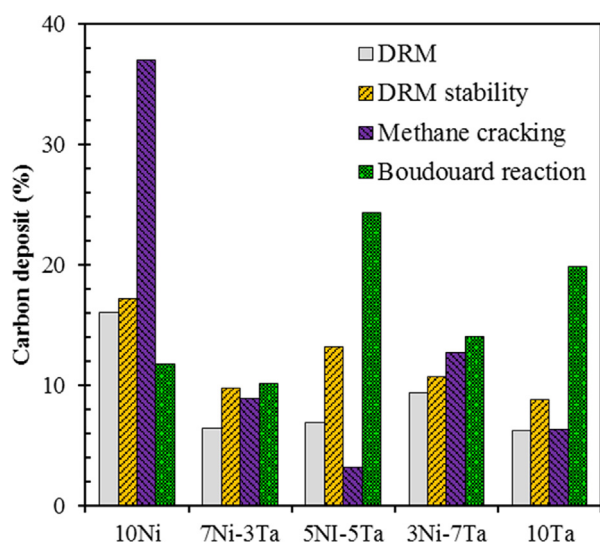


Fig. 6. Carbon deposits from Dry reforming of methane and other side reactions.

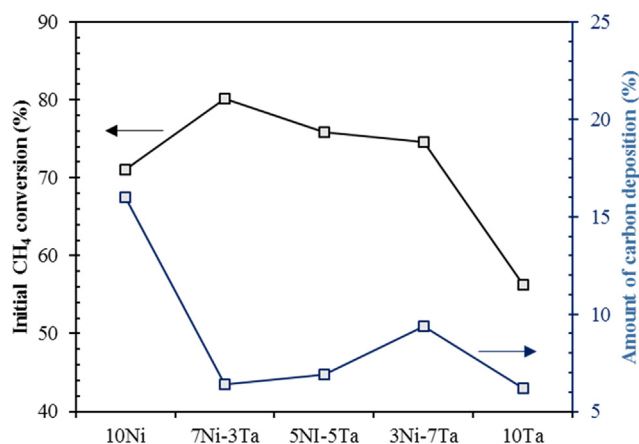


Fig. 7. Influence of Ni-Ta ratio on the initial CH₄ conversion and the amount of carbon deposition.

Arrhenius plots, as displayed in Fig. S5. The activation energies of both reactants are summarized in Table 1. The activation energies could vary within a broad range from 20 kJ/mol to 250 kJ/mol (Tang et al., 2014). The activation energies calculated reveal that the activation barrier for CO₂ consumption is to some extent lower than that of methane consumption over the Ni catalysts. The 10Ni catalyst gives activation energies of 34.2 kJ/mol and 33.4 kJ/mol for CH₄ and CO₂ respectively. The obtained activation energies are lower than those reported in the work of Tang et al. (2014) for a Ni/ZSM-5 catalyst. We ascribe the difference to better dispersion of metal species on the fibrous structured catalyst (Hambali et al., 2020a; Jalil et al., 2019). For the 7Ni-3Ta catalyst, a decrease in the reactants' activation energies was recorded. This could stem from the high basicity (Fig. 3), which could further promote the elimination of carbon deposits on the 7Ni-3Ta catalyst. This also explains the stable performance of the 7Ni-3Ta catalyst throughout the 100 h TOS. In the case of 5Ni-5Ta and 3Ni-7Ta, slight increase in activation energies were recorded. The kinetic studies reveal that Ta-rich catalysts do not seem very active for DRM, while catalytic performance is favored for promoted catalyst with small Ta content. The increased basicity induced by the addition of small amounts of Ta seems enough to lower the reactants' activation energies.

The amounts of carbon deposition of spent xNi-yTa catalysts was measured using TGA. The results (Fig. 6) show that 7Ni-3Ta exhibited the strongest coking resistance, with a total carbon content of 9.8%. The other two bimetallic catalysts also exhibited slight resistance to carbon deposition, with 5Ni-5Ta and 3Ni-7Ta containing 11 and 13.2 wt% carbon, respectively, while monometallic 10Ni and 10Ta possessed 17.2 and 8.9 wt% carbon, respectively. This signals that even low Ta loading enhances carbon resistance (Guerrero-Pérez, 2019). Aiming to shed light on the promoting attributes of Ta, Raman analysis was conducted on selected spent catalysts after 100 h on stream. Fig. S6 displays the Raman spectra of representative spent 7Ni-3Ta and 10Ni catalysts. Two distinct peaks were observed at 1350 cm⁻¹ and 1580 cm⁻¹ corresponding to disordered and graphite carbon bands, respectively (Abdulrasheed et al., 2019b). The degree of graphitization of carbon deposits is measured from the I_G/I_D ratio, with I_G and I_D being the intensities of bands of G to D band (Fig. S6). Generally, the higher the I_G/I_D ratio, the higher the graphitic carbon deposited with high potential to cause catalyst deactivation (Abdulrasheed et al., 2019b). I_G/I_D ratios of 0.96 and 0.87 were obtained for 10Ni and 7Ni-3Ta, respectively, signifying that graphitic and amorphous carbon species are present in both catalysts. The spectra for the

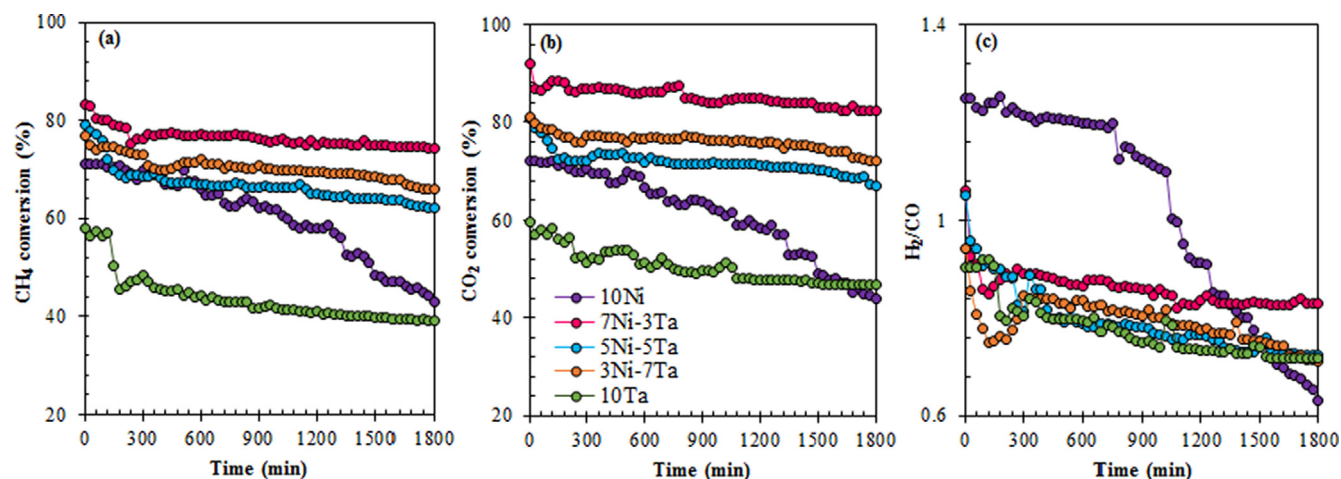


Fig. 8. Dry reforming of methane stability test over the synthesized catalysts (a) CH_4 conversion; (b) CO_2 conversion; and (c) H_2/CO ratio, Reaction conditions: 700 °C, GHSV = 30 $\text{L g}^{-1} \text{h}^{-1}$, 100 h, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 1/1/3$.

7Ni-3Ta catalyst produced a low I_G/I_D ratio as compared to the 10Ni catalyst. This implies that the degree of graphitization of carbon on 7Ni-3Ta is lower than on 10Ni. These observations are concomitant with literature which suggests that graphitic carbon species form more readily on Ni-based catalysts than their Ta-based counterparts (Bawah et al., 2018; Guerrero-Pérez, 2019).

The retained sphericity of fibrous ZSM-5 (Fig. 9) after a long time of performance merits attention, as it affirms its robustness, as reported in a previous study (Hambali et al., 2020a). As seen from the TEM images in Fig. 9a, carbon deposits on 7Ni-3Ta are mostly in the form of amorphous carbon located close to Ni parti-

cles, as marked by yellow arrows. In the spent 10Ni catalyst (Fig. 9b), encapsulating carbon could be observed, as marked by red arrows, which is in good agreement with TGA and Raman results. This suggests that the addition of Ta changed the amount and type of the deposited carbon species, which, in turn, enhanced the coke-tolerant properties. Table 2 shows the comparison of 7Ni-3Ta with other bimetallic catalysts. The activity and degree of deactivation of 7Ni-3Ta were competitive with literature data, and the longer TOS considered to examine its stability, exceeded most of the catalysts mentioned (Table 2). However, despite the shorter time on stream considered by Estephane et al. (2015) and

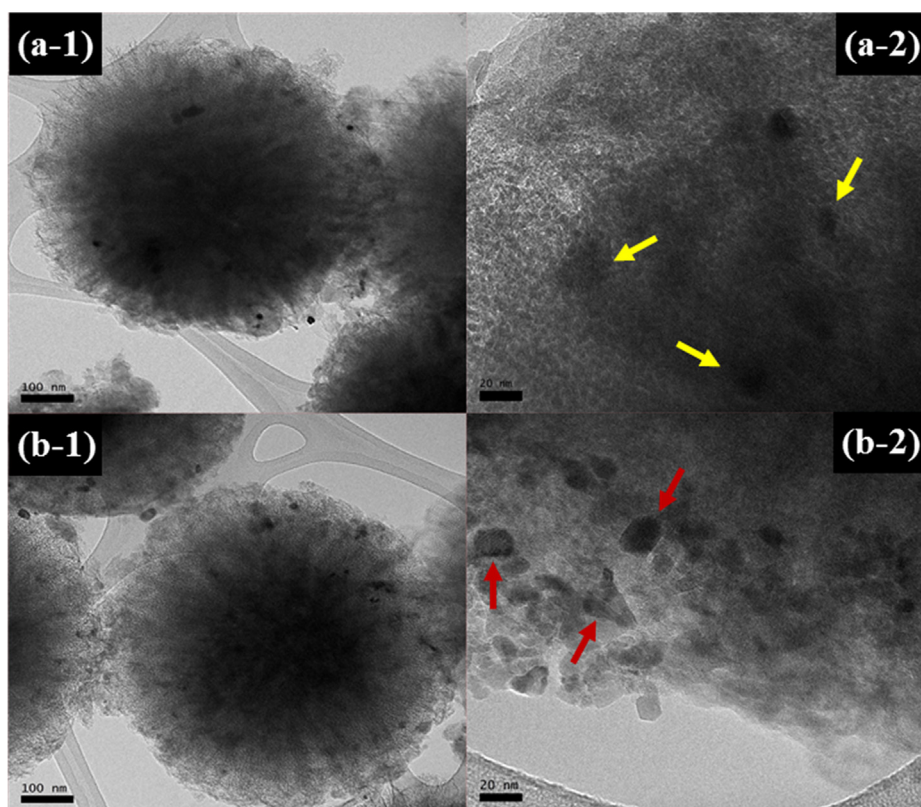


Fig. 9. Representative TEM images of spent 7Ni-3Ta (a); and spent 10Ni (b) catalysts, Amorphous and encapsulating carbon are designated by yellow and red arrows, respectively.

Table 2

Comparison of performance of bimetallic catalysts applied in dry reforming of methane.

Catalyst	T (°C)	GHSV (L g ⁻¹ h ⁻¹)	X _{CH₄}	X _{CO₂}	H ₂ /CO ratio	TOS (h)	Deactivation degree (%)	Refs.
10Ni-15La/illite clay	800	60	80.0	63.0	0.82	25	1.2	(Akri et al., 2017)
Ni _{0.8} -Co _{0.2} /H-ZrO ₂	700	275	74.2	76.1	0.74	80	22.8	(Sheng et al., 2019)
10Ni-7Ce/MgO	700	12	47.8	88.6	–	5	1.4	(Khajenoori et al., 2015)
10Ni-5.6B/Ni/Al ₂ O ₃	700	30	54.6	62.5	–	24	11.7	(Fouskas et al., 2014)
10Ni-2La/SBA-15	700	30	83.0	86.5	0.9	10	0.7	(Oemar et al., 2016)
Ni _{0.5} -Ce _{0.5} /ZSM-5	800	15	97.0	91.0	1.0	24	–	(Tang et al., 2014)
5Ni-10Co/Al ₂ O ₃	700	36	67.0	71.0	0.9	4	–	(Siang et al., 2018)
10Ni-11.9W/Al ₂ O ₃	700	30	51.0	62.5	0.8	24	3.5	(Vroulias et al., 2019)
Ni-Co/ZrO ₂	800	120	85.0	92	0.9	160	42.3	(AlSabban et al., 2017)
10Ni-3Y ₂ O ₃ /SBA-15	700	12	70.8	74.4	0.7	12	1.3	(Taherian et al., 2017)
2Ni-1Co/ZSM-5	800	60	66.0	71.9	0.9	12	13.6	(Estephane et al., 2015)
7Ni-3Ta/FZSM-5	700	30	83.1	92.0	0.94	100	7.1	This work

Sheng et al. (2019), their degree of deactivation was quite high. The outstanding performance of the 7Ni-3Ta catalyst can be attributed to the small Ni particle size and high reducibility, in addition to its ability to form more readily oxidized carbon species. Moreover, the unique fibrous morphology gives the catalyst the required coking resistance as reported in our previous work (Hambali et al., 2020a). Substantiated findings have shown that core-shell structured support could to some extent protect the active metal phase from coke deposition (Sheng et al., 2019; Chong et al., 2020; Abdurashed et al., 2019b). Bawah et al. (2018) reported that the existence of low acidity on a hierarchical zeolite supported Ni-Ce catalyst suppressed catalyst deactivation.

3.5. Catalytic test of xNi-yTa catalysts for the competing side reactions

Dynamically, surface carbon formation is expected in DRM due to the high operating temperature that raises the molecular energy to cleave the C-H bonds in CH₄. The side reactions responsible for carbon deposition on the reforming catalyst are MC and BD. In addition, the occurrence of RWGS was also reported to affect the purity of syngas produced during DRM (Pakhare and Spivey, 2014; Wittich et al., 2020). The plot of Gibbs free energy (ΔG) as a function of temperature was depicted in Fig. S7. HSC Chemistry 6.0 software was used for computation of the effect of change of

ΔG on spontaneity of DRM and various reactions at 1 atm and 500–1000 °C. All the reactions were highly endothermic in nature except for BD reaction (Pakhare and Spivey, 2014). Different reactants (CH₄, CO, CO₂, H₂) were interacted with the synthesized catalysts to gain further insight on the influence of the Ni-Ta ratio on these side reactions. The same reaction temperature of 700 °C was used for the side reaction tests for better comparison with the DRM stability test.

The MC reaction involves the formation of solid carbon and H₂ via complete dissociation of CH₄, with its occurrence leading to massive deactivation of the catalyst (Ayodele and Abdullah, 2019; Wittich et al., 2020). The conversion of methane over each of the synthesized catalysts is shown in Fig. 10. Initial CH₄ conversion of 55% and 23.8% is observed for monometallic 10Ni and 10Ta catalysts, respectively. In addition, 7Ni-3Ta, 5Ni-5Ta, and 3Ni-7Ta achieved initial conversions of 63%, 32%, and 19.7%, respectively. For all catalysts, CH₄ conversion decreased over the first few minutes on stream, with complete deactivation recorded after 25–50 min. TGA of the catalysts post reaction (Fig. 6) revealed that 10Ta had a content of 6.3 wt%, while 10Ni had a total carbon content of 37 wt% signaling that MC contributed to catalyst deactivation. 7Ni-3Ta, 5Ni-5Ta and 3Ni-7Ta had carbon contents of 8.9, 3.2 and 12.7 wt%, respectively. This may be related to the presence of high concentration of BAS on 10Ni as compared to the Ta containing catalysts (Fig. 4). This is consistent with our previous study, which concluded that a high concentration of BAS induces severe carbon deposition on the 10Ni catalyst suggests its high inclination to CH₄ activation and dissociation. The formed carbon species diffuses into the Ni lattice which finally produces encapsulating carbon (Fig. 9) which is responsible for the inferior performance of 10Ni catalyst during DRM. It is obvious that addition of Ta to Ni hindered this process, as the 7Ni-3Ta catalyst formed a more readily oxidized carbon species. Furthermore, the DRM stability test shows less carbon formation on 10Ta, which suggests any graphitic carbon formed is easily removed. The improved resistance of Ta to coking could be attributed to the presence of abundant O* or OH* species, which readily oxidize and remove surface carbon on the Ta containing catalysts (Chong et al., 2020; Guerrero-Pérez, 2019; Usman et al., 2015). Thus, a balance between deposition and removal of carbon species resulted in the stable performance of the 7Ni-3Ta catalyst.

The BD reaction occurs when CO breaks down via a disproportionation process, producing C and CO₂. The formation of surface carbon via the BD reaction contributes to catalyst deactivation via coking or reactor plugging (Ayodele and Abdullah, 2019; Pakhare and Spivey, 2014). The conversion of CO is displayed in Fig. 11. An initial conversion range of 36 and 56% was observed for all catalysts except 7Ni-3Ta, which achieved a 23% initial

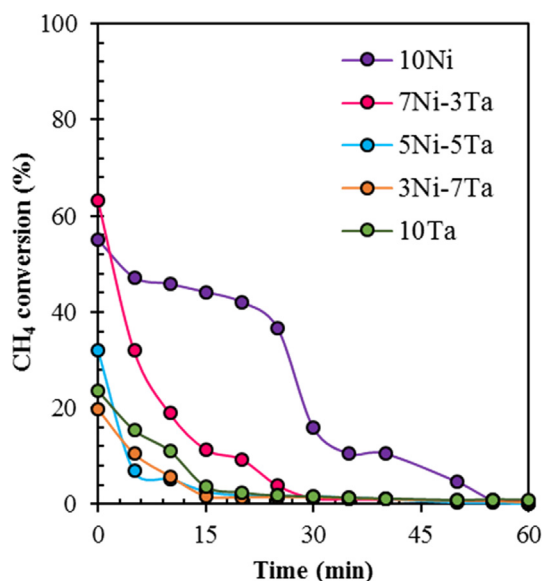


Fig. 10. Effect of Ni-Ta ratio on CH₄ conversion during CH₄ cracking reaction test. Reaction conditions: 700 °C, GHSV = 30 L g⁻¹ h⁻¹, 60 min, CH₄/N₂ = 1/2.

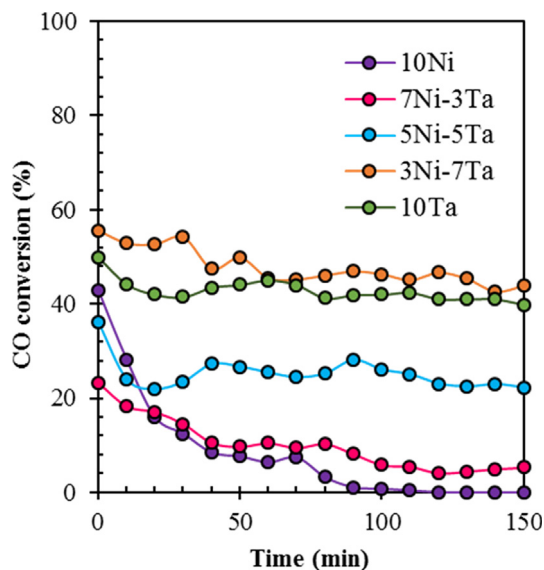


Fig. 11. Effect of Ni-Ta ratio on CO conversion during Boudouard reaction test, Reaction conditions: 700 °C, GHSV = 30 L g⁻¹ h⁻¹, 150 min, CO/N₂ = 1/2.

conversion. The CO conversion of all catalysts decreased steadily over the first few minutes on stream. The 10Ni catalyst completely deactivated after 90 min on stream, while 7Ni-3Ta showed a slightly decreasing trend and remained stable from around 100 min onwards. In the case of 5Ni-5Ta, 3Ni-7Ta and 10Ta, CO conversion increased and later stabilized, possibly due to transformation of the carbonaceous species on the catalyst surface. Similar observations were reported in literature (Guczi et al., 2010; Horlyck et al., 2018). The total carbon content follows the trend: 7Ni-3Ta (10 wt%) < 10Ni (11.7%) < 3Ni-7Ta (14%) < 10Ta (19.8%) < 5Ni-5Ta (24.3%). It is worth pointing out that Ta containing catalysts displayed stronger resistance to deactivation than the Ni catalyst. This implies that Ta containing catalysts are most likely producing disordered amorphous carbon species, as this has been found to have little or no impact on deactivation, whereas monometallic Ni may be deactivated by a graphitic form of carbon. This finding is consistent with the TEM and Raman results. Contrastingly, CH₄ conversion during the MC reaction is lower than the CO conversion observed during the BD reaction for all catalysts with the exception of 10Ni. This suggests that 10Ni is more selective towards MC, while 10Ta has a high inclination towards the BD reaction.

The RWGS reaction involves the formation of H₂O and CO via the consumption of H₂ and CO₂. Unlike BD and MC, which invoke carbon formation on the catalyst surface during DRM, RWGS consumes product H₂. This influence the purity of product syngas, resulting in a H₂/CO ratio less than unity (Pakhare and Spivey, 2014; Wittich et al., 2020). As observed in Fig. 12 10Ni and 10Ta showed initial conversions of 79 and 62%, respectively. For 7Ni-3Ta, 5Ni-5Ta, and 3Ni-7Ta, the conversion was 68, 71 and 84%, respectively. The conversion of H₂ was within 42 and 50% for all catalysts (not shown here). It is interesting to note that during RWGS, 10Ta exhibited the lowest CO₂ conversion, suggesting the presence of more surface oxygen species on Ta surfaces than Ni (Wittich et al., 2020; Zhang et al., 2020). It was reported that the removal of carbon depends on a stable oxygen intermediate being formed on the surface of the catalysts (Ayodele and Abdullah, 2019; Das et al., 2019). Hence, different Ni-Ta ratios altered the surface oxidation and are responsible for the increase in CO₂ conversion. It is interesting to note that for 7Ni-3Ta with stronger interaction of catalyst components, intermediate BAS as well as

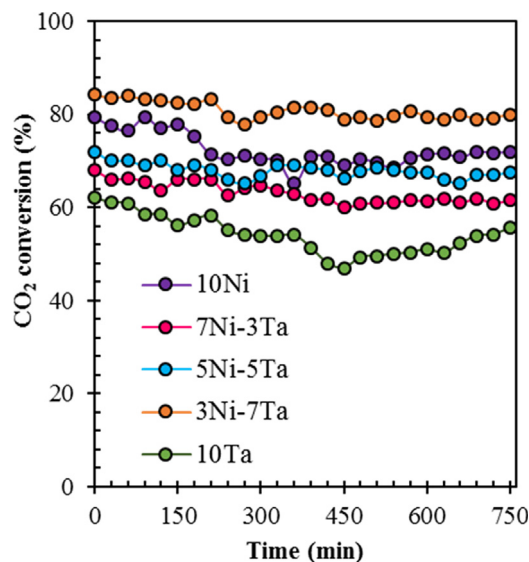


Fig. 12. Effect of Ni-Ta ratio on CO₂ conversion during RWGS reaction test, Reaction conditions: 700 °C, GHSV = 30 L g⁻¹ h⁻¹, 750 min, CO₂/H₂/N₂ = 1/1/4.

abundant basic sites which boost availability of surface O₂ with the removal of carbon species upon the Ni particles, thus provide higher stability. This corroborates the pattern observed during DRM stability tests (Fig. 8), where 7Ni-3Ta produced a stable performance.

From the above findings, the differences between catalysts in terms of conversion, selectivity, and carbon formation can be correlated to the differing properties of the Ni and Ta catalysts during DRM and competing side reactions. As expected, Ni was found to be more active than Ta, but exhibited inferior stability. Nonetheless, the bimetallic Ni-Ta catalysts gained the activity of Ni while retaining the stabilizing effects of Ta. The highest carbon deposition on 10Ni during the MC reaction corroborates the stability test observations, which can be attributed to the strong surface acidity. The BD reaction shows that the 10Ta, 3Ni-7Ta, and 5Ni-5Ta catalysts produce more carbon deposits than 10Ni but remain active, while 10Ni rapidly deactivated. This indicates that carbon formed on 10Ta and Ni-Ta catalysts are predominantly of the amorphous type which easily gasified. The RWGS reaction illustrates that 10Ni had stronger affinity for CO₂ than 10Ta, but the DRM stability of the latter still supersedes the former. This can be rationalized by the fact that catalytic performance in DRM is not only dictated by a better interaction with CO₂. Thus, the addition of small amounts of Ta cations were able to dilute Ni surface, thereby impeding agglomeration and formation of stable and ordered carbon, which is a prerequisite for stable performance in DRM.

4. Conclusion

A series of xNi-yTa catalysts were evaluated for the dry reforming of methane. The differences between the xNi-yTa catalysts in terms of conversion, selectivity and carbon formation were attributed to the differing properties of Ni and Ta. As expected, 10Ni was found to be more active than 10Ta, but exhibited inferior stability. Ta species were able to prevent sintering of Ni particles and facilitated CO₂ chemisorption to counteract coke formation. The kinetic studies revealed that Ta-rich catalysts were not very active for DRM, while catalytic performance was enhanced for catalysts with low Ta content. The increased basicity induced by the addition of small amounts of Ta seem enough to lower the reactants'

activation energies. Furthermore, results obtained from the side reaction (MC, BD and RWGS) tests, indicated that 10Ni had a high inclination towards MC reaction. The 7Ni-3Ta catalyst showed the best performance among the bimetallic xNi-yTa catalysts. Enhanced reducibility, small Ni crystallite size, strong interaction of catalyst components as well as abundant basic and Lewis acid sites were found to significantly contribute to the remarkable performance of the 7Ni-3Ta catalyst. Thus, the addition of small amount of Ta to Ni catalyst was able to dilute Ni surface and limit the formation of stable and ordered carbon for better stability.

CRedit authorship contribution statement

H.U. Hambali: Investigation, Data curation, Writing - original draft. **A.A. Jalil:** Conceptualization, Supervision, Methodology. **A. A. Abdulrasheed:** Investigation, Data curation, Writing - review & editing. **T.J. Siang:** Investigation, Data curation, Writing - review & editing. **B.B. Nyakuma:** Data curation. **W. Nabgan:** Data curation. **T.A.T. Abdullah:** Data curation.

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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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ces.2020.115952>.

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