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Syngas production via CO₂ reforming of CH₄ over Ni-based SBA-15: Promotional effect of promoters (Ce, Mg, and Zr)

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ABSTRACT

The promotional effect of different types of metals (Ce, Mg, and Zr) over Ni/SBA-15 which synthesized using ultrasonic co-impregnation technique were scientifically evaluated via CO₂ reforming of CH₄ (CRM). Characterizations including XRD, BET, FTIR, CO2-TPD were done to examine their physical attributes, metal-support interactions, and basicity properties. XRD results suggested that NiO particles were not distributed homogeneously within the confined framework of SBA-15 for Ni-Ce/SBA-15. Nevertheless, Mg and Zr promoters could effectively improve Ni dispersion over the SBA-15's siliceous framework and controlled the NiO crystallize sizes. The smallest NiO crystallite size of 9.3 nm was obtained by Ni-Zr/SBA-15. BET results verified the alteration of pore structure without changing the ordered structure of SBA-15 upon promoter addition. FTIR results suggested the partial transformation of Si–OH groups to the Si–O–X bond (X = Ce, Mg and Zr), whereas, CO_2 -TPD results confirmed the moderate basic sites present in Ni-Zr/ SBA-15. H₂-TPR evidenced the strongest metal-support interaction in Ni-Zr/SBA-15 owing to its high temperature reduction behaviour. At operating condition of P = 1.0 bar and WHSV = 15,000 mLg⁻¹h⁻¹, catalytic performance and stability ascended the trend of un-promoted < Ce-promoted < Mgpromoted < Zr-promoted Ni/SBA-15, in which Zr-promoted Ni/SBA-15 manifested the best catalytic activity (CO₂ conversion = 93.8%; CH₄ conversion = 88.3%; H₂/CO ratio = 0.82). The ascendency catalytic activity and stability of Ni-Zr/SBA-15 catalyst were attributed to its favourable properties such as strong Si -O-Zr bond formation, smallest NiO crystallite size and a moderate amount of basic sites, which crucial for sintering restriction of NiO particles and carbon deposition, thus facilitated CRM reaction.

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1. Introduction

Global warming issue remains the main apprehensions of humanity in recent century. Methane (CH₄) and carbon dioxide (CO₂), known as main contributors to greenhouse gases (GHGs) and global warming, thus, facilitated the multitudinous investigation among researchers for the utilization of CO₂ and/or CH₄ to advantageous products, via steam reforming [1,2], autothermal reforming of CH₄ [3], partial oxidation of CH₄ [4], and CO₂ reforming of CH₄ (CRM) [5,6]. Undoubtedly, CRM emerged as marvellous discovery to yield syngas (CO + H₂) from the adoption of two primary greenhouse gases (CH₄ and CO₂), and the syngas yielded from this

https://doi.org/10.1016/j.mtener.2019.04.001 2468-6069/© 2019 Elsevier Ltd. All rights reserved. process is a building block for the carbonyl and Fischer-Tropsch synthesis [5,6].

Innumerable investigations have been undertaken on CRM reaction such as the effects of the active metals, supports, preparation techniques, and calcination temperature, throughout the decades [7], which have resulted in preeminent achievements. Nonetheless, the problem of catalyst deactivation by coke accumulation and metal sintering due to the catalysts' poor thermal stability delayed the CO₂ reforming technology commercialization. In addition, accompanied undesired reactions in CRM are the main culprits for coke deposition such as methane decomposition (CH₄ \rightarrow C + 2H₂) and CO disproportionation or Boudouard reaction (2CO \rightarrow C + CO₂) [6]. Moreover, the existence of reverse water gas shift (RWGS) reaction (CO₂ + H₂ \rightarrow CO + H₂O) affected the unity of H₂/CO ratio [1].

An enormous range of metal supported catalysts have been investigated substantially in order to minimize the coke formation.







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In general, two major classes of catalyst, i.e., nickel (Ni)-based catalysts [8] and noble metal catalysts [9] were often applied in CRM. From an industrial standpoint, the first-mentioned class is more recommendable due to its economic cost and preferable catalytic performance [9]. Regrettably, Ni-based catalysts are susceptible to fast deactivation with notable coke deposition and sintering effect incurred by a high temperature of reaction and oxidation of metal, thus restrict its practical application in the industry. The pore walls' confinement effect, strong mechanical endurance, high thermal durability as well as firm-aligned framework enabled the mesoporous silica SBA-15 to be a perfect support for allocating the active metals onto the pore channel of SBA-15 [10]. Nonetheless, these two-dimensional hexagonal materials unable efficaciously suppress Ni nanoparticles aggregation at high temperature, thus sintering and coke deposition still unavoidable [10]. For the purpose of addressing this challenge, stabilization of Ni nanoparticles in the nano-tubular channels within twodimensional silica can be achieved upon the introduction of a second metal as a promoter. An appropriate introduction of promoters will produce a promising catalyst that has the ability to boost catalyst stability and attenuate carbon deposition.

Regardless previous literature reported on the adoption of promoters in the Ni-based catalyst [11], there is almost no report on the comparison studies of different categories of metal in the periodic table over Ni-based catalysts for CRM. Based on aforementioned considerations, three different metals from different groups were proposed as promoters, which can be categorized into rare earth metal (Cerium, Ce), alkaline earth metal (Magnesium, Mg) and transition metal (Zirconium, Zr). Upon the addition of alkaline earth metal oxides, it is acknowledged that the coke deposition could possibly minimize with the reaction the active oxygen species with the deposited carbon species [12]. Interestingly, sintering of metallic Ni species can also be impeded using Mg as promoter whereby strong Ni-support interaction urged the MgO layer coated on silica surface [13]. According to Huang et al. [14], MgO addition could greatly influence the catalyst's reduction attributes and increased catalyst's basicity as compared to the unpromoted catalyst. The ameliorate basicity of the catalyst could facilitate the formation of strong CO₂ adsorption and better Ni incorporation. Furthermore, its characteristics such as high thermal endurance, high melting point, and relatively inexpensive made MgO as a promising component in endothermic reactions, particularly in the DRM process [15].

Meanwhile, rare earth metals such as cerium (Ce) has unique chemical nature, owing to its 4f orbitals with electron vacancy and lanthanide contraction [16]. The existence of rare earth metal in catalyst are able to enhance the lattice oxygen reactivity, oxygen storage capability, active metal incorporation and thermal endurance of the material. In addition, the Ce doping could eventually improve the available basic sites for CO₂ adsorption which aid in gasification of carbon deposits, thus reduces carbon deposition [17]. These advantages may lead towards a considerable enhancement in catalyst activity. On the other hand, Shanmugam and co-workers (2016) also reported on the ascendancies of CeO₂ and ZrO₂ as the promoter for Ni/SBA-15 [18]. The plentiful surface oxygen species on the CeO₂ and ZrO₂ catalysts' surface successfully enhanced propylene glycol activity by suppressing the sintering and carbon deposition, as well as absorbing and releasing oxygen under oxidizing and reducing conditions, respectively. Another study [19] found that the ZrO₂ addition onto Ni/Al₂O₃ led to high catalytic activity as compared to un-promoted Ni/Al₂O₃. This result was related to the CO₂ dissociation enhancement and intimate contact amidst Ni nanoparticles and the Al₂O₃ surface which hindered the Ni/Al₂O₄ formation sequentially inhibited Ni particles agglomeration during the reaction. Therefore, the gasification increment of segregated oxygen and unsaturated intermediates subsequently ameliorated stability and suppressed coke deposition.

In conjunction with the argument on the best promoter candidate for Ni-based catalysts, the focus of this study is to explore on the influential of metal additives (Mg, Ce, and Zr) on the catalysts' behaviour. With the introduction of the promoters, Ni particles are expected to disperse homogeneously within the SBA-15's siliceous framework and thus resist towards metal sintering and carbon accumulation. In concise, the pre-requisites of uniform Ni dispersion coupled with a high accessibility of Ni as the active sites are prerequisites for an excellent catalytic activity.

2. Methodology

2.1. Catalyst preparation

Facile procedures reported by Zhao et al. [20] were employed as the guideline for the SBA-15 support preparation with triblock copolymer P123 (EO₂₀PO₇₀EO₂₀, M = 5800, Sigma–Aldrich) as template accompanied with tetraethylorthosilicate (TEOS, Merck) as silica precursor. The TEOS/P123 ratio used was 2.21 [8]. Concisely, deionized water and concentrated hydrochloric acid (HCl, Merck, 37 wt %) solution were used to dissolve triblock copolymer P123 under vigorous stirring for 1 h at 40 °C. Thereafter, an exact quantity of TEOS was dropped gently to the solution before being agitated vigorously for 1 day at 40 °C. The slurry was then fed to a reflux set for hydrothermal treatment at 80 °C for 6 h. The white powder acquired was rinsed repeatedly until pH ~5 using deionized water before oven-dried 0.5 days at 110 °C and finally calcined at muffle furnace at 550 °C for 3 h in air to eliminate the P123.

Ultrasonic-impregnation assisted technique was employed for catalyst preparation, using a commercial ultrasonic generator furbished with an ultrasonic probe [5] In brief, SBA-15 was intermixed with 5 wt% aqueous solution of promoter salt precursors of cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, Sigma–Aldrich), magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, Sigma–Aldrich) and zirconium (IV) oxide (ZrO₂, Sigma–Aldrich) under ultrasonic irradiation for 3 h, followed by air-dried for 0.5 days at 100 °C and calcined for 3 h at 550 °C, to synthesize Ce/SBA-15, Mg/SBA-15 and Zr/SBA-15, respectively. Thereafter, these powders were added to 5 wt% nickel (II) nitrate hexahydrate (Ni(NO₃)₃·6H₂O, Merck) aqueous solution using the same technique mentioned above, to synthesize Ni-X/SBA-15 (X = Ce, Mg, Zr). Likewise, Ni/SBA-15 was also prepared using the same method mentioned above in the absence of a promoter to act as a reference for comparison purpose.

2.2. Catalyst characterization

X-ray diffraction (XRD) profiles were acquired via powder diffractometer (Philips X' Pert MPD, 3 kW) equipped with the CuK α source ($\lambda = 1.5405$ Å), recorded at low ($2\theta = 0.5-3.0^{\circ}$) and wide ($2\theta = 10-80^{\circ}$) angles. The average NiO nanoparticle sizes were computed by the Scherer equation at $2\theta = 37.2^{\circ}$.

AUTOSORB-1 model AS1 MP-LP specific surface area and porosity analyser were employed to ascertain the specific surface areas, total pore volume, and pore size at -196 °C. Prior to measurement, the samples were evacuated under nitrogen flow at 300 °C for 3 h. Pore size distribution was evaluated using Barrett–Joyner–Halenda (BJH) method, meanwhile Brunauer–Emmett–Teller (BET) method was adopted to assess the specific surface area and adsorption isotherms.

The metal-support interactions and functional groups present in the samples were determined via FTIR spectra obtained on a Thermo Nicolet Avatar 370 DTGS model in KBr matrix with the scanning range of $1300-400 \text{ cm}^{-1}$.

The catalysts' basicity behaviours were identified using CO₂ temperature programmed desorption (CO₂-TPD). At first, the sample (50 mg) were flushed with 20 mL/min N₂ flow at 50 °C for 0.5 h and then cooled to room temperature. The sample was then contacted to CO₂ for 1 h and purged with He for 1 h to withdraw physically adsorbed CO₂. At last, the samples were heated from ambient temperature to 900 °C at 10 °C ·min⁻¹ of heating rate and CO₂-TPD was quantified using a calibrated TCD.

Thermo Scientific TPDRO 1100 equipped with TCD detector was used for H₂ temperature-programmed reduction (H₂-TPR) analysis to appraise the reducibility of as-synthesized bare and promoted Ni-based catalysts. Prior to analysis, the samples were pre-treated by evacuating 0.1 g catalysts under an inert atmosphere (25 mL/min He) at fixed-bed micro-quartz reactor (120 °C, 2 h), and then cooled to ambient temperature. Then, the catalysts were gradually heated to 900 °C at 10 °C/min rate under 50 mL/min 5%H₂/95%N₂. The hydrogen consumption during the reduction was analyzed online by a TCD detector.

The morphology and metals distribution of the samples were observed via transmission electron microscopy (TEM) using JEM-2100 Electron Microscope. Prior to the viewing process, the sample was firstly ultrasonicated in ethanol solution to obtain homogeneous solution. The sample was then dropped onto a porous and hollow carbon grid.

2.3. Catalyst evaluation

Activity assessments were accomplished in a packed-bed continuous flow reactor (i.d. = 11 mm, length = 417 mm) at ambient pressure with 0.2 g catalyst located amidst two quartz wool sheets in a stainless-steel tube. Before reaction, evacuation of the catalyst in flowing H₂ (50 mL min⁻¹) at 600 °C for 1 h was done. The total flow rate of feeding gas (reactants (CH₄ + CO₂) and carrier (N₂)) towards the reactor were specified at 50 mL min⁻¹, with N₂: CH₄: CO₂ = 1:1:1 proportion and 15,000 mL·gcat⁻¹·h⁻¹ was the corresponding weight hourly space velocity (WHSV). The gas reactants and products' constitution were analyzed by a TCD-gas chromatograph (Agilent 6890 Chromatograph). The catalytic CRM was taking place at 800 °C within 30 h time-on-stream (TOS). The quantity of coke accumulated on the catalysts during the experimental run was verified by XRD analysis. Formulas for CH₄ and CO₂ conversions were defined as the following equations:

$$CO_2 \text{ Conversion}, X_{CO_2} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100\%$$
(1)

$$CH_4 Conversion, X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\%$$
(2)

where *F* represents the specific component's molar flow rate. The H_2/CO , syngas ratio was defined according to equation (3).

$$\frac{H_2}{CO} = \frac{F_{H_2}}{F_{CO}} \tag{3}$$

3. Results and discussion

3.1. Characterization of the catalysts

Fig. 1(A) illustrates the low angle XRD profiles of fresh unpromoted and promoted Ni/SBA-15 catalysts. Within the region of $2\theta = 0.5-3.0^{\circ}$, each pattern manifested one perfect-resolved diffraction peak, which was indicated to the (100) diffractions

that represented to the typical p6mm hexagonal symmetry nature of mesoporous silica materials [20]. From the figure, it can be observed that even with the addition of the promoters (Ce, Mg, and Zr), the d₁₀₀ peak of promoted Ni/SBA-15 catalysts have almost the same intensity with Ni/SBA-15. This indicated that all promoters were well distributed within the meso-structure of Ni/SBA-15 without hindering the primary silica configuration of the parent Ni/SBA-15 [21]. The wide-angle XRD pattern of un-promoted and promoted Ni/SBA-15 catalysts are illustrated in Fig. 1(B). The apparent wide amorphous silica peak located at approximately 23° is accredited to the silica frameworks belongs to SBA-15 support for all catalysts, which is in conformity with another study [21]. The patterns also show the existence of peaks for cubic crystalline structure NiO at $2\theta = 37.2^{\circ}$, 43.1° , 62.8° , which corresponding to the (111), (200), (220) facets [22]. Moreover, the peaks' intensities for NiO phase in Ce promoted catalysts are more intense than that of the bare Ni/SBA-15 catalyst. It is proposed that NiO particles were not dispersed homogeneously over the confined mesopores of SBA-15 for Ce promoted SBA-15. Meanwhile, for Mg and Zr promoted catalysts, the peaks intensities are weaker than the Ni/SBA-15 catalyst, suggesting that Mg and Zr promoters could effectively ameliorate Ni dispersion [21].

For promoters peaks analysis, the CeO₂ characteristic peak was found at $2\theta \approx 28.5^{\circ}$ for Ce promoted catalyst, corresponding to the (111), which signifies the attribute of the CeO₂ cubic fluorite configuration [23]. Meanwhile, the MgO phase peak for the Ni-Mg/ SBA-15 was observed at 42.2° [24]. For the Ni-Zr/SBA-15 catalyst, almost no notable peak for ZrO₂ phases could be detected from the XRD profiles, suggesting the perfect distribution of ZrO₂ over the Ni/SBA-15 catalyst's surface.

By applying the line broadening of Scherrer equation over the XRD pattern, the (111) plane Ni crystal size was computed and the results are tabulated in Table 1. The NiO nanoparticles size for fresh Ni/SBA-15 was 9.5 nm. Intriguingly, the overall NiO crystallite sizes were reduced upon the addition of promoters. The crystallite size of NiO of the samples was reduced in the trend of un-promoted > Ce-promoted > Mg-promoted > Zr-promoted SBA-15, and the smallest NiO crystallite was marked by Ni-Zr/SBA-15 with 9.3 nm. The decrement in the NiO crystallite size might be related to a better distribution of metal over the support, which minimize the metals agglomeration that tend to enhance the active sites accessibility. In fact, a highly active metal distribution over the support is known to be an effective attempt to minimize carbon accumulation [25].



Fig. 1. (A) Low-angle and (B) wide-angle XRD profiles of Ni/SBA-15 and Ni-X/SBA-15 (X = Ce, Mg, and Zr) catalysts.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Crystallite size (nm)		
				Fresh (NiO) ^a	Fresh (Ni ⁰) ^b	Spent (Ni ⁰)
SBA-15	856	0.99	7.45	_	_	_
Ni/SBA15	407	0.89	8.57	9.8	8.23	11.2
Ni-Ce/SBA-15	323	0.50	6.73	9.5	7.98	10.0
Ni-Mg/SBA-15	203	0.31	6.50	9.7	8.15	10.1
Ni-Zr/SBA-15	323	0.58	7.52	9.3	7.81	9.5

Table 1 Physical properties of Ni/SBA-15 and Ni-X/SBA-15 (X = Ce, Mg, and Zr) catalysts.

^a NiO crystallite size was calculated from Scherrer equation.

^b Ni⁰ crystallite size was computed from d (Ni⁰) = 0.84d (NiO).

The catalysts consist of fine metal crystallite size as well as better metal-support interaction will improve the stabilization of Ni particles, and thereby impeding Ni particles sintering. Therefore, the smallest NiO nanoparticle sizes in Ni-Zr/SBA-15 was substantially advantageous to promote better sintering resistance for the catalyst, on account of the wall's confinement effect [26]. This can be also related to the existence of an intense interaction between ZrO_2 and NiO particles, which aid in impeding the agglomeration of NiO crystallites. In addition, the use of ZrO_2 as a promoter could strengthen the thermal endurance of SBA-15 and suppresses the sintering process, thus resulting in smallest particle size of NiO [27]. The calculated NiO crystalline size was correlated to the size of reduced metallic Ni⁰ particle sizes ($d(Ni^0)$) by the equation of $d(Ni^0) = 0.84d$ (NiO) [12] and the data was tabulated in Table 1 as well for its growth comparison purpose with the spent catalysts.

Regrettably, the relatively larger NiO crystallite size in Ce and Mg-promoted Ni/SBA-15 was suspected on lack of the interaction of Ce and Mg with NiO particles, thus resulted in minor agglomeration by metal sintering, which will be further discussed in the next section. The TEM images of Ni-Zr/SBA-15 (Fig. 2) also evidenced the homogeneous metal distribution and incorporation onto the framework and pore channel of parent SBA-15. It can be obviously observed that the dark spots which represented on the metals were small in size and distributed evenly along the hexagonal rod-like lattice of SBA-15.

The textural attributes (BET surface area, average pore volume, pore diameter and crystallite size of NiO) of the promoted and un-promoted catalysts are summarized in Table 1. The specific surface area, pore volume and pore diameter of SBA-15 support were 856 m² g⁻¹, 0.99 cm³ g⁻¹ and 7.45 nm, respectively. The apparent decrement in the physical properties of Ni/SBA-15 as compared to parent SBA-15, implying that the entrance of definite Ni species and blockage of the confined pores of SBA-15 [21]. The ineluctable and significant drop in surface area, pore size and pore



Fig. 2. TEM image of Ni-Zr/SBA-15.

volume upon the incorporation of Ce, Mg, and Zr symbolizes the felicitous scattering of both active metal and promoters on the aligned SBA-15 support's mesoporous channels. Moreover, in term of Ni-Ce/SBA-15 and Ni-Mg/SBA-15, the small pore size and pore volume can be linked to the possibility of pore blockage due to the NiO nanoparticles agglomeration at the pore entrances that prompted a drastic decline in their textural virtues. This was in parallel to the finding on the relatively larger NiO crystallize sizes found on both Ni-Ce/SBA-15 and Ni-Mg/SBA-15. On the other hand, the appropriate physical attributes shown by Ni-Zr/SBA-15 claimed that the Ni species were perfectly dispersed over the framework of mesoporous SBA-15, which are favourable to the excellent catalytic performance and stability of the samples [28].

Fig. 3 (A) illustrates the nitrogen adsorption-desorption isotherms of the promoted and un-promoted Ni/SBA-15 catalysts. As can be observed from Fig. 3 (A), isotherms type IV with perfectdefined hysteresis H1-type and parallel adsorption and desorption branches were demonstrated by all of the samples, which are distinctive for cylindrical channels filled mesoporous materials [29]. H1 hysteresis loop signifies the typical mesoporous materials with consistent pores size for all Ni/SBA-15 samples [30]. The hysteresis loop's upper region ranges from $P/P_0 = 0.6-0.8$ which alike with the parent SBA-15 host corresponds to the bare section of nano-channels [20]. Another N₂ capillary condensation set of Ni/ SBA-15 was evidenced by the lower region of the hysteresis loop [31]. Obviously, Ni/SBA-15 loaded with promoter species (Ce, Mg, and Zr) showed markedly smaller hysteresis loops than that of Ni/ SBA-15, signifying to a decline in the pore volume and specific surface area [21]. In the case of Ni-Ce/SBA-15 and Ni-Zr/SBA-15, it was observed that their adsorption branch of nitrogen isotherms



Fig. 3. (A) N_2 adsorption-desorption isotherms and (B) pore size distribution of Ni/SBA-15 and Ni-X/SBA-15 (X = Ce, Mg and Zr) catalysts.

virtually superimposed entirely with the desorption branch, evidencing reversible pore clearance and filling [32]. The steep rise of H1 hysteresis loop (P/P_0 range of 0.55–0.65) for both Ce and Zr promoted SBA-15 indicated that the regular size of spherical NiO nanoparticles was distributed uniformly on the mesoporous material. This property also symbolized a feature of capillary condensation within uniform pores [33]. After promoters' incorporation, distinct isotherms were found for all the samples than that of Ni/SBA-15, evidencing the considerable effects on the porous structure upon the addition of promoters [28]. A pore structure alternation in the confined spaces of SBA-15 after immobilizing promoter species was verified. Nonetheless, no alternation on the SBA-15 hexagonally aligned structure and remain intact. The results obtained are in conformity with the results shown by low-angle XRD patterns.

The pore size distribution of all samples is displayed in Fig. 3 (B). All the samples showed monomodal pore size scattering. The Ni/SBA-15 catalyst exhibited the pore size dispersion which scattered within the range between 2.5 nm and 22 nm, and a greatest centered at approximately 12.5 nm. Mostly pores of Ni-X/SBA-15(X = Ce, Mg, Zr) were centered less than 10 nm, which were finer than un-promoted Ni/SBA-15.

Fig. 4 displays the FTIR spectra of all the samples. Si-O-Si bond asymmetrical stretching vibration at about 1060 cm⁻¹ and symmetrical stretching vibration at 801 cm⁻¹ can be recognized from the FTIR spectra. Meanwhile, the 961 cm⁻¹ band represented the Si–OH (silanol group) asymmetrical stretching vibration. The 463 cm^{-1} band ascribed to the Si–O bonds bending vibration [34]. The band at 1060 cm⁻¹ and 801 cm⁻¹ for all promoted samples showed lower peaks intensity relative to the Ni/SBA-15. These alternations in Si-O-Si bond asymmetric and symmetric stretching vibration can be related to the partial amalgamation and distribution of promoter species over the mesoporous SBA-15 porous structures. In addition, the band at 961 cm⁻¹ also can be used to demonstrate the strength of Si-O-Ni interaction [5], whereby the increment in the interaction amidst metal and support led to a decline in the band intensity. It can be speculated that Ni-support interaction in the bare Ni/SBA-15 was the weakest among all the catalysts. The absence of the peak for the stretching

vibration of the Si-OH bond at 961 cm⁻¹ in the Ni-X/SBA-15 (X = Ce, Mg, and Zr) samples but shifted to the higher wavenumber proposed the occurrence of a conformation alteration in the Si-OH group surface upon the introduction of promoter species. This can be claimed to the absence of Si-OH groups due to the formation of $(Si-O)_n X = O$ species, proposing that certain Si-OH species have been altered or depleted, and converted to the Si–O–X bond (X = Ce, Mg, and Zr) [28]. This was proven by shifting of the band at 961 cm⁻¹ for un-promoted samples to the higher wavenumber side, in which to 965 cm⁻¹ for Si-O-Zr bonds [35] and 970 cm⁻¹ for Si–O–Ce bonds [36]. Meanwhile, in the case of Ni-Mg/SBA-15, no Si-O-Mg bond can be detected which can be claimed on the relatively inappropriate Mg loading (5 wt%), thus led to the comparatively weak Mg-support interaction. The similar phenomenon observed by Arora and Prasad [37] who stated that carbon accumulation on the Mg-promoted catalyst appearance can be deterred via strong metal-support interactions, which only existed at low Mg loadings and a fine particle size.

The basicity natures of bare Ni/SBA-15 and bimetallic Ni-X/ SBA-15 (X = Ce, Mg, Zr) catalysts were evaluated via CO_2 -TPD characterization. The CO2-TPD patterns of all the synthesized catalysts are displayed in Fig. 5. Generally, the strength and the basicity natures of the samples can be revealed from the desorption temperature and respective area for the particular CO₂ desorption peaks [38]. The desorption peaks observed within the temperature ranges of 100–300 °C, 400–600 °C and >700 °C can be assigned to weak, moderate, and strong basic sites, respectively. From Fig. 5, bare SBA-15 displayed the only peak at 500 °C (moderate basic site), meanwhile, the additions of Ce, Mg, and Zr proved to promote the basic site's formation with the existence of several new peaks at all basicity regions. The enhanced basicity by the incorporation of promoters is advantageous as CO₂ adsorption affinity can be ameliorated, which in turn affect the activity stability and CO_2 conversion [14]. It is also acknowledged that the CO₂ adsorption and dissociation can be strengthened upon the increment in surface basicity of the catalyst, which subsequently suppresses the coke accumulation at the catalyst surface and catalyst deactivation [19].



Fig. 4. FTIR spectra of Ni/SBA-15 and Ni-X/SBA-15 (X = Ce, Mg, and Zr) catalysts.



Fig. 5. CO2-TPD profiles of (a) Ni/SBA-15 and Ni-X/SBA-15 (X= (b) Ce, (c) Mg and (d) Zr) catalysts.

As can be illustrated from Fig. 5, Ni-Ce/SBA-15 exhibited desorption peaks at 220 °C, 480 °C, and 800 °C which corresponds to weak, moderate and strong basic sites regions respectively. Regrettably, the relatively weak desorption peak at 800 °C can be claimed on the unsatisfactory ability of Ni-Ce/SBA-15 to promote the formation of strong basic sites. Meanwhile, similar peaks were also found for Ni-Mg/SBA-15, with the minor distinction over the desorption peak of strong basic, which was marked at 750 °C instead of 800 °C. Moreover, it can be detected that Ni-Mg/SBA-15 instigated the additional moderate basic sites when extra desorption peak was observed at 540 °C. In a case of Ni-Zr/SBA-15, this catalyst exhibited desorption peaks at 220 °C (weak basic site), 480 °C and 540 °C (moderate basic site) as well as 750 °C (strong basic site). In addition, the quantity of basic sites was calculated and tabulated in Table 2. The basicity strength of the samples was inclined with the trend of Ni/SBA-15 (5.8128 mmol/g) < Ni-Ce/SBA-15 (6.3253 mmol/g) < Ni-Zr/SBA-15 (8.0882 mmol/g) < Ni-Mg/SBA-15 (8.7060 mmol/g). On the contrary, previous report [39] indicated that excessive basicity of the catalyst itself is detrimental to catalytic activity as it will stimulated higher extent of the CO₂ dissociation ($CO_2 \rightarrow C + O_2$) to be happened and thereupon deactivating the catalyst. The phenomenon worsens when Boudouard reaction $(2CO \rightarrow C + CO_2)$ start to happen at high temperature due to the enriched composition of CO upon CRM activity, thus resulted in higher quantity of coke deposited on the catalyst surface. In general, excessive basicity of the catalyst is not favourable over CRM due to the coke and metal-oxides formation [39,40]. Thus, it was deduced that Ni/SBA-15 and Ni-Mg/SBA-15 were less favourable for CRM activity due to their insufficient and excessive basicity. respectively.

Fig. 6 illustrates the H₂-TPR profiles of Ni/SBA-15 and Ni-X/SBA-15 (X = Ce, Mg, and Zr) catalysts to determine their reducibility as well as metal-support interactions. According to the literature [41], bulky NiO and Ni₂O₃ species tended to reduce at temperature lower than 400 °C, whereas NiO interacted with support was reduced at the temperature > 400 °C. The reduction of NiO and Ni₂O₃ can be represented by NiO + H₂ \rightarrow Ni + H₂O and Ni₂O₃ + 3H₂ \leftrightarrow 2Ni + 3H₂O, respectively. Generally, weak interaction NiO-support strength can be deduced from peaks present at temperature in range of 400-500 °C while peaks at temperature zone 500-600 °C were representing the medium NiO-support strength reduction [42]. In addition, peaks detected at temperature >600 °C symbolize strong NiO-support strength reduction [5]. Indeed, the existence of multiple peaks at corresponding temperatures are crucial in verifying the degree of reducibility and metal-support interactions present in the catalysts [5,43]. For un-promoted Ni/SBA-15, its deconvoluted TPR patterns consist of four reduction peaks centered at 388, 419, 456 and 528 °C. The absence of peak at temperature >600 °C evidencing the lack of strong metal-support interaction in

Table 2 Amount CO₂-TPD of Ni/SBA-15 and Ni-X/SBA-15 (X = Ce, Mg, and Zr) catalysts.



Fig. 6. H₂-TPR profiles of (a) Ni/SBA-15 and Ni-X/SBA-15 (X = (b) Ce, (c) Mg, and (d) Zr) catalysts. The dotted lines represent the Gaussian peaks.

Ni/SBA-15. In the meantime, the reduction peaks for all promoted Ni-X/SBA-15 (X = Ce, Mg, Zr) were shifted towards higher temperature, demonstrating an enhancement on the metal-support interactions as higher reduction temperatures are required for the reduction of Ni species [44]. Previous literature [5] claimed the presence of peak at approximately 748 °C for Ni-Ce/SBA-15 was related to the CeO₂ oxide crystalline reduction from Ce^{4+} to Ce^{3+} . Meanwhile, the shifting of all peaks for Mg promoted Ni/SBA-15 towards higher temperature was in parallel to the finding reported by Bian et al. [44] for Ni-MgPSNTs, in which the introduction of Mg shifted the Ni species reduction peak to a higher temperature. In addition, the peaks located at roughly 575 °C, 650 °C, 763 °C and the absence of peak at lower temperature for Ni-Zr/SBA-15, indicating a strong interaction of the Ni species with the SBA-15 support or in other words Ni species incorporated into the SBA-15 meso-structures [45]. Overall, the metal-support interactions of the catalysts can be recognized based on temperature of the peak and thus the general order of metal-support interaction followed the ascending order of Ni/SBA-15 < Ni-Ce/SBA-15 < Ni-Mg/SBA-15 < Ni-Zr/SBA-15. This fact indicates strongest Ni species interaction with the SBA-15, which further verified the XRD, TEM and FTIR findings and this factor aids in hindering metal sintering in Ni-Zr/SBA-15. The strong metal-support interaction in Ni-Zr/SBA-15 was indeed resulted from the formation of Ni-O-Zr bond,

Catalysts	Desorption Temperature [°C]	Desorbed CO ₂ [mmol/g]	Total desorbed CO ₂ [mmol/g]
Ni-SBA-15	<250	0.6144	5.8128
	250-600	3.1148	
	>600	2.0836	
Ni-Ce/SBA-15	<250	1.0142	6.3253
	250-600	3.8319	
	>600	1.4792	
Ni-Mg/SBA-15	<250	1.0373	8.7060
	250-600	4.0199	
	>600	3.6488	
Ni-Zr/SBA-15	<250	1.3647	8.0882
	250-600	4.0133	
	>600	2.7102	

homogenously distribution and incorporation over SBA-15 support. From this finding, it can also conclude that addition of promoters was able to enhance the thermal stability of the catalysts with their high temperature reduction behaviours.

3.2. Catalytic activity

Fig. 7 presents the catalytic evaluation of promoted and unpromoted Ni/SBA-15 catalysts in the CO₂ reforming of CH₄ (CRM) at 1.0 bar, 800 °C and 15,000 mL g⁻¹ h⁻¹ of WHSV. According to Chein et al. [46], the equilibrium conversions for both CH₄ and CO₂ at operating conditions (reaction temperature = 800 °C, CO₂/ CH₄ = 1.0, and reaction pressure = 1 bar) were found to be at 97% and 92%, respectively. Intriguingly, in spite of promoted and unpromoted catalysts, the CH₄ conversion was higher to that of CO₂, suggesting the occurrence of reverse water gas shift (RWGS) as a secondary reaction [17]. As can be illustrated in Fig. 7(A) and (B), CH₄ and CO₂ conversions were ameliorated with promoters' addition ascending in the trend: un-promoted < Ce-promoted < Mg-promoted < Zr-promoted Ni/SBA-15 catalysts. Among all, Ni-Zr/SBA-15 exhibited the most excellent performance with average CH₄ and CO₂ conversions were 93.8% and 88.3%, respectively (Fig. 7 (D)). While, the worst performance was demonstrated by Ni/SBA-15 (CH₄ Conv. = 77.7%, CO₂ Conv. = 69.0%). Particularly, Ni/SBA-15



Fig. 7. (A) CH₄ conversion (B) CO₂ conversion and (C) H₂/CO ratio (D) average catalytic performance of the Ni/SBA-15 catalysts with Ce, Mg, Zr promoters towards 30 h time-on-stream (TOS). (Reaction conditions: P = 1 bar, WHSV = 15,000 mLg⁻¹h⁻¹, T = 800 °C, CH₄: CO₂: N₂ = 1:1:1).

catalyst lost its stability since the 7th h in the stability test, which resulted in a decreasing of CO₂ and CH₄ conversions. In this circumstance, the insufficient oxygen mobility rapidly deactivating the catalyst and led to a decreased in the catalytic activity regardless of controllable Ni nanoparticles size and dispersion by ultrasonic co-impregnation technique. The lowest stability of Ni/SBA-15 might also be related to the large NiO crystallite size (evidenced by XRD) due to sintering and highest coke formation, as well as due to the poor Ni-support interaction (evidenced by FTIR).

On the other hand, it was observed that all promoted Ni/SBA-15 catalysts performed better stability in CRM reaction might be due to the promotional effect of the Ce, Mg, and Zr in preventing active species sintering at high temperature. Even though the reduction in stability can be observed on promoted Ni/SBA-15 catalysts, however, the reduction was insignificance as compared to the Ni/SBA-15. An excellent catalytic performance of promoted Ni/SBA-15 catalysts was related to an increased in the Ni-support interaction and provided oxygen capacity active sites, thus yielded smaller NiO particles on spent catalysts, and prevented the occurrences of sintering and even coking [21]. It was also observed that there is the difference in catalytic performance and stability among the promoted Ni-catalysts. These distinctions are mainly because of the availability of active metal for reaction. Based on the proposed mechanism for CRM, CO₂ activation mainly happened on the support whereas the stepwise CH₄ adsorption accompanied with its CH_x fragments decomposition on active metal sites [47]. It can be discerned that the highest activity and stability shown by Zr promoted Ni/SBA-15 as compared with the other promoted Ni/SBA-15 catalyst. The superior catalytic performance of Ni-Zr/SBA-15 catalysts could be ascribed by uniform fine Ni nanoparticles dispersion with strong interaction between Ni and Zr promoter that impede the sintering, (ii) structural stability of SBA-15 support, and (iii) existence of Si-O-Zr bond formation. In general, there are two types of surface active oxygen which are surface adsorbed oxygen and lattice oxygen [19]. When Zr was distributed uniformly over SBA-15 support, Ni-Zr mixed oxides were formed which led to more vacant active sites for the reactant gases, thus led to the superior activity. Moreover, the capability of ZrO₂ to ameliorate CO₂ dissociation owing to its high basicity (evidenced by CO₂-TPD) also prompted the excellent catalytic activity and stability of Ni-Zr/SBA-15. These may also resulted from an increased in unsaturated intermediates and dissociated oxygen gasification [19]. Additionally, there is no significant in Ni⁰ growth was observed due to its outstanding sintering resistance arose from the strong metal support interaction and Si-O-Zr bond formation.

Previously, Li et al. (2015) reported that Ce incorporation onto the SBA-15 framework was able to demonstrate anti-coking potential and reduce the metallic Ni nanoparticles size [48]. Furthermore, it was acknowledged that Ce possessed the ability to release mobile oxygen with its high oxygen storage to react with the carbonaceous species, thus inhibited the carbon accumulation at the catalyst appearance and subsequently increased the overall stability of the catalyst by preventing catalyst deactivation [16]. Meanwhile, the beneficial effect of Mg introduction enhanced the Ni-support interaction and catalyst's basic attributes [15]. The strong basicity of Mg is able to eliminate the carbonaceous species at the surface such as CH_x (x = 0-3) by activating the CO₂, increasing the CO₂ adsorption capacity, thereupon improving carbon formation resistance of the catalysts. The occurrence of CO disproportionation reaction can be avoided as well with MgO addition [13]. Although the previous works of literature reported on the beneficial effect of Ce and Mg onto the catalysts, however in this study, Ni-Zr/SBA-15 possessed superiority over Ni-Ce/SBA-15 and Ni-Mg/SBA-15. This statement was proven from the characterization results and catalytic performance, whereby the activity and stability for both Ce and Mg-promoted SBA-15 were left behind of Ni-Zr/SBA-15. This circumstance probably linked to the possibilities of the agglomerated Ni particles in the Ni-Ce/SBA-15 and Ni-Mg/SBA-15 catalysts due to the low homogeneity of Ni particles scattered over the mesoporous silica's exterior surface, and thus led to the NiO growth and thereupon altered the ordered framework of SBA-15. This structural degradation of the mesoporous SBA-15 support boosted the Ni particles sintering at the harsh reaction circumstances [18].

In brief, the catalytic activity of Ni-Mg/SBA-15 was probably influenced by the high ability of CO oxidation $(2CO + O_2 \rightarrow CO_2)$ by alkaline earth metal, Mg. This was in accordance with the finding by Yang and co-researchers who declared the CO oxidation $(2CO + O_2)$ \rightarrow CO₂) reaction was initiated upon the incorporation of alkaline earth metal oxide into TiO₂ [49]. In addition, inappropriate Mg loading (5 wt %) led to the absence of Si-O-X bond as seen in FTIR result further justified the performance of Ni-Mg/SBA-15. Mg, an alkaline earth metals, may even disintegrate into the base formation and cover the active sites surface from the catalyst structure at high temperature, which resulted in catalyst deactivation [14]. Meanwhile, the cubic fluorite structure of CeO₂ is one of the high oxidation state rare earth dioxides, in which the coordination number of the Ce^{4+} cation is 8 and while the oxygen anion is 4. The electronic configuration of rare earth elements is very unique that it can be claimed as reversible reaction activators [16]. The potential of Ce as reversible reaction activators prompted the undesirable catalytic activity of Ni-Ce/SBA-15.

In term of H₂/CO proportion, the high H₂/CO ratio values (>1) can be claimed to the existence of CO disproportionation, meanwhile, low H₂/CO values (<1) are ascribed to the small extent of the RWGS [50]. In fact, all of the catalysts showed lower H₂/CO ratio than that of the stoichiometric H₂/CO ratio (\approx 1) except the bare Ni/SBA-15, indicating the co-existence of RWGS reaction (Fig. 6(C)). Furthermore, the ratio of H₂/CO on un-promoted Ni-catalyst fluctuated between the 1.08–1.32 within 30 h TOS, might be due to the alternate reaction of coking and carbon elimination, indicating the catalytic instability at high temperature. Although RWGS occurred in Ni-Zr/SBA-15, the H₂/CO ratio of this catalyst almost reach the unity, which approximately at 0.82 and almost constant during 30 h of reaction. This result further confirmed the favourable catalytic performance of Ni-Zr/SBA-15, which in good agreement with its favourable catalytic properties.

In conclusion, the overall analysis and investigation have proved that adoption of Zr promoters plays a pivotal role in deactivation resistance and suppressing the Ni nanoparticles sintering through reinforcement of the interaction amidst Ni and Zr and also with SBA-15 support. Owing to its smallest Ni nanoparticle size, strongest metal-support interaction, highest oxygen capacity, vast Ni active sites quantity, strongest CO₂ adsorption capability and best catalytic performance in CRM, thus Ni-Zr/SBA-15 is proven its beneficial effect over CRM.

3.3. Characterization of spent catalyst

Fig. 8 indicates the XRD patterns of spent promoted and unpromoted Ni/SBA-15 samples. As expected, pronounced peaks were detected with strong intensity at $2\theta = 26.6^{\circ}$ disclosed the presence of graphite for all spent catalysts, suggesting the carbon nanotubes was built on the catalyst surface after 30 h TOS [38]. It can be implied that largest quantity of carbon nanotubes was marked by Ni/SBA-15 catalyst with the highest graphite peak intensity observed, revealed the weak Ni-silica SBA-15 support interaction, and thus resulted in the catalyst deactivation under high temperature reaction conditions [18]. The large crystallite size of NiO as indicated in Table 1 resulted from weak external silica



Fig. 8. XRD patterns of spent Ni/SBA-15 and Ni-X/SBA-15 (X = Ce, Mg, and Zr) catalysts.

surface interaction, as shown in FTIR analysis, are prone to carbon layers encapsulation.

Meanwhile, the lower peak intensity of $2\theta = 26.6^{\circ}$ on the spent promoted Ni/SBA-15, implying less amorphous carbonaceous or graphitic coke accumulated on the catalyst surface. It is also acknowledged that the coke deposition resulted in poor metalsupport interaction will result in catalyst deactivation. The quantity of carbon deposited which indicated from the peak intensities at $2\theta = 26.6^{\circ}$ decreased with the trend of Ni/SBA-15 > Ni-Ce/SBA- $15 > Ni-Mg/SBA-15 \approx Ni-Zr/SBA-15$. The incorporation of magnesium and zirconia promoters accelerate the coke gasification rate [18] while decelerating the coke formation rate and thereby aid in exceptional stability within 30 h TOS in the CRM reaction. Intimate interaction between Ni and ZrO₂ accompanied with spacious active oxygen species provided by higher oxygen storage capacity to inhibit coke deposition on Ni-Zr/SBA-15. In addition, this also can be linked to the high potential of Zr to improve oxygen mobility, thus favouring carbon gasification and lastly inhibiting the coke deposition on Ni-Zr/SBA-15 [19]. Meanwhile, highly basic nature of MgO also increased Ni dispersion which minimized the coke accumulation on the catalyst surface [14]. Meshkani and Rezae (2010) proclaimed that carbon formation resistance of the catalyst can be ameliorated with strong basic sites by preventing the CO disproportionation reaction (2CO \rightarrow C + CO₂) from taking place [51].

In addition, characteristics peaks of metallic Ni⁰ were also observed at $2\theta = 44.6^{\circ}$ (111), 51.9° (200), and 76.4° (220) (JCPDS No. 04–0850) for both Ni-based catalysts [52,53], implying the complete NiO reduction into metallic Ni⁰ phase upon H₂ pre-treatment. The metallic Ni⁰ phase from (111) plane of spent catalysts was also being computed by Scherrer equation and the data are tabulated in Table 1. Significant Ni⁰ growth was observed on Ni/SBA-15 from 8.23 nm to 11.2 nm, an increment of 2.97 nm other than formation of carbon nanotubes. This can be directly related to the poor metal-support interaction as well as poor sintering resistance in Ni/ SBA-15. The Ni⁰ growth was decreased with the trend of unpromoted > Ce-promoted > Mg-promoted > Zr-promoted SBA-15. The least Ni⁰ growth was found on Zr promoted Ni/SBA-15 catalyst, revealing its superb sintering resistibility.

4. Conclusion

In this study, a series of homogeneously dispersed bare Ni/SBA-15 and Ni-(Ce, Mg, Zr)/SBA-15 catalysts were synthesized by ultrasonic co-impregnation technique and evaluated for the CO₂ reforming of CH₄ at WHSV = 15,000 mLg⁻¹h⁻, T = 800 °C and P = 1 bar. It is obvious that the Ce, Mg, and Zr promoted Ni/SBA-15 performed better catalytic activity than bare Ni/SBA-15, in which the catalytic performance and stability followed the order of un-promoted < Ce-promoted < Mg-promoted < Zr-promoted Ni/SBA-15. Ni-Zr/SBA-15 exhibited the highest activity (CO2 conversion = 93.8%; CH₄ conversion = 88.3%, H_2/CO ratio = 0.82) and demonstrated the highest stability within 30 h of long-term stability test. Characterizations results of XRD and BET convinced the addition of zirconia into SBA-15 is able to manipulate the Ni nanoparticles and even facilitate the NiO nanoparticles distribution over the siliceous framework of SBA-15, which ameliorated the availability of Ni active sites. FTIR spectroscopy revealed the increment of the interaction amid active metals and support with the assistance of Si–O–X bond (X = Ce, Mg, and Zr), in which crucial to prevent metal sintering and ameliorated the catalytic performance and stability. The strongest metal-support interaction was marked by Ni-Zr/SBA-15 with its strong confinement effect, further disclosing the excellent sintering resistance. The CO₂-TPD analysis evidenced the basicity of the Ni/SBA-15 surface was significantly ameliorated upon the introduction of Zr. Moreover, the highest coke resistance of Ni-Zr/SBA-15 catalysts prohibited catalysts deactivation, thereby prolong its stability. Hence, the energy barrier of the reaction can be lowered and resulted in excellent catalytic activity. In conclusion, the modification of Ni/SBA-15 by Zr promoter successfully improved the properties of Ni/SBA-15 towards promising catalytic properties (small NiO particles, well Ni distribution, high Ni active sites accessibility and moderate basic sites, strong active metal-support interaction, strong anti-sintering and coke resistance). The Zr promoted Ni-based catalyst accompanied with ultrasound treatment can be the accepted techniques to achieve well-suited catalysts for reforming reactions which currently struggling in coke formation and sintering.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also from part of an ongoing study.

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