

RESEARCH ARTICLE

Fibrous spherical Ni-M/ZSM-5 (M: Mg, Ca, Ta, Ga) catalysts for methane dry reforming: The interplay between surface acidity-basicity and coking resistance

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Summary

A highly active and robust fibrous spherical ZSM-5-supported nickel catalyst with different promoters (Mg, Ca, Ta, Ga) have been synthesised by micro-emulsion method for dry reforming of methane (DRM). The structural framework provided by the unique fibrous spherical ZSM-5 aided confinement of Ni particles. Catalytic activity was improved by homogenous distribution of surface acid-basic sites, thereby reducing the propensity of coke deposition. Bimetallic Ni-Ta catalyst produced the highest CH₄ and CO₂ conversions at 93% and 98%, respectively, with H₂/CO ratio closer to unity (0.97). The nature of acid sites and bimetallic Ni-Ta synergism amplified interaction of catalyst components, resulting in improved interaction with the reactants, thus impeding metal sintering and coke deposition. Consequently, the Ni-Ta/FZSM-5 catalyst shows long-term activity (80 hours) for the DRM reaction at 800°C.

KEYWORDS

dry reforming, methane, Ni/ZSM-5, nickel, tantalum

1 | INTRODUCTION

Synthesis gas (syngas), a versatile feedstock, has been widely used in the chemical industry as a starting material for the production of liquid energy carriers and high value-added chemicals.^{1–3} One of the environmentally benign pathways for syngas production is dry reforming of methane (DRM): $\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$, $\Delta H^\circ_{298\text{ K}} = 260.5\text{ kJ mol}^{-1}$. DRM is considered an archetypical CO₂ transformation route, considering that CO₂ and CH₄ are problematic greenhouse gases as well as abundant chemical materials.^{4,5} Due to its endothermicity,

high temperature is required to reach suitable CH₄ and CO₂ conversions. Thus far, nickel-based materials have demonstrated high DRM performance from an industrial perspective due to their high activity, availability and low cost.² However, there suitability to loss of activity and heavy carbon deposition due to sintering at harsh reaction conditions, leading to abrupt and massive deactivation of catalysts, remains an intractable problem.

As we recently reviewed, the nature of the support has a strong influence on the activity, selectivity and stability of supported Ni catalysts in DRM reaction.⁶ Support materials such as SiO₂,⁷ KCC-1,⁸ KIT-6,⁴ Al₂O₃,⁹ CeO₂,¹⁰

perovskites¹¹ and zeolites^{6,12} have been investigated in DRM. In general, zeolites are microporous crystalline aluminosilicates. Their application is directly related to their well-defined pore architecture, intralattice pore volumes, plentiful supply and tunable-active sites.^{13,14} However, zeolites encompass varying levels of hydration, which results to structure collapse at high-temperature conditions.¹⁵ Hence, the extreme conditions of DRM reaction necessitate the need to develop zeolite support with high thermal stability. Systematic investigation by Tang et al¹⁶ points out that ZSM-5 support has a weak effect on stabilisation of Ni particles and reactant adsorption. High acidity of the Ni/ZSM-5 was responsible for the significant catalyst coking, limiting the long time on stream performance of the catalyst. Similarly, large amount of filamentous carbon deposited on Ni/BEA zeolite during DRM reaction was attributed to weak metal support interaction and acidity of the support.¹⁷

In recent times, fabrication of fibrous materials provides a viable route in producing catalysts with large pore system capable of accelerating diffusion of reactants and maintaining stable catalytic performance.⁶ Abdurashed et al⁸ synthesised a fibrous KCC-1 silica material via one-pot hydrothermal method producing a highly active and stable DRM catalyst. The fibrous morphology not only offer high surface area but also reinforced confinement of Ni particles, exhibiting remarkable performance much better than conventional SiO₂ support. In addition, the dispersion and stabilisation of active metals in reactions where coking and sintering are prone can also be controlled by the acid sites, especially Lewis acid sites (LAS).^{18–20} The LAS serves as anchoring sites for stabilisation of active metals in reactions such as CO methanation,²¹ CO oxidation²² and hydrazine decomposition.²³ Further, Ni et al²⁰ reported that LAS-stabilised Ni metal from high temperature sintering due to enhanced metal-support interaction. Thus, structuring of zeolite support can enhance the catalytic properties.

A plethora of metals have been considered as promoters for Ni catalysts.^{24–27} Basic metal oxide additives improve CO₂ chemisorption to catalyst surface, which expedites gasification of deposited carbon to form CO ($\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$). Generation of basic sites on materials could be beneficial to inhibit carbon accumulation, thus ameliorating catalytic activity.^{28,29} The incorporation of rare earth promoters also impedes severe carbon deposition.²⁴ Similarly, the presence of transition metal in the close vicinity of active Ni sites hinders the diffusion of monoatomic carbon into the Ni particles, which improve the resistance of DRM catalysts.²⁴ Tantalum is a transition metal widely applied in catalysis. It was shown that the promoting effect of Ta is mainly due to its unique surface acidity, ability to form alloy with many metal oxides

and high thermal resistance.^{30–32} The incorporation of small amount of Ta into NiO impedes enlargement of NiO particles which enhances catalytic stability.³¹ In addition, Ni-Ta interaction led to better dispersion of Ni species on the catalyst surface.³³ DFT computations predict that Ta is energetically favoured to react with zeolite support framework.³⁴ Although Ta promoted catalysts are expected to show improved performance, DRM over these catalysts has not been investigated.

In this work, fibrous spherical ZSM-5-supported Ni catalyst with different promoters (Mg, Ca, Ta, Ga) have been synthesised. Comparative studies between chemical, surface and structural properties of resulting catalysts were conducted. The goals are to determine the role of the promoters in enhancement of catalytic performance and to identify possible interplay between surface acidity–basicity and coking resistance in DRM. This research is a strive towards addressing the shortcomings of zeolite-supported Ni catalysts due to severe coke deposition. To the best of our knowledge, the impact of fibrous spherical ZSM-5 morphology and Ta promoter has not been reported before for DRM reaction.

2 | EXPERIMENTAL

2.1 | Catalyst preparation

Fibrous spherical ZSM-5 (FZSM-5) catalysts were prepared by microemulsion coupled with zeolite seed crystallization technique.^{35,36} In brief, the FZSM-5 support was prepared by microemulsion templating technique using cetyltrimethylammonium bromide (CTAB) as the templating material. Tetraethyl orthosilicate (TEOS) was employed as the silica precursor. First, a certain amount of TEOS was dissolved in an aqueous solution containing toluene and 1-butanol. Then, the zeolite seed was added to the mixed solution and stirred at ambient condition for 30 minutes. Subsequently, the mixed solution containing CTAB, urea and distilled water were constantly stirred. The suspension was then microwaved (400 W) for 4 hours. The obtained cake after centrifugation (4000 rpm) was washed five times with acetone and distilled water. Finally, the solid product was dried overnight at 120°C. The template was burned off with calcination for 6 hours at 800°C.

The zeolite seed (ZSM-5, Si/Al ratio of 23) used was supplied by Zeolyst. The series of the metal-based catalysts were prepared by the incipient wetness impregnation method. The aqueous solution of Ni and each metal precursor was incorporated to FZSM-5. Nominal Ni loading amount was fixed at 5 wt% and the promoter at 1 wt%. The following metal nitrates were used as precursors in

TABLE 1 Metal loadings and textural properties of the catalysts

Catalyst	Metal loading [wt%] ^a	NiO crystal size [nm] ^b	H ₂ consumption [mmol H ₂ /g _{cat}] ^c	Surface area [m ² /g] ^d	Pore volume [mL/g] ^d		
					Micropore	Mesopore	Total
FZSM-5	—	—	—	603	0.028	0.946	0.974
Ni/ZSM-5	Ni: 4.97	20.98	0.504	278	0.123	0.035	0.158
Ni/FZSM-5	Ni: 5.01	13.85	1.697	494	0.023	0.698	0.720
Ni-Mg/FZSM-5	Ni: 4.98, Mg: 0.97	11.87	2.067	483	0.030	0.681	0.711
Ni-Ca/FZSM-5	Ni: 4.92, Ca: 1.01	15.11	1.788	292	0.074	0.264	0.339
Ni-Ta/FZSM-5	Ni: 4.96, Ta: 0.98	16.62	2.298	460	0.026	0.578	0.604
Ni-Ga/FZSM-5	Ni: 5.02, Ga: 0.96	—	1.006	377	0.045	0.354	0.399

^aICP-OES measurements.^bScherer equation at (111) reflection.^cH₂-TPR peaks.^dBET surface area.

fabricating the catalysts: nickel (II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O] (99%, Sigma-Aldrich), magnesium nitrate [Mg(NO₃)₂·6H₂O] (99%, Sigma-Aldrich), calcium nitrate tetrahydrate [Ca(NO₃)₂·4H₂O] (99%, Sigma-Aldrich), tantalum (V) oxide [Ta₂O₅] (99%, Sigma-Aldrich) and gallium (III) nitrate hydrate [Ga(NO₃)₃·xH₂O] (99.9%, Sigma-Aldrich). The impregnated samples were dried at 110°C in an atmospheric oven overnight and calcined at 550°C for 3 hours with heating rate of 10°C min⁻¹. In total, 6 catalysts were prepared and listed in Table 1, where the textural properties are shown.

2.2 | Catalyst characterisation

Powder X-ray diffraction (XRD) patterns of fresh and spent samples were obtained using D8 X-ray powder diffractometer with Cu-Kα radiation (λ = 1.54060 Å). The average crystallite sizes were computed from the full width at half maximum intensity of the more intense diffraction peaks and the Scherrer equation. Metal contents in the catalysts were determined by Vista-MPX analyzer. Morphology of the support materials was investigated using field emission scanning electron microscopy (FESEM) (Zeiss Supra, VP35) and transmission electron microscopy (TEM) (JEOL, JEM-2100F). Beckman Coulter SA 3100 analyzer was used to investigate surface areas from N₂ adsorption-desorption at -196°C. Before analysis, all samples were degassed at 300°C. Brunauer-Emmett-Teller (BET) method was used to compute surface areas values.

The catalysts' reducibility was determined using Micromeritics Chemisorb-2720 chemisorption analyser through H₂-TPR measurements. Sequel to that, treatment of catalyst (25 mg) with helium (20 mL min⁻¹, 1 hour and 300°C) was conducted to remove moisture and other impurities. H₂-TPR profiles were recorded within 50-800°C temperature

range through temperature ramping of 10°C min⁻¹ and 20 mL min⁻¹ of 10% (vol.) H₂/Ar flow. The NH₃ and CO₂ temperature-programmed desorption measurements were obtained using the same instrument. Next, H₂ desorption curves were recorded at a rate of 10°C min⁻¹ and temperature range of 30°C to 850°C. To examine the carbon deposits on the catalyst surface, thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) via Mettler Toledo thermogravimetric analyzer (operated under flow of air at the heating rate of 10°C min⁻¹) were carried out. At a furnace temperature range of 30-900°C, the exothermic mass loss was discovered. X-ray photoelectron spectroscopy (XPS) was measured by DLD Spectrometer (Shimadzu Axis), using a monochromatic Al Ka X-ray radiation.

2.3 | Catalytic activity

The methane dry reforming catalytic tests were conducted in a stainless-steel continuous flow fixed bed reactor (at atmospheric pressure and temperature range of 500°C-800°C). The catalyst (0.2 g) was placed within the quartz wool support to retain a fixed bed position. Before the tests were carried out, packed catalyst was exposed to O₂ flow (50 mL min⁻¹) at temperature of 850°C for 1 hour, then H₂ reduction (50 mL min⁻¹) was conducted for 3 hours. Thereafter, the reactor was cooled to reaction temperature under N₂ flow. The reactant gases composed of 1:1:3 ratio for CH₄:CO₂:N₂ with a total flow of 100 mL min⁻¹. The reactant and product gases (H₂ and CO) were continuously recorded online via gas chromatograph analyser (7820-N, Agilent GC). Prior to sampling for the considered temperatures, the reaction was left running at steady-state mode for 1 hour. CH₄ and CO₂ conversion and H₂/CO ratio were calculated as follows:

$$X_{\text{CH}_4} = \frac{F[\text{CH}_4]_{\text{in}} - F[\text{CH}_4]_{\text{out}}}{F[\text{CH}_4]_{\text{in}}} \times 100 \quad (1)$$

$$X_{\text{CO}_2} = \frac{F[\text{CO}_2]_{\text{in}} - F[\text{CO}_2]_{\text{out}}}{F[\text{CO}_2]_{\text{in}}} \times 100 \quad (2)$$

$$\frac{\text{H}_2}{\text{CO}} = \frac{F[\text{H}_2]_{\text{out}}}{F[\text{CO}]_{\text{out}}} \times 100 \quad (3)$$

3 | RESULTS AND DISCUSSION

3.1 | Characterisation of the catalyst systems

3.1.1 | Morphology and structural composition

Figure 1 shows the XRD patterns of commercial and fibrous spherical ZSM-5 (FZSM-5)-supported nickel catalysts. A detailed examination reveals diffractograms within peak range of $2\theta = 7\text{--}10^\circ$ and $22\text{--}25^\circ$, which is allotted to ZSM-5 phase (JCPDS file number 37-359).^{1,35} In addition, formation of NiO cubic phase around $2\theta = 37.28$, 43.2 and 62.5 , which corresponds to the (111), (200) and (220) reflections were observed for all supported Ni catalysts.^{24,37} All promoted catalysts portrayed different NiO crystallites sizes (see Table 1). However, additional peaks corresponding to the structure of promoters were observed

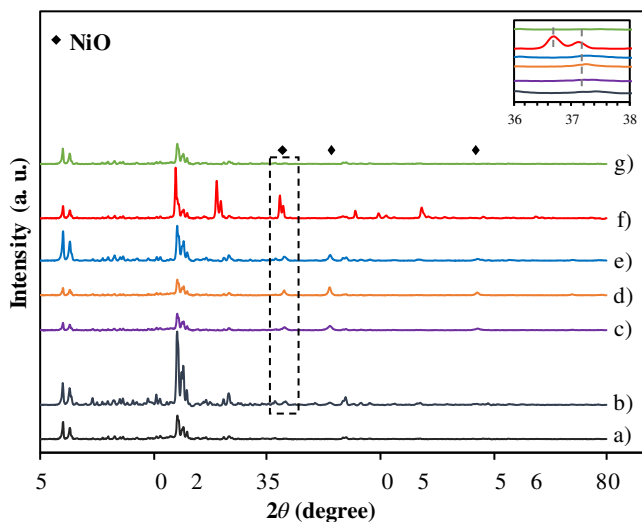


FIGURE 1 XRD patterns of A, FZSM-5; B, Ni/ZSM-5; C, Ni/FZSM-5; D, Ni-Mg/FZSM-5; E, Ni-Ca/FZSM-5; F, Ni-Ta/FZSM-5; and G, Ni-Ga/FZSM-5 catalysts. FZSM, fibrous spherical ZSM-5; XRD, X-ray diffraction [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/er.5527)]

for all bimetallic catalysts except for Ga-promoted catalyst. Nevertheless, the β -Ta₂O₅ peak at 36.5° seems to overlap with NiO (111) peak (inset Figure 1), suggesting strong interaction between NiO and Ta. This may be due to their comparable ionic radii (Ni = 0.69Å and Ta = 0.74Å) and ability of Ta to easily react with metal oxides.³¹ Conversely, the NiO peak slightly shifted, suggesting formation of alloy.^{32,38}

Liu et al.³⁹ also affirmed enhancement of catalyst structure offered by Ta promoter. Hence, Ni-Ta/FZSM-5 demonstrates better bimetallic synergism, thus can curtail Ni particles agglomeration.^{6,32} Basically, the nature of support material dictates the kind of synergy that exist within catalyst components. The FESEM images (Figure 2A) show the coffin shape morphology of commercial ZSM-5 support. Figure 2B,C shows the core shell morphology of fibrous ZSM-5.^{35,40} The TEM micrograph (Figure 2D) reveals the presence of dendrimers covering the core of FZSM-5 support.^{41,42} Literatures^{6,24,35,43} reported that core shell morphology was responsible for enhanced catalytic activity due to the confinement of active metal species in the support framework.

The synthesized catalysts were characterised by ICP-OES to ascertain the metal content in the catalysts, and results are summarised in Table 1. The total metal content for mono and bimetallic catalysts was almost close to the nominal Ni loading (5 wt%) and target promoter loading (1 wt%). The textural properties of the catalysts were assessed via nitrogen physisorption. The corresponding adsorption/desorption isotherms and pore size distribution plots were displayed in Figure 3. The FZSM-5 catalyst exhibited type IV isotherms with H3-type hysteresis loop (Figure 3A) which is typical for mesoporous materials. However, commercial ZSM-5-supported Ni catalysts showed a type I isotherm, characteristic for microporous MFI structure.^{21,35} Based on the isotherms shown in Figure 3, the results are compiled in Table 1. The lowest surface area of about 278 m²/g obtained for Ni/ZSM-5 is attributed to the microporous nature of commercial ZSM-5 support.^{6,7,16}

Generally, support materials with high surface area promote better dispersion of active metals for better activity.⁶ It could be observed that the fibrous structured catalysts had significantly higher surface area; their mesoporous nature is responsible for this enhancement. The surface area of FZSM-5 was 603 m²/g. Incorporation of Ni contributed in reduction (18%) of the surface area, while addition of promoters showed different effects on the catalysts. The decrease in the surface area was found in the order: Ni-Mg/FZSM-5 (2%) < Ni-Ta/FZSM-5 (7%) < Ni-Ga/FZSM-5 (24%) < Ni-Ca/FZSM-5 (40%). Both Mg and Ta promoted catalyst displayed slight decrease in surface area, which could be attributed to cooperative interaction between the catalyst components.^{44,45}

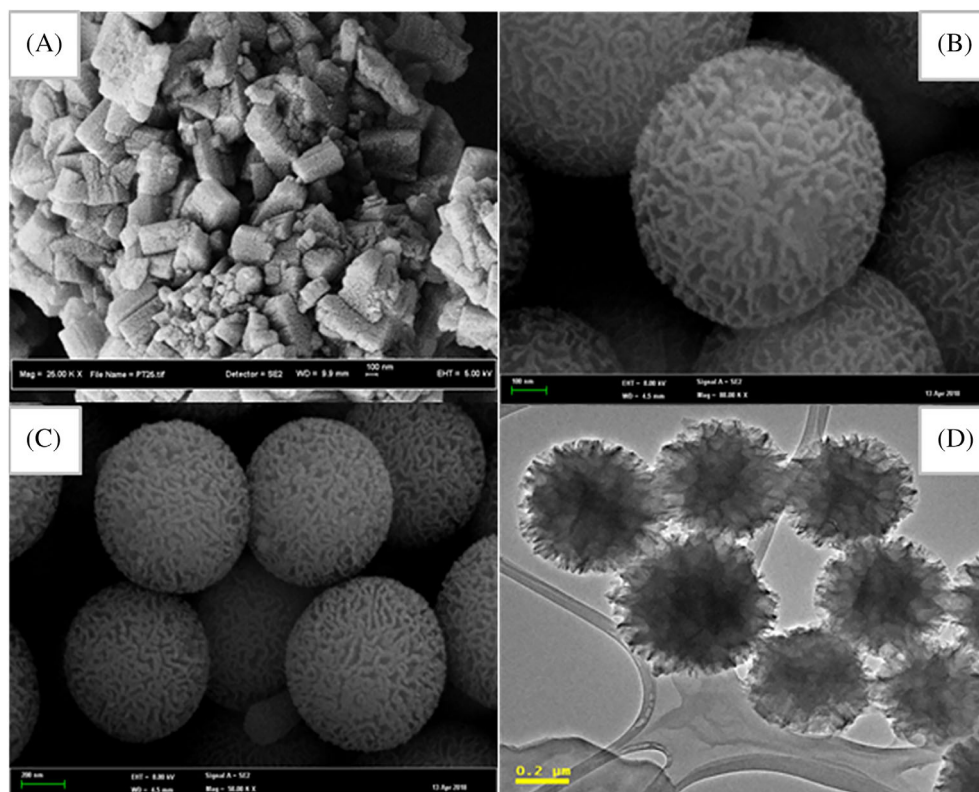


FIGURE 2 A, ZSM-5; B and C, fibrous spherical ZSM-5 (FZSM-5) support field emission scanning microscope (FESEM) images; D, transmission electron microscopy (TEM) image of FZSM-5 [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/er.5527)]

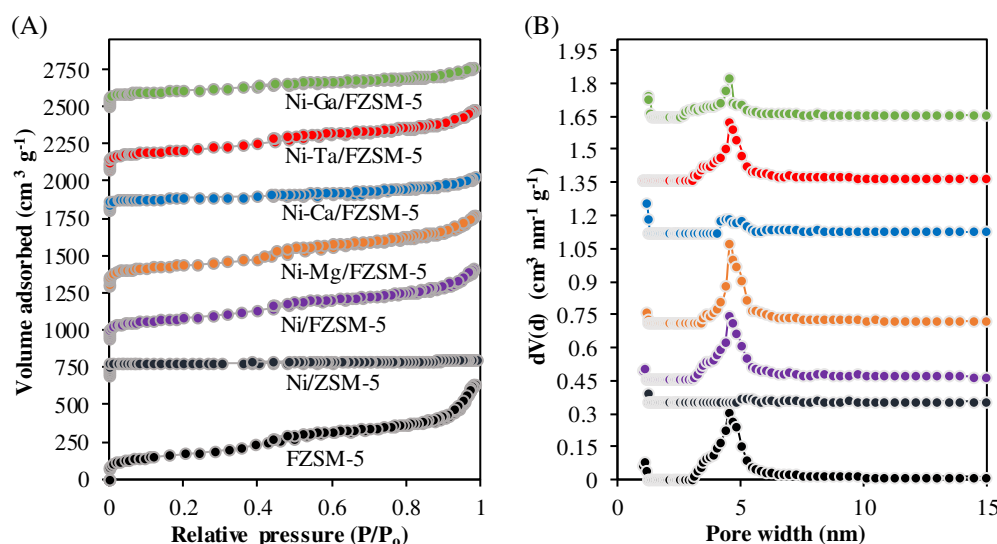


FIGURE 3 A, Nitrogen adsorption-desorption isotherms and B, pore size distribution for the catalysts [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/terms-and-conditions)]

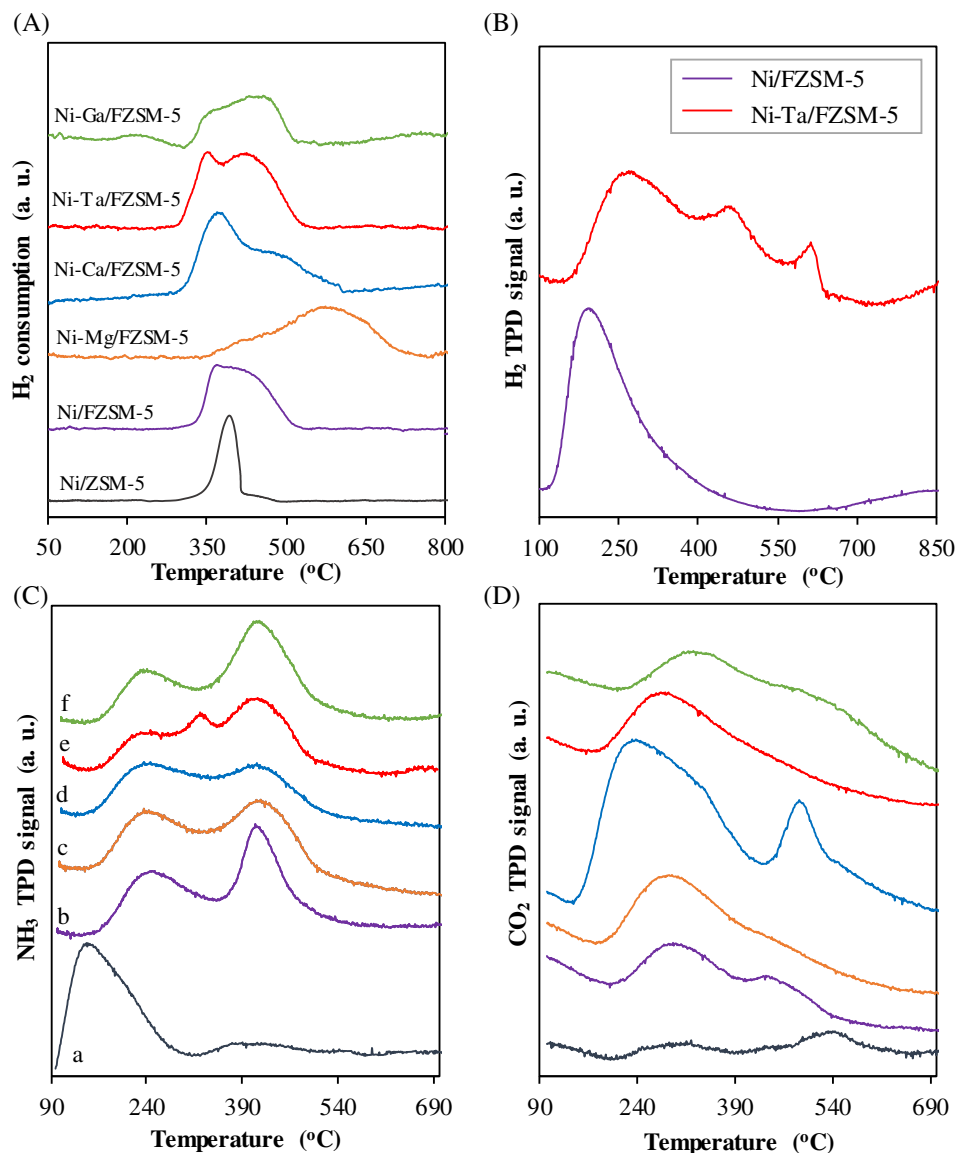
The nonlocal density functional theory (NLDFT) method was used to derive the pore size distribution. FZSM-5 displayed pore size distribution in the range of 1.1–1.6 nm and 3–6 nm. However, Ni/ZSM-5 portrayed narrow pore distribution in the range of 1.2–1.4 nm and 4.7–5.9 nm. Intriguingly, the fibrous-supported Ni catalysts displayed higher mesopores (around 89–97%). This can be attributed to their mesoporous nature induced by the synthesis condition as observed in Figure 3. It was obvious that the metal nanoparticles were homogeneously dispersed within the mesopores, leading to the

slight decrease in mesopore volume. However, variation in pore size distribution of the promoted catalysts suggests that the textural properties could be crucial in enhancement of catalytic performance.

3.1.2 | Reducibility studies

The reducibility of NiO to its metallic state (Ni^0) has a crucial influence on catalytic activity.⁴⁶ Figure 4A shows the H_2 -TPR profile of the mono and bimetallic catalysts.

FIGURE 4 A, H_2 -TPR; B, H_2 -TPD; C, NH_3 -TPD; and D, CO_2 -TPD profiles of the catalysts of A, FZSM-5; B, Ni/FZSM-5; C, Ni-Mg/FZSM-5; D, Ni-Ca/FZSM-5; E, Ni-Ta/FZSM-5; and F, Ni-Ga/FZSM-5. FZSM, fibrous spherical ZSM-5 [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]



The quantitative H_2 consumption is presented in Table 1. Ni/ZSM-5 displayed a small asymmetric peak centred at a temperature of 400°C , which correspond to the reduction of NiO to elemental Ni.^{7,46} For Ni/FZSM-5, broader peak (from 310 to 500°C) was displayed. The fibrous structured catalyst had higher H_2 consumption than the conventional ZSM-5-supported Ni catalyst. This is due to its morphology, high surface area and possible contribution of inherent oxygen vacancies.⁴⁷ However, Mg-promoted catalyst displayed peak shift from 500°C to high reduction temperature (610°C). This is in accord with similar investigation.⁴⁸ The high peak intensity for Ta promoted catalyst signifies more reducibility which can be attributed to bimetallic synergism. Zhu et al³¹ reported that introduction of Ta significantly enhanced reducibility of Ni-Ta oxide catalysts. Similarly, the reduction pattern of Ni-Nb/ TiO_2 studied in H_2 atmosphere revealed broad reduction signal.³³ In addition, a previous

work on Ni-V/ Al_2O_3 catalyst showed that vanadium doping induces higher rate of Ni reduction.^{49,50}

The H_2 -TPD profile shown in Figure 4B provides insights on enhanced reducibility of NiO on Ni-Ta/FZSM-5. Basically, the magnitude of H_2 -TPD peak reveals the extent of H_2 uptake by metallic Ni atoms.³³ The presence of wide peak in temperature range of 120°C to 370°C for Ni/FZSM-5 corresponds to desorbed H_2 from the exposed Ni atoms. For Ni-Ta/FZSM-5, two peaks appeared around 400°C to 650°C . This convincingly suggests the presence of strong H_2 binding sites. Bang et al⁵¹ found that strong H_2 -binding sites are pivotal for expediting chemisorption of H_2 atoms induced from the dissociative adsorption of H_2 molecules. The addition of Ta altered the H_2 adsorption behaviour as can be envisaged from the slight peak shift to the higher temperature. Weatherbee et al⁵² reported that the addition of promoter on Fe/ SiO_2 led to H_2 desorption peaks shift to higher

TABLE 2 Summary of TPD profile of the catalysts

Catalyst	Acid sites [mmol/g (NH ₃)]			Basic sites [mmol/g (CO ₂)]		Acid/base ratio
	Weak	Strong	Total	Weak	Total	
FZSM-5	2.802	0.129	2.931	0.280	0.451	6.498
Ni/FZSM-5	0.763	1.191	1.954	0.723	0.908	2.153
Ni-Mg/FZSM-5	0.804	1.052	1.805	2.094	2.094	0.886
Ni-Ca/FZSM-5	0.904	0.408	1.312	4.334	5.640	0.286
Ni-Ta/FZSM-5	0.696	0.965	1.661	1.905	1.905	0.872
Ni-Ga/FZSM-5	0.583	1.522	2.105	1.326	1.326	1.588

temperature, and Lin et al⁵³ concluded that the shift of H₂ desorption peaks to higher temperatures signals good dispersion of metal particles, better intermolecular interactions and increase in surface coverage. Generally, CH₄ adsorption on reduced Ni surface is the rate-determining step for DRM, which is fostered by stable H₂ atoms adsorption on strong H₂ binding sites of the reduced Ni atom. Thus, it is expected that the Ta promoted catalyst with strong H₂ binding sites would exhibit larger CH₄ adsorption capacity as well as better catalytic performance.

3.1.3 | Acid-base properties characterization

Acidity and basicity of as-synthesised catalysts were determined by NH₃ and CO₂ TPD analysis as provided in Figure 4C,D. The amount of adsorbed NH₃ and CO₂ were computed from the area produced from the TPD signal (Table 2). FZSM-5 produced a large peak around 100°C to 300°C which correspond to weak acid sites. The Ni/FZSM-5 present desorption peaks around 250°C and 405°C which represent weak and strong acid sites respectively (Figure 4C). Addition of promoters altered surface acidity of the catalysts. The total acidity follows the trend Ni-Ga/FZSM-5 > Ni/FZSM-5 > Ni-Mg/FZSM-5 > Ni-Ta/FZSM-5 > Ni-Ca/FZSM-5. Johnson et al⁵⁴ proposed that a relationship exists between surface acidity and distribution of metal particles, where catalyst system with high amount of medium-weak acid sites promotes microscopic dispersion. In our current case, after addition of Ta, the strong acid sites were engulfed; thus, the number of strong acid sites decreased. Accordingly, a new type of acid site was observed around 332°C which could be regarded as medium acid sites.^{20,55} Essentially, medium-weak acid sites could facilitate formation of distinct adsorptive sites that stabilise metal nanoparticles and aid redispersion of Ni particles. For Mg- and Ca-promoted catalysts, concentration of weak acid sites increased by

5% and 19%, respectively. According to literature,^{6,7,16} there is a significant decrease in concentration of acid sites due to addition of alkaline earth promoters. The addition of Ga species incited 28% increase in concentration of strong acid sites. This may be attributed to weak interaction between Ga and Ni particles as observed in H₂-TPR, thus Ga species form Ga₂O₃ granules with strong acidity.⁵⁴ High-surface acidity has been found to promote side reactions resulting to carbon formation.⁷ Thus, incorporation of Ta species could positively influence activity and stability of Ni catalyst during DRM.

FTIR spectroscopy is an effective means for assessment of surface chemical species.⁵⁶ Surface acidity of as-synthesised catalysts was further examined by in situ FTIR pyridine analysis as shown in Figure S1. The pyridine was adsorbed at 150°C to ascertain its interaction with the acid sites on the catalyst (Figure S1A). Bronsted acid sites (BAS) peaks at 1640, 1540-1546 cm⁻¹ and Lewis acid sites (LAS) peaks at 1612, 1595, 1489, 1442-1445 cm⁻¹ were observed.^{21,41,57} The computed amount of acid sites based on appropriate molar extinction coefficients is displayed in Table S1.⁵⁸ For all catalysts, the amount of acid sites reduced on increasing outgassing temperature (Figure S1B,C).⁵⁹ Fibrous-supported Ni catalysts possessed lower amount of BAS acidity than Ni/ZSM-5 because of their inherent mesoporosity and enhanced surface area. Ta-promoted catalyst had higher LAS than other bimetallic catalysts, probably due to the ability of Ta to create new type of acid sites.³⁴ The result is in accordance with the NH₃-TPD observation, suggesting Ni-Ta/FZSM-5 has moderate surface acidity. This agrees with previous study on the presence of more LAS on SiO₂-Ta₂O₅ materials.⁶⁰ Similarly, Kyriienko et al⁵⁹ reported enhancement of LAS due to incorporation of Ta ions in the vacant T-atom sites of SiBEA zeolite catalyst.

The CO₂-TPD profile showing the basic properties is displayed in Figure 4D. The basic sites of fibrous-supported catalysts were significantly induced by different promoters. The peak around 300°C and 500°C represents the weak and strong basic sites, respectively. The increase in adsorbed CO₂ was significant for Ni-Ca/FZSM-5, with

slight peak shift to lower desorption temperature. It can be seen that addition of Ca induced a towerly desorption pattern. This implies that CO₂ interaction with the catalyst is intensified, which might be related to the ability of CaO to adsorb CO₂.⁶¹ The surface basicity was found in the order: Ni-Ca/FZSM-5 > Ni-Mg/FZSM-5 > Ni-Ta/FZSM-5 > Ni-Ga/FZSM-5 > Ni/FZSM-5. In addition, the acid/base ratio (Table 2) shows homogeneous distribution of acid–basic sites on Ni-Ta/FZSM-5 and Ni-Mg/FZSM-5. The in situ FTIR pyridine analysis exhibited no peaks of adsorbed pyrrole over all the studied catalysts (not shown here). Considering the BET, TPR, TPD and FTIR results, it can be concluded that the inherent fibrousity and bimetallic Ni-Ta synergism play a significant role in modifying the catalyst system. These phenomena may favour dispersion of active Ni sites. Thus, bimetallic Ni-Ta catalyst may influence interaction with the reactants, resulting in suppression of side reactions with inferior stability in the DRM.

3.1.4 | XPS characterisation

Figure 5A displays XPS results of the Ni 2p signals of Ni/FZSM-5 and Ni-Ta/FZSM-5. The Ni 2p^{3/2} peaks at 856 eV and Ni 2p^{1/2} peaks at 870.2 eV as well as satellite peaks were observed.¹⁶ These reveal the presence of Ni²⁺ on both catalysts.⁴⁴ The small peaks intensity observed could be attributed to dispersion of Ni particles into the pores of the highly mesoporous fibrous support; therefore, only the few Ni particles located on the external catalyst surface were detected by photoelectrons during the analysis.⁶²

The large XPS O1s signals with broad peak centred at 531.2 eV (Figure 5B) suggest the presence of different oxygen species. A slight increase is observed in the

binding energy of Ni-Ta/FZSM-5 as compared to Ni/FZSM-5, which is presumably due to the bonds formed after introduction of Ta into the structure. The O1s spectrum can be deconvoluted into component peaks to show the presence of bridging oxygen species. The peak observed on Ni/FZSM-5 at 529.1, 530.8 and 532.1 corresponds to Si - O - Ni, Si - O - Al and Si - O - Si bonds, respectively.⁸ In the case of Ni-Ta/FZSM-5, additional peak at 532.9 eV belonging to Si - O - Ta bond was observed.⁶³ In addition, small Ta 4f^{7/2} peak (Figure 5C) around 26.1 eV is attributed to Ta⁵⁺ presence on Ni-Ta/FZSM-5 catalyst.³¹

3.2 | Catalytic performance

The catalytic activity for DRM reaction over the catalysts was shown in Figure 6. In all the catalysts tested, conversion of both reactants considerably increased with increase in temperature due to endothermicity of the process.⁶ The CO₂ conversion was higher than the CH₄ conversion due to high activation energy of C-H bond compared to C-O bond and conceivable occurrence of the RWGS side reaction (CO₂ + H₂ ⇌ CO + H₂O).⁶¹ The bare zeolite catalysts produced low activity which is in agreement with findings in literature.^{6,26} The catalytic activity of mono and bimetallic catalysts follows the order: Ni/ZSM-5 < Ni/FZSM-5 < Ni-Ga/FZSM-5 < Ni-Ca/FZSM-5 < Ni-Mg/FZSM-5 < Ni-Ta/FZSM-5. The fibrous-supported Ni catalyst had better conversions than Ni/ZSM-5, due to the higher surface area, mesoporosity and low surface acidity.^{26,45}

As expected, addition of Mg promoter increases availability of Ni active sites and affinity for CO₂ adsorption. Although, there is a slight difference in alkaline earth

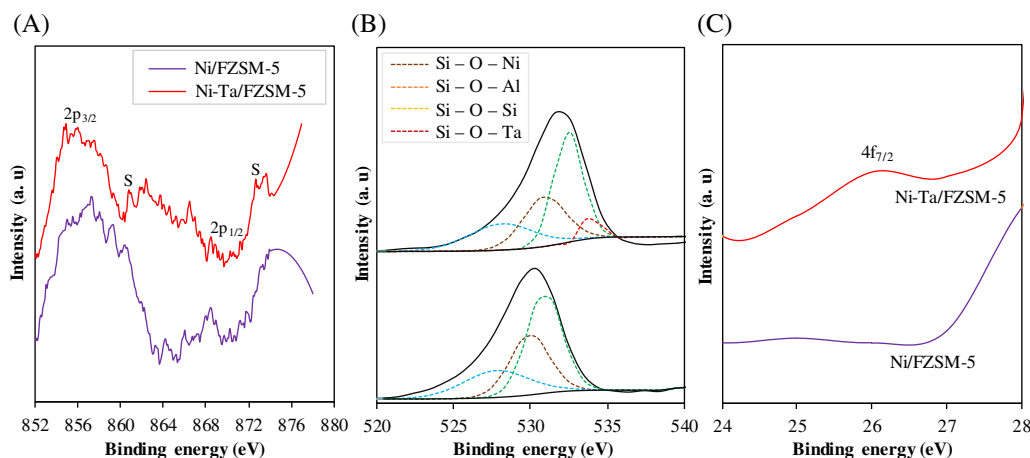


FIGURE 5 A, Ni 2p spectrum; B, O1s spectrum; and C, Ta 4f core level spectrum of Ni/FZSM-5 and Ni-Ta/FZSM-5 [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

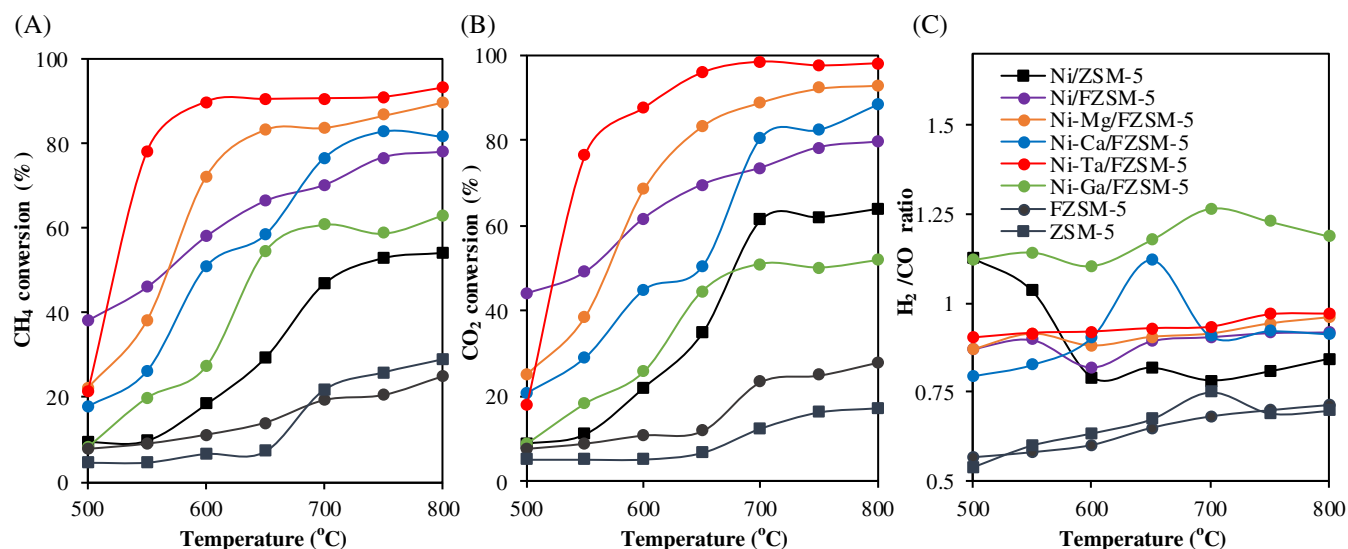


FIGURE 6 Dry reforming of methane activity over the catalysts A, CH₄ conversion; B, CO₂ conversion; and C, H₂/CO ratio [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/er.5527)]

Ca and Mg promoted catalysts, in that the former show higher basicity than the latter, but the activity of the latter still supersedes as shown in Figure 6A,B. This can be rationalised by the fact that not only basicity influence performance of catalysts for DRM. Among the promoted catalysts, Mg and Ta promoted catalysts possessed higher surface area, which is crucial in attainment of highly active catalyst.⁶⁴ Furthermore, incorporation of Ga promoter shows a negative influence on catalytic activity. This could be ascribed to its high acid/base ratio, low porosity and reducibility as evidenced by NH₃-TPD, CO₂-TPD, N₂ adsorption/desorption and H₂-TPR findings. The higher conversions for the Ta-promoted catalyst correlate to the existence of medium-weak acid sites, more reducibility and bimetallic Ni-Ta synergism. Valentini et al⁵⁰ reported enhanced performance of bimetallic Ni-V for DRM. The H₂/CO (Figure 6C) stream ratio showed a linear dependence on conversions (Figure 6A,B). The difference in catalytic activity between the catalysts suggests that surface acidity–basicity influence performance of catalysts for DRM.

3.3 | Catalytic stability

In addition to the catalytic activity, impeding catalyst deactivation during the harsh DRM condition is of great importance. To gain some insight on interplay between surface acidity–basicity and coking resistance in DRM, the catalysts were subjected to 80 hours continuous time on stream at reaction temperature of 750°C. The results are presented in Figure 7. Ni/ZSM-5 was only stable for the first few hours on stream, with severe activity loss of

64% and 62% obtained for CH₄ and CO₂ conversion, respectively. Sarkar et al⁶⁵ reported rapid deactivation of Ni/ZSM-5 catalyst in CO₂ reforming of methane. This is due to the acidic nature of zeolite support, which promotes RWGS as side reaction.⁷

For Ni/FZSM-5, activity loss of CH₄ and CO₂ conversion was 26% and 7%, respectively. The fibrous-supported Ni catalysts achieved better stability than Ni/ZSM-5. This can be correlated to the presence of large pore sizes which is desirable for stable performance because complete pore plugging is impeded. Furthermore, addition of Ga promoter did not improve stability, with rapid deactivation resulting in 64% and 66% activity loss for CH₄ and CO₂ conversion, respectively. This may be related to its high acid/base ratio (Table 2), which favours deactivation by severe carbon deposition on catalyst surface. The Ni-Ta/FZSM-5 was stable throughout the 80 hours TOS, while for Ni-Mg/FZSM-5 catalyst, slight sign of deactivation was noticeable. Both Mg and Ta promoted catalysts exhibited near unity acid/base ratio, thus boosting CO₂ chemisorption beneficial for consequent carbon gasification. Incorporation of Ta was responsible for almost complete hindrance of coke formation. This can be explained by the ability of Ta species to act as physical barrier between Ni particles, which hindered the formation of deactivating carbon.³⁴

3.4 | Carbon deposition studies

To ascertain the structural changes after DRM reaction, XRD patterns were recorded, as shown in Figure 8A. In comparison to the fresh catalysts, Ni/ZSM-5 and Ni/FZSM-5 show diffraction peaks ascribed to carbon species around

FIGURE 7 Time on stream performance of the catalysts [Colour figure can be viewed at wileyonlinelibrary.com]

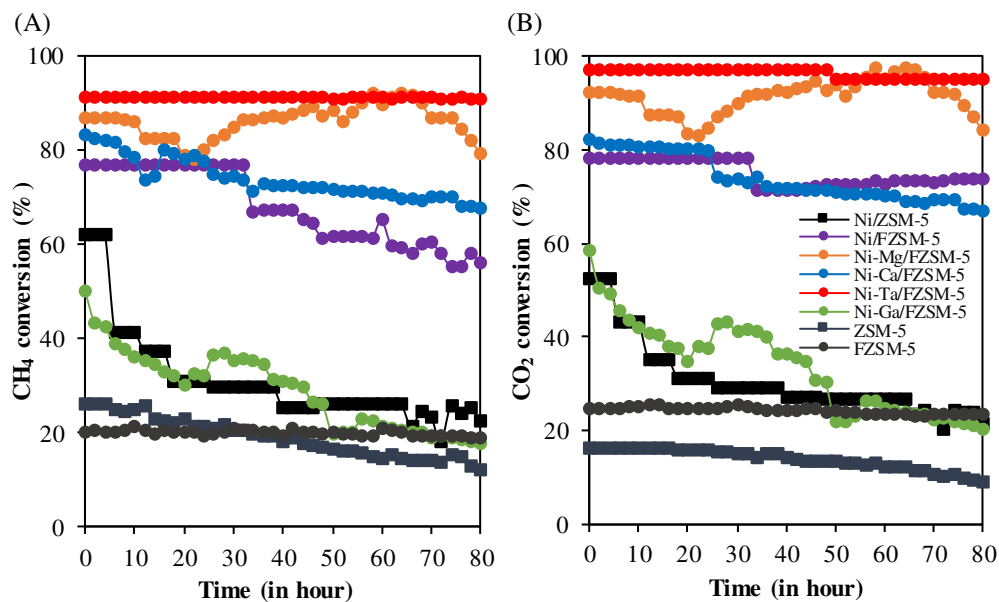
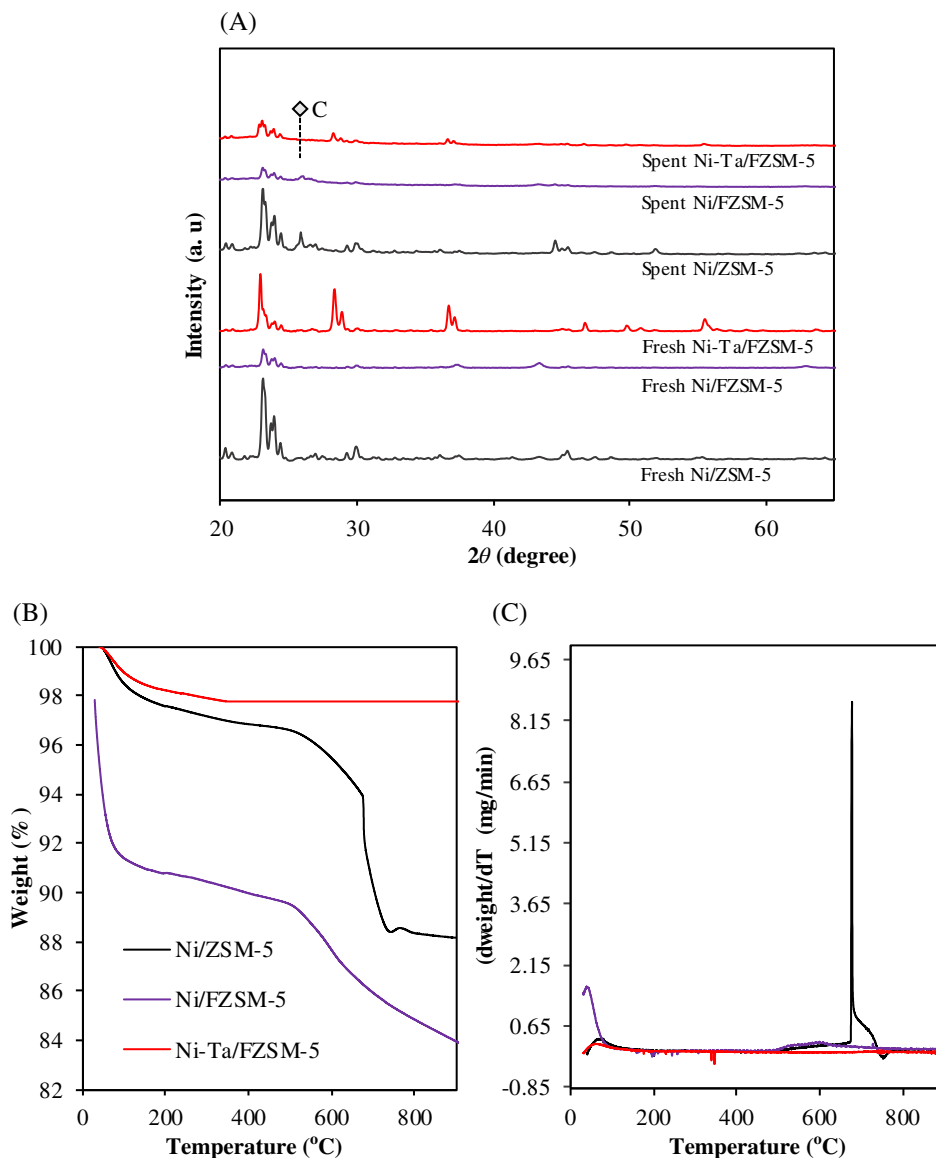


FIGURE 8 Analysis of carbon deposited on spent catalysts by A, X-ray diffraction (XRD); B, DGA; and C, DTA profiles [Colour figure can be viewed at wileyonlinelibrary.com]



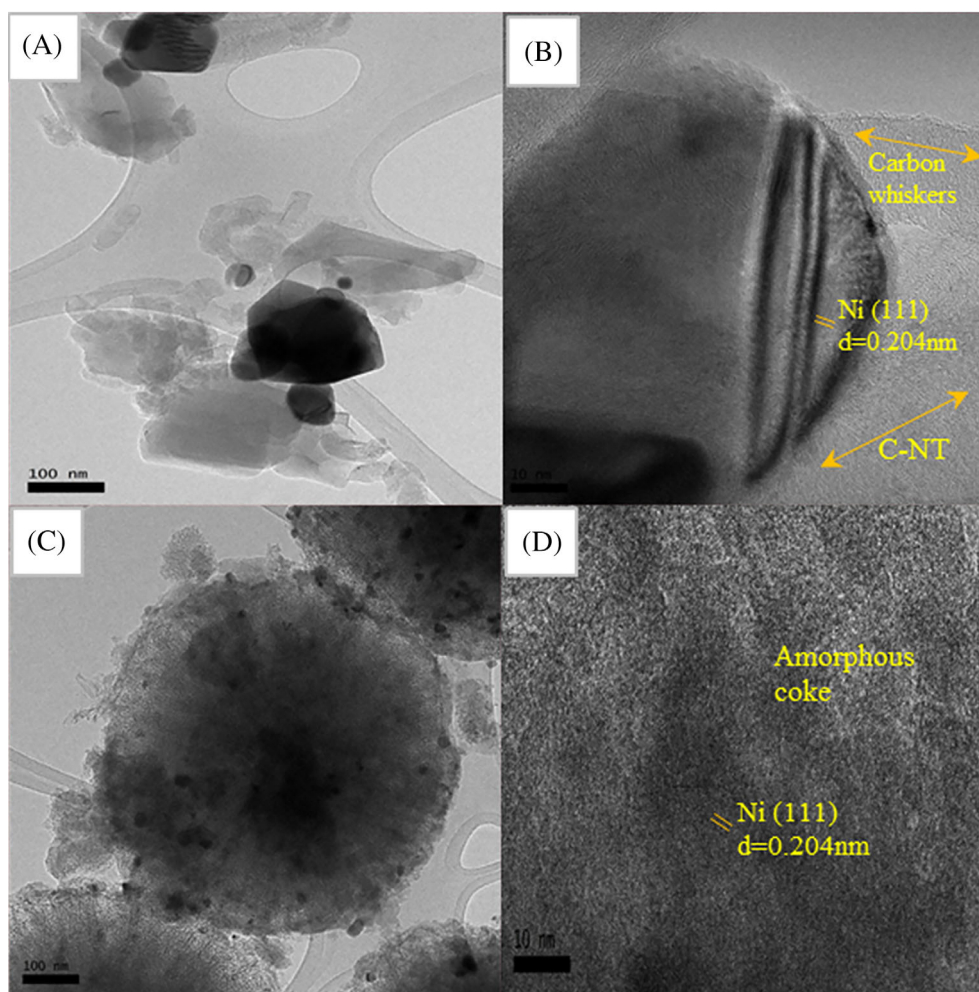


FIGURE 9 Transmission electron microscopy images of spent (A,B) Ni/ZSM-5 and (C,D) Ni-Ta/FZSM-5 catalysts [Colour figure can be viewed at wileyonlinelibrary.com]

2θ value of 26°. The carbon peak intensity of Ni/ZSM-5 is relatively higher compared to Ni/FZSM-5, suggesting more carbon deposition on Ni/ZSM-5. However, Ni-Ta/FZSM-5 shows no reflection of carbon species, possibly due to low carbon graphitisation level. The TGA/DTA technique was employed to elucidate the degree and type of coke deposited on the spent catalysts. As shown in Figure 8B, weight loss below 250°C was observed over the spent catalysts. The weight loss results from trapped water molecules within the catalyst channels or those generated from RWGS side reaction.⁶ Spent Ni/FZSM5 displayed a peak in the 250°C to 600°C region (Figure 8B), representing burning of surface carbon.⁸ For Ni/ZSM-5 catalyst, there was notable weight loss in the 250°C to 850°C region. This implies that most of the carbon deposits are graphitic in nature, which are difficult to burn off.⁶⁶ This is in good agreement with the spent XRD results (Figure 8A). Previous study reported similar findings for zeolite-supported Ni catalyst.^{16,26}

Generally, strong acid sites impede CO₂ chemisorption due to the formed dehydrogenated carbon species leading to high degree of carbon graphitisation which renders catalyst inactive. Bawah et al⁷ reported the presence of high

acidity on zeolite-supported Ni catalysts favours severe carbon formation which propagates catalyst deactivation. Moreover, the DTA profile in Figure 8C displays a sharp peak with a minimum at around 680°C for Ni/ZSM-5 catalyst, signifying formation of graphitic carbon.⁸ The addition of Ta influenced Ni-support interaction, and the medium-weak acid sites serves as anchoring sites for Ni particles stabilization. According to previous report, medium acid sites of Ni/KF-Al₂O₃ could effectively inhibit coke deposition and sintering due to improved metal-support interaction.²⁰ Hence, carbon deposition was less on Ni-Ta/FZSM-5, which supports its stable performance in DRM as discussed earlier.

TEM images of spent Ni/ZSM-5 (Figure 9A,B) showed formation of carbon nanotubes (C-NT) and whiskers. This type of carbon results in pore width shrinkage, morphology change and fracture of the support during DRM.⁶ This is consistent with the XRD and TGA/DTA results. The carbon deposits on Ni/ZSM-5 surface were difficult to gasify and responsible for the swift deactivation of Ni/ZSM-5 (Figure 7). From Figure 9C,D, spent Ni-Ta/FZSM-5 retained the fibrous morphology after the 80 hours TOS,

TABLE 3 Performance of different prevailing catalysts in DRM

Catalyst	Feed	Activity			Conditions	Carbon deposits [%]	Ref.
		X _{CH₄}	X _{CO₂}	H ₂ /CO ratio			
20Ni/ZnS-1	CH ₄ :CO ₂ :He = 1:1:1	84.5	75.4	1.87	750°C, 51.4 ^a , 0.3 ^b , 12 hours	38.3	7
Ni/fumed SiO ₂	CH ₄ :CO ₂ :He = 1:1:3	66	68	NR	600°C, 1440 ^a , 0.15 ^b , 24 hours	~26	62
SiO ₂ @Ni@SiO ₂	CH ₄ :CO ₂ :He = 1:1:1	50	58	NR	600°C, 60 ^a , 24 hours	7.6	68
05Ni05Ce/ZSM-5	CH ₄ :CO ₂ = 3:3	97	91	1.01	800°C, 15.6 ^a , 0.1 ^b , 24 hours	64	16
Ni/KIT-6	CH ₄ :CO ₂ :Ar = 1:2:2	65.1	37	NR	600°C, 40 ^a , 0.3 ^b , 100 hours	NR	4
2Ni1Co/ZSM5	CH ₄ :CO ₂ :Ar = 1:1:3	60	68	0.82	700°C, 60 ^a , 0.1 ^b , 12 hours	25.6	13
Ni/ZSM-5	CH ₄ :CO ₂ :N ₂ = 1:1:3	53	62	0.80	750°C, 30 ^a , 0.2 ^b , 80 hours	12	This work
5Ni-Ta/FZSM-5	CH ₄ :CO ₂ :N ₂ = 1:1:3	91	97	0.97	750°C, 30 ^a , 0.2 ^b , 80 hours	~5	This work

Abbreviation: DRM, dry reforming of methane; NR, not reported.

^aGHSV [Lg⁻¹ hour⁻¹].

^bCatalyst weight [g].

with formation of amorphous carbon species. This form of carbon is reported to have little or no impact on deactivation.^{6,7} The lattice fringes of Ni (111) were noticed on both catalysts.^{62,67} In addition, there was noticeable agglomeration of Ni particles on the ZSM-5-supported catalyst. The Ni-Ta/FZSM-5 displayed remarkable resistance to sintering after the long time on stream. Li et al³⁰ reported that Ni-Ta₂O₅ catalyst showed persistent resistance to carbon deposition for long-term operation.

The coking resistance of fibrous-supported Ni catalysts is attributed to the possible confinement of Ni particles to the support structure driven by the mesoporous spherical architecture.⁶ This confinement played a crucial role in controlling agglomeration of Ni particles. Among the promoted catalysts, Ni-Mg/FZSM-5 and Ni-Ta/FZSM-5 exhibited relatively stable DRM performance. Ni-Mg/FZSM-5 is believed to be resistant to coking due to smaller Ni particle size and increased basicity which boosted chemisorption of CO₂ beneficial for consequent gasification of the formed carbon at high temperature. Besides, slight deactivation was noticeable during the 80 hours duration of the stability experiment. However, Ni-Ta/FZSM-5 displayed excellent stability due to bimetallic Ni-Ta synergism and inherent ability of Ta species to act as physical barrier between Ni particles resulting to sintering resistance.^{31,34} In addition, homogeneous distribution of surface acid and basic sites was able to keep balance between CH₄ decomposition and CO₂ dissociation, thus improving stability. Table 3 shows comparison of our results with prevailing catalysts. It is evident that Ni-Ta/FZSM-5 showed higher reactant conversions and stability than the reported literature results under comparable conditions.

Figure 10 shows DRM catalytic activity dependence on reducibility of nickel species (quantified by H₂-TPR) and the number of acid sites (quantified by NH₃-TPD),

respectively. It can be observed that conversions (CH₄ and CO₂) increase with the increase in H₂ consumption (Figure 10A). The Ta-promoted catalyst produced higher conversions, signifying stronger metal-support interaction due to bimetallic Ni-Ta synergism. Valentini et al⁵⁰ reported that superior DRM performance of Ni-V/Al₂O₃ resulted from the ability of vanadium species to induce vacancies in the active metal phase thereby creating new active sites. It is worth examining the activity of the studied catalysts with respect to number of acid sites (Figure 10B). As discussed earlier, dispersion of Ni particles is related to the amount of acid sites. In a previous study, it was found that dispersion of active metal species on the support is linked to LAS abundance.⁶⁸ This feature is noticeably gathered on the Ta promoted catalyst. This fact shows that anchoring metal particles on these sites boost synergism of catalyst components, which have a positive influence on the observed DRM activity. It is also noteworthy correlating the activity of the investigated catalysts with number of basic sites (quantified by CO₂-TPD). It can be clearly seen in Figure 10C that, relationship exists between basicity and the conversions. It seems that high basicity of Ca promoted catalyst was not advantageous for the catalytic activity. It can be rationalised that even though surface basicity favours CO₂ adsorption, their excess abundance under our present experimental conditions does not improve DRM performance. Basically, catalyst with high basicity is susceptible to RWGS side reaction, leading to by-product water formation that inhibits catalytic activity.⁶ It was reported that despite the beneficial basic character of alkaline earth-modified Ni catalysts, their performance does not significantly improve reactants conversion and lead to deactivation through Boudouard or RWGS reaction as well as agglomeration of metal oxides.^{18,63} Thus, the

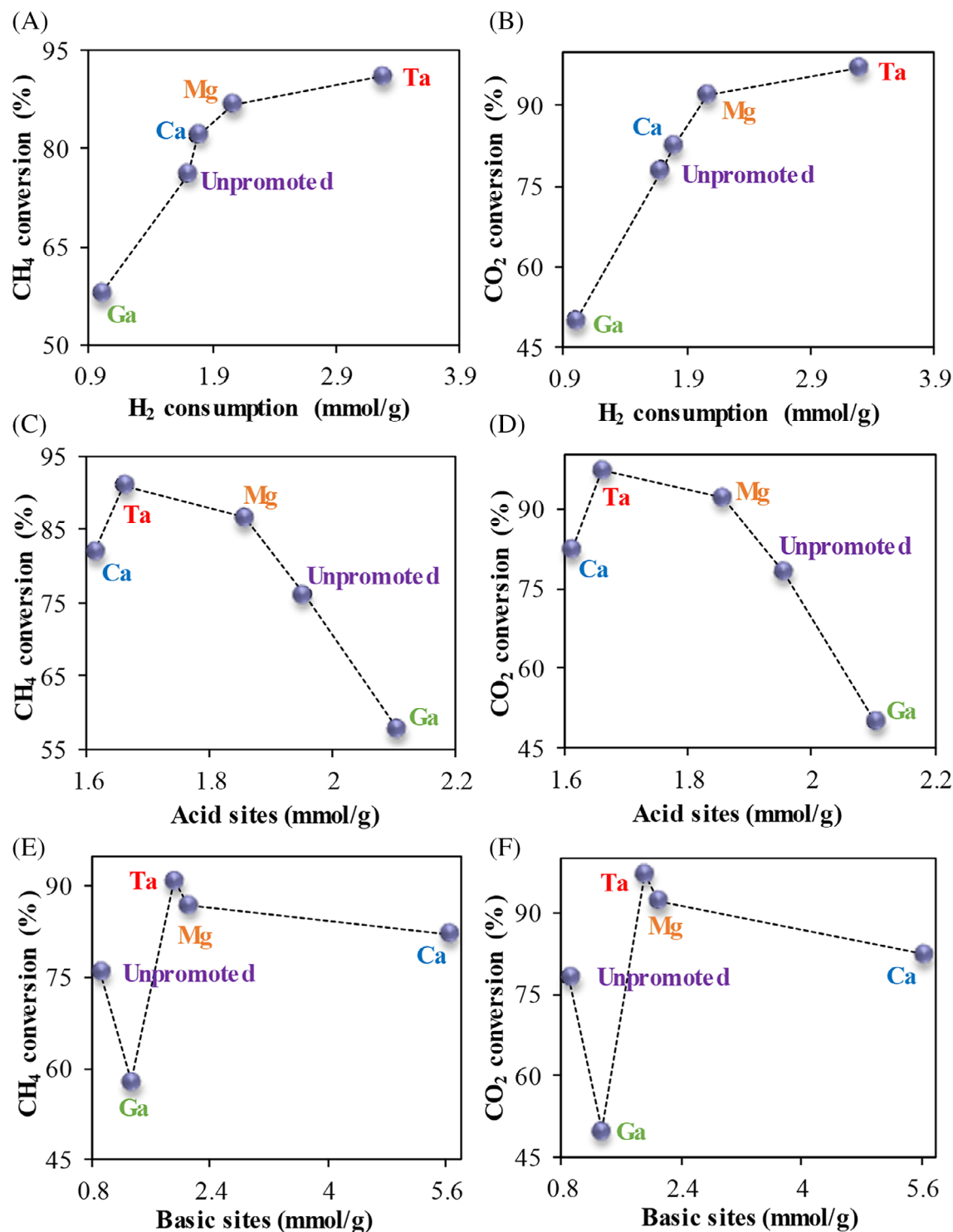


FIGURE 10 Dry reforming of methane catalytic activity dependence on (A,B) reducibility of nickel species, (C, D) number of acid sites and (E,F) number of basic sites [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/er.5527)]

surface acidity–basicity has been found to play a vital role on catalytic activity. Besides the acid–base properties, synergistic relationship between bimetallic Ni–Ta contributed to enhanced DRM performance. It can be outlined that a balance must be established between acid–basic sites to

limit the tendency of swift deactivation of zeolite support Ni catalysts. Hence, the present finding shows that a subtle interplay between acidity–basicity functions and bimetallic synergism may be beneficial to the development of an optimally performing DRM catalyst.

4 | CONCLUSION

fibrous spherical Ni-M/ZSM-5 (M: Mg, Ca, Ta, Ga) catalysts were synthesised by microemulsion method for DRM. The fibrous morphology in comparison to the coffin-shaped commercial ZSM-5 provides larger surface area and pore volume which influenced accessibility of reactants to active Ni sites. Addition of promoters altered the distribution of surface acid–basic sites and Ni-support interaction. Catalysts with high surface acidity/basicity were more vulnerable to rapid deactivation. The activity follows the order: Ni/ZSM-5 < Ni/FZSM-5 < Ni-Ga/FZSM-5 < Ni-Ca/FZSM-5 < Ni-Mg/FZSM-5 < Ni-Ta/FZSM-5. As expected, the alkaline earth promoted catalysts exhibited high concentration of basic sites, leading to strong CO₂ adsorption. Nevertheless, the excessive basicity of Ca promoted catalyst had negative influence on activity, leading to deactivation via RWGS side reaction.

Strikingly, bimetallic Ni-Ta catalyst produced the highest CH₄ and CO₂ conversions at 93% and 98%, respectively, with H₂/CO ratio closer to unity (0.97). This outstanding performance was attributed to enhanced reducibility, presence of medium-weak acid sites and improved Ni-support interaction resulting in suppression of side reactions with inferior stability in DRM. Thus, subtle interplay between acidity–basicity functions and bimetallic Ni-Ta synergism amplified interaction of catalyst components which is beneficial to the development of an optimally performing DRM catalyst.

We believe that the obtained activity and stability could be improved by tuning the feed ratio concentration. An extended study should focus on the coke deposition mechanism of this catalyst. Future study on Ni-Ta alloy formation needs to be carried out in order to get more insights on its influence on the performance of this bimetallic catalyst.

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SUPPORTING INFORMATION

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