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Validation of Consecutive Coke and SiC Formation on Ni Core–Shell Microspheres During Methane Decomposition

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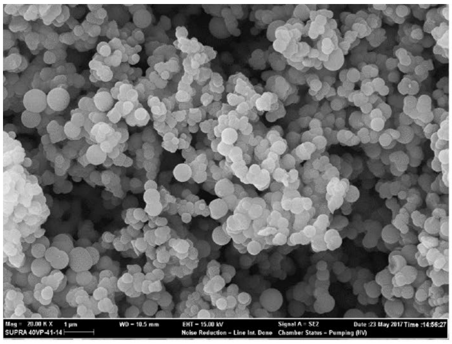
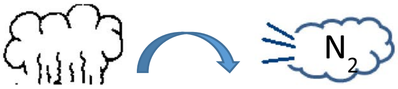
Abstract

Nickel based MCM-41(Ni/MCM-41) and silica microsphere (Ni/SiO_2) were synthesized and tested against consecutive coke deposition and SiC formation in a model methane decomposition reaction. Results indicated coke deposition on both (Ni/MCM-41 and Ni/SiO_2) catalysts and exclusive SiC formation due to utilization of coke deposited on Ni/SiO_2 catalyst.

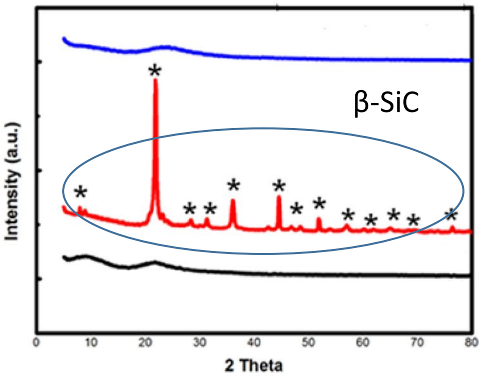
Graphical Abstract



SEM image of 5% Ni/Si microsphere after 2 hours of reaction (stable structure with no structural changes)



Heat treatment at 1200 °C under nitrogen flow to convert amorphous SiC to crystal β-SiC structure for XRD visualization.



Increased β-SiC amount on structure due to coke utilization brought self-cleaning property to the catalyst

Keywords Silicon carbide · Microspheres · Nickel · Methane decomposition · Self-cleaning · Sustainable

1 Introduction

Silicon carbide (SiC) has long been utilized as a support material in catalyst synthesis due to its excellent chemical and physical properties. The chemical inertness of the compound along with its high thermal conductivity, high

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resistance, mesoporous structure and affordable price increased its use in catalyst applications [1–8]. Having said that, SiC formation on catalyst surface was detected by chance in our previous study [9] in which Nickel (Ni) based silica microspheres (Ni/SiO_2) had been utilized in dry reforming of methane. Time on stream performance of the catalyst during reaction indicated a negligible (5%) decrease in catalytic activity without coke formation. Ni based catalysts were notorious for their affinity toward coke deposition and our results were unexpected compared with literature [10]. It was our belief that coke, formed during methane decomposition, had further reacted with Silica to give SiC. Dry reforming of methane was conducted at 750 °C, at close range of the onset of SiC crystallization and XRD analyses of used catalyst was inconclusive probably due to the presence of an amorphous SiC structure. Nevertheless, evidences of SiC could have been illustrated by interpretation of TGA and ATR-FT-IR results [9].

The present study was conducted to show that SiC formation had been exclusive to microsphere catalysts. To the best of our knowledge this was the first report on evidence of SiC formation related to dry reforming of methane.

Molecular structure of SiC varied according to the temperature of reaction. SiC was observed as ß-SiC at low (< 1400 °C) temperature while α-SiC was the main configuration at higher (> 1800 °C) temperatures [11]. SiC was formed by a gas–solid reaction between gaseous SiO (Eq. 1) and the solid carbon (C) with formation of CO as a by-product (Eq. 2) [11]. These reactions constituted the main pathway for the production of β-SiC at low temperature (> 1400 °C).

$$\mathrm{Si_{(s)} + SiO_{2(s)} \rightarrow 2SiO_{2(g)}} \tag{1}$$

$$\mathrm{SiO_{(g)} + 2C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)}} \tag{2}$$

$$\mathrm{CH_4} \rightarrow C + \mathrm{2H_2} \quad \Delta H^{\circ}{}_{298} = 75\ \mathrm{kj/mol} \tag{3}$$

Dry reforming of methane was conducted at 750 °C in our previous study [9]. Literature survey revealed that the main reaction leading to coke deposition in dry reforming of methane had been methane decomposition for a temperature interval of 650–1000 °C [12, 13]. Coke deposition through Boudard reaction was reported to be 20 times less compared to methane decomposition [13]. As a consequence, it was assumed that coke deposition during dry reforming of methane had been emanated from methane decomposition [Eq. 3] and hence we have selected this as our model reaction. Dry reforming of methane in our previous work [9] was conducted at 750 °C which was near the onset of SiC crystallization and formation of an amorphous structure was more likely to occur in these conditions. Having said that, amorphous SiC could easily be transformed to either of the crystal states by simply applying certain heat treatment procedures. The heat treatment procedure used in this study was elaborated in "Experimental" section.

The experimental layout of this study was designed as an extension of our previous study to validate coke and/or SiC formation on catalyst structure. Elimination of coke deposition during syngas production could be achieved via SiC formation which would lead to sustainable use of the catalyst. It was our belief that SiC formation could have been exclusive to microsphere structure and the best way to prove this thought was to conduct experiments in the presence of Ni containing silica catalyst other than microsphere. Consequently, Ni based MCM-41 (Ni/MCM-41) was synthesized and utilized in methane decomposition to provide a comparison. Blank SiO_2 microsphere (SiO_2) was also synthesized and used in the same reaction to indicate the sole effect of Ni on coke formation.

2 Experimental

2.1 Catalyst Preparation

2.1.1 Blank (SiO_2) and Ni Based Silica (Ni/SiO_2) Microspheres

SiO_2 and Ni/SiO_2 microspheres were prepared by a modified sol–gel microencapsulation method reported in previous studies [9, 14]. The method involved dispersion of 0.5 g hexadecyl cetyl trimethyl ammonium bromide (CTAB, Merck) with pre-determined amount of $Ni(NO_3)_2{\cdot}6H_2O$ (Merck) in 20 ml deionized water by ultra-sonication for 15 min which was followed by homogenization of the solution in a mixture of 50 ml ethanol and 10 ml 25 wt% ammonia solution. 5 ml of TEOS (tetraethylorthosilicate, Merck) was added dropwise into the solution in the final step. The amount of Ni inside the microsphere was determined as 5% based on its superior performance in our previous study [9]. The theoretical amount of Ni inside the microsphere was determined based on calculation of SiO_2 in TEOS and Ni in its salt. Synthesis solution was stirred for 6 h at room temperature and the solid product was washed with ethanol and deionized water for three times prior to drying at room temperature (24 h). Blank SiO_2 was calcined at 750 °C for 6 h to remove impurities. Ni based catalysts were initially calcined at 750 °C for 6 h to remove impurities and maintain nickel oxide (NiO) formation at the same time. These catalysts were then treated with hydrogen at 750 °C for 3 h to reduce NiO to Ni. Hydrogen treatments was applied prior to reaction.

2.1.2 Ni Based MCM-41 Catalyst (Ni/MCM-41)

Ni/MCM-41 catalyst was synthesized at room temperature according to a method recently published in literature [15]. 1.28 g of sodium hydroxide (NaOH, Merck) was dissolved in 288 ml distilled water with 500 rpm stirring at 30 °C. NaOH solution was then added to the surfactant (CTAB, 4.56 g) and the solution was mixed until observation of a clear surfactant solution. TEOS, utilized as silica source, was added dropwise to this solution under identical conditions and synthesis was conducted for 2 h which was followed by consecutive filtering and washing steps. The remaining gel was washed with deionized water until the pH of the washing solution became neutral. MCM-41 like structure was obtained after drying at room temperature for 24 h and calcination at 550 °C for 6 h. Ni/MCM-41 catalyst was synthesized via wet impregnation of Ni salt into the structure. The amount of Ni was identical in both catalysts. Impregnation was conducted by addition of Ni salt in 15 ml methanol which was followed by dropwise addition of 0.5 g MCM-41 under stirring. The mixture was kept on the magnetic stirrer for 12 h at room temperature. The catalyst was then dried in oven at 90 °C. Ni/MCM-41 catalyst was also reduced at identical conditions prior to reaction experiments.

2.2 Characterization of Blank Si Microsphere and Ni Based Catalysts Before/After Use in Methane Decomposition Reaction

XRD analyses of synthesized and used catalysts were conducted on a Panalytical Empyrean instrument ($\lambda = 1.5418$ Å) at 200 kV, 50 mA and in the range of 5–80° 2θ values (10°/min). SEM images of spent catalysts were recorded on a Zeiss Supra 40V device. TGA analysis of spent catalysts were performed on a Hitachi Exstar SII TG/DTA 7300 device (25–900 °C) with an air flow rate of 10 °C/min. Raman spectroscopy on spent catalysts was performed on a Bruker FRA 106/S Raman instrument using a $\lambda = 532$ nm Nd-YAG laser.

An additional treatment procedure was applied prior to XRD analyses for both synthesized and spent catalysts. As previously stated, amorphous SiC was obtained at the end of methane decomposition which was impossible to detect with XRD analyses. In order to validate SiC formation in catalyst structure, a practical procedure based on literature was applied to convert amorphous SiC to its crystal β form. The applied procedure was simply treatment of catalyst at 1200 °C for 16 h in the presence of nitrogen prior to XRD analyses [16–19].

2.3 Catalytic Testing

Catalysts were tested in methane decomposition reaction conducted at 750 °C for 2 h. Experiments were performed in a fixed bed reactor fitted inside a quartz tube (inner diameter of 6 mm). 0.1 g of reduced catalyst was used in experiments. 1/1 CH_4/Ar mixture was fed to the system at a flow rate of 40 ml/min which corresponded to a space velocity of 36,000 ml/(g_{cat} h). The effluent gases were analyzed online in a gas chromatograph containing a thermal conductivity detector and a Carbosphere column.

3 Results and Discussions

Decomposition of methane was selected as the model reaction with the intention of observing coke and/or SiC formation on catalyst structure. Experiments were performed in the presence of blank SiO_2, Ni/SiO_2 microsphere and Ni/MCM-41 catalyst at 750 °C for 2 h. Methane conversion and hydrogen selectivity, at the end of 3 h and in the presence of Ni/SiO_2 microsphere were determined as 72 and 1.62%, respectively. This catalyst has demonstrated a slightly higher activity compared to Ni/MCM-41 and no activity was observed in the presence of blank SiO_2 microspheres, as expected. Initial characterization of spent catalysts were conducted by TGA analyses to detect coke formation during reaction. As seen in the figure, weight losses through 200 °C were due to loss of water and/or CO_2 adsorbed on catalyst surface. Coke formation on catalyst surface was characterized by two regions of weight losses which were roughly determined between 200–400 and 400–700 °C [20–22]. The weight losses of spent catalysts between 200 and 700 °C were calculated as 0.063, 1.625 and 1.879% for SiO_2 microsphere, Ni/MCM-41 and Ni/SiO_2 microsphere, respectively. The amount of coke deposited on catalyst surface was negligible for blank microsphere as expected. On the other hand, coke amounts were almost identical for Ni/MCM-41 and Ni/SiO_2 microsphere which implied that their activity be identical in reaction (Fig. 1). TGA analyses was performed in the presence of air and formation of nickel oxide should be validated by weight increase regions in Figure. Having said that the main regions of nickel oxidation, previously determined as 250–500 [23], 500–700 and 700–1000 °C [24] in literature, was in the range of weight losses characterized by coke formation. Methane decomposition reaction was especially selected for promoting coke formation and in our opinion, the coke formed during reaction has been accumulated both on silica and nickel surfaces of the catalyst. Since nickel oxidation has been reported to be diffusion controlled [23], the absence of weight increase regions between 200 and 700 °C was an expected result. In temperature interval of 700–1000 °C a sub-parabolic behavior of oxidation kinetics,

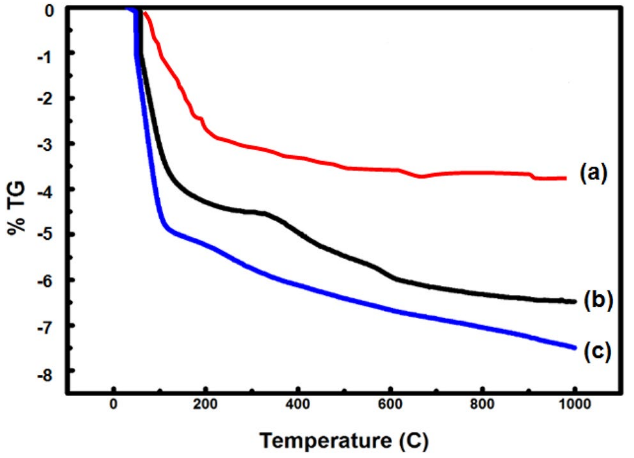

Fig. 1 TG analysis of the spent catalysts. *a* Blank (SiO_2) microsphere *b* 5% Ni/SiO_2 microsphere *c* 5% Ni/MCM-41

in other words a rapid decrease of reaction rate with time was reported [24]. Hence TGA profile obtained for catalysts utilized in methane decomposition has been found consistent with literature.

Catalysts removed at the end of 2 h were analyzed by Raman spectroscopy to further validate coke formation on their structure. Coke formation on Ni/SiO_2 catalyst could be seen in the wavelength interval of 1200–1800 per cm. The two weak bands at 1337 and 1584 per cm, corresponded to defect D band and graphite G band, respectively [25]. The G band was characteristic of graphitic carbon corresponded to C–C stretching vibration of sp^2 carbon pairs [25] and the D band was defective graphite indicating the presence of different carbonaceous materials (Fig. 2) [2, 26]. Coke regions for Ni/MCM-41 catalyst could not be determined due to the amount of coke which was probably lower or at the vicinity of device's calibration.

Visual determination of coke or SiC could not be possible from SEM images of spent catalysts (Supplementary Fig. 1). This was an expected result considering the low amount of coke formed in a relatively shorter reaction time. SEM images of pure SiC powder (Supplementary Fig. 1d) has also been obtained to determine the presence of a distinguishing feature, if any. However SiC had also a spherical form and it was impossible to distinguish SiC presence on spent catalysts. On the other hand, these images were useful in showing the microsphere structure of Ni/SiO_2 microsphere and wheat-like morphology of Ni/MCM-41 exclusive to MCM-41 structure [27].

High angle XRD patterns of the fresh catalysts along with low angle XRD pattern of Ni/MCM-41 were presented in Fig. 3. Low angle XRD pattern of Ni/MCM-41 (small figure) was given to validate formation of hexagonal structure [28]. As previously mentioned, a treatment procedure in the presence of nitrogen was applied to all (fresh and spent) catalysts in order to facilitate crystalline β-SiC formation. In the case of fresh catalysts, results indicated that SiC had already existed in microsphere structure (Ref. Code 98-002-8310 hexagonal silicon carbide). Both catalysts (Ni/MCM-41 and Ni/SiO_2) were synthesized with identical amounts of Si and Ni, the only difference between these were the method applied in syntheses and it was our belief that the distinct conditions applied in the synthesis of Ni/Si microsphere had played a crucial role in SiC formation and this result was one of the highlights of this study as SiC had already existed as a support ingredient in catalyst structure.

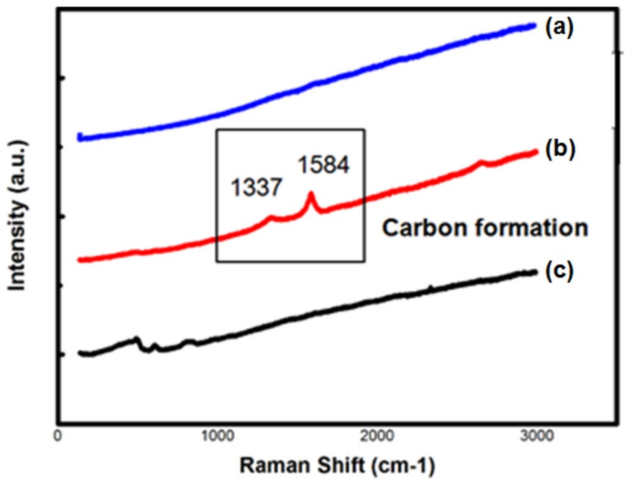

Fig. 2 Raman spectra on the spent catalysts *a* Blank microsphere *b* 5% Ni core–shell microsphere *c* 5% Ni MCM-41

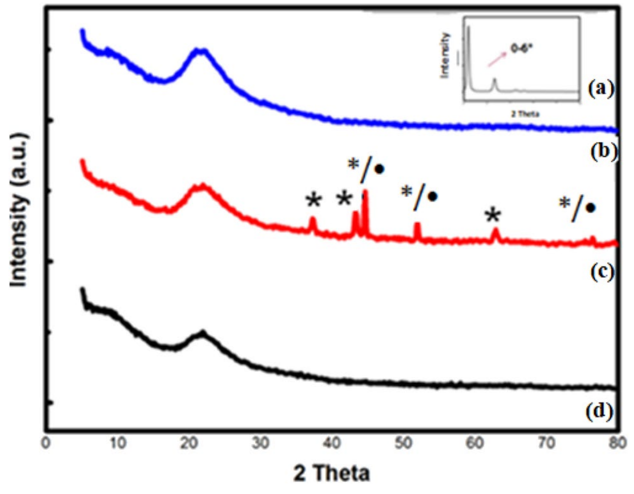

Fig. 3 XRD analysis of the fresh catalysts (after 1200 °C in a nitrogen flow for 16 h) (* = ß-SiC, • = Ni) *a* Low angle XRD pattern of a MCM-41 *b* Blank microsphere *c* 5% Ni core–shell microsphere *d* 5% Ni MCM-41

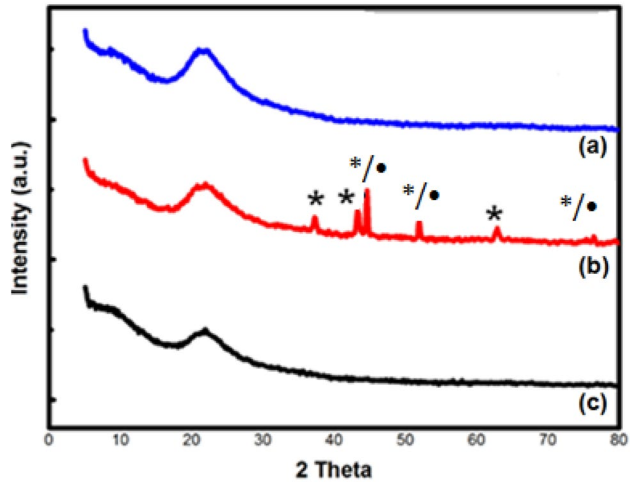

Fig. 4 XRD analysis of the used catalysts (after 1200 °C in a nitrogen flow for 16 h) (* = ß-SiC, • = Ni) *a* Blank microsphere *b* 5% Ni core–shell microsphere *c* 5% Ni MCM-41

SiC was not present in structures of blank SiO_2 microsphere and Ni/MCM-41 catalyst as seen from the figure.

XRD patterns of fresh and spent SiO_2 and Ni/MCM-41 catalyst were identical which implied that SiC be not present in their structure. In the case of spent microsphere (Ni/SiO_2) catalysts, an increase in intensity and the number of peaks distinctive for SiC could clearly be seen from Fig. 4 (Ref. Code 98-002-8310 hexagonal silicon carbide). This result indicated an ongoing SiC formation during reaction and only possible carbon source for SiC formation could be the coke generated during methane decomposition. This should also be the case for DRM reaction investigated in our previous study [9] in which coke deposition, in our opinion, was eliminated by SiC formation. The peak values identifying Ni presence on catalyst structure has overlapped with SiC peaks as seen from Figs. 3 and 4.

SiC formation was especially presented as an improvement in elimination of coke deposition since coke presence covering active Ni sites could be decreased which would increase time on stream performance of the catalyst. The negligible decrease in the activity of Ni/SiO_2 microsphere during time on stream experiments validated our conclusion [9].

4 Conclusion

Ni based microsphere catalyst showed distinct properties prior to and after methane decomposition reaction. This difference was mainly characterized by SiC formation during synthesis and the increase of SiC crystal sites after methane decomposition implied an ongoing SiC formation. The presence of SiC, exclusive to microspheres could only be explained by the procedure followed during synthesis. This was one of the highlights of the study as microsphere formation resulted in formation of a more improved structure compared to Ni/MCM-41. The crystal sites identifying SiC on catalyst structure has increased due to an ongoing SiC formation during methane decomposition. Based on the results obtained in our previous [9] study, this should also be the case in dry reforming of methane. The only possible explanation for the carbon source in SiC formation was the coke deposited on the catalyst surface and based on its fine performance of time on stream analyses, it was concluded that this catalyst had self-cleaning property. Based on literature survey, this was the first report on the presence of a self-cleaning microsphere catalyst and the synthesized catalyst was concluded to have a great potential for sustainable use in dry reforming of methane.

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Compliance with Ethical Standards

Conflict of interest The authors declared no conflict of interest related to this study.

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