Pd Supported on ZSM-5 with different ratios of Si/Al as catalysts for direct catalytic decomposition of methane

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ABSTRACT
Hydrogen and filamentous carbon have been produced by direct catalytic decomposition of methane. ZSM-5 Zeolite with ratios of Si/Al (25, 140, and 750) was used as a support in 0.5 wt% Pd/ZSM-5 catalysts. Fresh and spent Pd/ZSM-5 catalysts were characterized by XRD, SEM, TGA and CHN analyses. The hydrogen formation rates for the catalysts were Pd/ZSM-5 (25) < Pd/ZSM-5 (140) < Pd/ZSM-5 (750). The CHN analysis showed wt% of the carbon that was deposited, over the catalysts, during the reaction run to be 15.6, 17.1, and 34.3 for Pd/ZSM-5 (25), Pd/ZSM-5 (140), and Pd/ZSM-5 (750), respectively. The SEM images revealed that filamentous carbon was produced. It appears that the zeolite support in different Si/Al ratios led to form different sizes of palladium particles and palladium dispersion over ZSM-5 support. It is suggested that the catalyst activity be ascribed to the palladium particles size and its dispersion over ZSM-5.

KEYWORDS
Methane; decomposition; hydrogen; filamentous carbon; ZSM-5; Si/Al ratio

1. Introduction
Because of growing global populations and economies, energy demand is increasing rapidly. The fossil fuels utilization in particular coal, oil, gasoline, and natural gas are considered environmental challenges. This is because its combustion causes severe negative effects on the climate and environments, for instance, the greenhouse effect, global warming, acid rains, and the hole in the ozone layer. Hydrogen is a more environment-friendly fuel than hydrocarbon and used in a variety of applications, such as non-polluting vehicles, as clean aircraft fuel, in fuel cells, and as rocket fuel, and water is the only product for the combustion of hydrogen. Furthermore, it can be used in various chemical processes, for example, in the industry of petroleum, production of ammonia, methanol synthesis, ethanol, and dimethyl ether, and hydrogenation of hazardous wastes. Therefore, it is predictable that it could be the fuel of the futures [1,2]. Hydrogen is not readily available in nature, unlike fossil fuels. Hence, it can be produced using a variety of processes and from several readily available materials [3].

Most of the hydrogen utilized globally is produced with steam-methane reforming (SMR). However, this process forms large quantities of CO2, which is one of the gases belonging to the greenhouse. Also, steam reforming is a multi-stage process that includes endothermic catalytic reforming of methane, a catalytic reaction of water–gas shift, reduction of CO concentration, and separation of the H2–CO2 mixture [4–6].

Methane is the primary component in natural gases, and because of its high availability and high C/H ratio compared to other hydrocarbons, it is an ideal source of hydrogen [7]. One of the promising methods for producing hydrogen is the direct catalytic decomposition of methane that would be a green process without the emission of CO or CO2. In this method, there are only two products of the reaction, hydrogen, and carbon, with the latter being in different forms such as filamentous carbon and carbon nanotubes [8]. Moreover, the carbon produced from this reaction is viable for many applications, such as sensors, structural reinforcement, catalyst support, and energy storage [9]. This reaction is represented by Equation (1):

\[ \text{CH}_4 (g) \rightarrow 2\text{H}_2 (g) + \text{C} (s) \quad \Delta H_{298^\circ C} = 74.8 \text{ KJ/mol} \]

(1)

Among the hydrocarbons, methane has the strongest C–H bond (440 kJ/mol). Consequently, its decomposition requires high processing temperatures of over 1200°C to obtain a reasonable yield of hydrogen. Hence, using transitional metal catalysts is a convenient approach for decreasing the temperature. Numerous studies have revealed that catalysts of iron (Fe), cobalt (Co), and nickel (Ni) are the ones used most commonly for the methane catalytic decomposition reaction because of their effectiveness. Most of these metals were supported on Al2O3, SiO2, MgO, TiO2 for increasing specific surface area of a catalyst, thus improving the catalytic performance. Nevertheless, their activity for...
methane decomposition is significantly reduced in the short term because carbon produced deposition on catalyst surface \([8,10]\). Several metal catalysts used in the catalytic methane decomposition have been summarized elsewhere \([2]\). Anjaneyulu et al. \([11]\) discussed the catalytic methane decompositions for hydrogen production over catalysts of Ni/ZSM-5 with ratios of Si/Al (40, 150, 300 and 485) at 550°C. They suggested that the rate of hydrogen production was related to the surface area of Ni in Ni/ZSM-5 catalyst. Majewska et al. \([12]\) studied the activity of a Co/ZSM-5 catalyst with two molar ratios that are different for SiO\(_2\):Al\(_2\)O\(_3\) (25–30, 300–350) and different concentrations of Co for catalytic methane decomposition to produce carbon and hydrogen. They stated that the high reaction temperatures, high content of silica, and high loading of Co result in a highly concentration of hydrogen and highly yield of carbon.

A review of the literature revealed that, in addition to reducing nitric oxide, the Pd/ZSM-5 catalyst was used for catalytic combustion of methane \([13–20]\). In addition, most studies that used palladium as a catalysts for hydrogen production by methane decomposition were in the form of a good promoter for other metal catalysts \([21–28]\).

Furthermore, the literature contains insufficient studies regarding methane decomposition on the catalyst of Pd/ZSM-5. Burns et al. \([29]\) advised the catalytic methane activation over 3%Pd/ZSM-5 and MoO\(_3\)/ZSM-5 catalysts at 700°C for carbon nanotube formation. They revealed that Pd/ZSM-5 remained more active than the MoO\(_3\)/ZSM-5 catalyst for methane decomposition and hydrogen yield. They also observed that carbon nanotubes were produced on the two catalysts.

Zhao and co-workers \([30]\) studied the formation of carbon nanotubes over plasma-reduced Pd/ZSM-5 and hydrogen (thermally)-reduced Pd/ZSM-5 catalysts at 700°C. They revealed that palladium particle dispersion in the plasma-reduced Pd/ZSM-5 catalyst was greater than with the hydrogen-reduced catalyst, which played a significant role in carbon nanotube formation. Unfortunately, they did not indicate the role of these catalysts in hydrogen formation.

Although as cited above, some studies regarding Pd-based ZMS-5 have been found in the literature regarding hydrogen production by methane decomposition. However, the significant of the current work is the effects of Si/Al ratios. The present study investigated Pd catalyst supported on ZSM-5 with various ratios of Si/Al and their catalytic achievement with the direct catalytic methane decomposition. The hydrogen formation rate, carbon deposited and deactivation behaviours of the Pd catalysts are discussed in detail in this paper.

2. Experimental methods and materials

2.1. Catalyst preparation

Three types of ZSM-5 powder with various Si/Al ratios (Zeolyst, Si/Al = 25; Zeolyst, Si/Al = 140; and Tosoh, Si/Al = 750) were used as received. Catalysts of supported Pd/ZSM-5 are prepared using the impregnation method. The ZSM-5 supports were impregnated with aqueous palladium nitrate hydrate (Aldrich, Pd(NO\(_3\))\(_2\)×H\(_2\)O) solution. The resultant samples dried at 100 0°C for 24 h and underwent calcination at 500°C for 6 h in air as elucidated earlier \([29]\) with some modifications. The desired loading of palladium was 0.5 wt% of the catalysts.

2.2. Catalysts’ characterization

Different approaches have been employed for the characterization of fresh and spent catalysts. X-ray powder diffraction (XRD) patterns were collected on an Ultima IV (Rigaku International Corp., Japan) with Cu K\(_\alpha\) radiation of \(\lambda = 1.543^{\circ}\) in the 2\(\theta\) ranged from 5 to 80°. TGA of spent catalyst samples was completed with a NETZSCH TG 209 F1 Libra (NETZSCH, Selb, Germany) in an air environment with a temperature range of room temperatures to 1000°C and the rate of heating 10°C/min. The morphology of carbons deposited on spent catalysts inspected with field emission (SEM; QUANTA 250 FEI; USA), and the content of deposited carbon were determined by combustion utilizing a PerkinElmer 2400 Series IICHNS analyser (PerkinElmer, Waltham, MA, USA).

2.3. Catalytic performance and analysis of product

The catalytic performance was studied in quartz reactor fixed-bed with 1.5 cm i.d., 50 cm length, where 0.5 g of catalyst powder was placed centrally inside a tube furnace between ceramic fibre plugs. A 25% nitrogen and 75% methane feed gas mixture (provided by AHG, 99.99%) was used. The nitrogen component in the mixture utilized as internal standard for the analysis. The mixture was introduced over the catalyst at a 16 mL/min rate of flow at temperature 800°C. All the catalysts were not exposed to a reduction pretreatment due to methane being a reductant. The products resulting from reactions were analysed with on-line Gas Chromatography Agilent GC Model 7890B, using 19043 Restek packed column, Shin carbon ST 80/100 2, 0.53 mm and TCD detector was used. The gas phases detected were unreacted methane, nitrogen and produced hydrogen.

3. Result and discussions

Figure 1 shows the percentage of conversion as a time function on stream (TOS) through the catalytic decomposition of methane at 800°C over 0.5 wt%Pd/ZSM-5 with different ratios of Si/Al. With all studied catalysts, the highest conversion rate was observed in the initial stages of reaction, during first 30 min of the reaction time. The Pd/ZSM-5 (750) catalyst achieved the
highest conversion rate with 37.40% after 30 min of TOS, whereas the Pd/ZSM-5 (140) catalyst demonstrated 31.03% when the reaction started. The Pd/ZSM-5(25) catalyst was the least active one and achieved 24.53% of conversion after 30 min of TOS. Beyond 30 min of TOS, it was apparent that for all catalysts, methane conversion rate was decreasing as a result of deactivation of catalyst, which ascribed to carbon deposition on the active sites on the surface of catalysts and/or accumulated at the pores' entrance, causing their blockage. The conversions were at the end of the reaction, after 300 min of TOS, the conversion rates were 1.41, 2.60, and 3.85% for the Pd/ZSM-5(25), Pd/ZSM-5 (140) and Pd/ZSM-5 (750) catalysts, respectively.

Figure 2 displays the hydrogen formation rate with TOS for decomposition of methane over Pd/ZSM-5 catalyst with different ratios of Si/Al. It became evident that the catalyst with high ratio of Si/Al (750) had the greatest hydrogen formation rate at 5.95 mol H$_2$ g$^{-1}$ min$^{-1}$, which corresponds to a 37.40% conversion, whereas the catalyst with lowest Si/Al ratio (25) had the lowest rate of hydrogen formation of 4.67 mol H$_2$ g$^{-1}$ min$^{-1}$, which corresponds to a 24.53% conversion. The catalysts’ performances were in the orders of Pd/ZSM-(25) < Pd/ZSM-5 (140) < Pd/ZSM-5 (750). However, as observed, the behaviours of the Pd/ZSM-(25) and Pd/ZSM-5(750) catalysts were quite similar in exhibiting an initial rush in the H$_2$ rate of formation rate which was declined later. Conversely, the Pd/ZSM-5 (140) catalysts demonstrated a different behaviour in showing a rapid decline with TOS following a gradual drop for the remaining part of the reaction run. It achieved the pace of hydrogen formation 5.44 mol H$_2$ g$^{-1}$ min$^{-1}$, which corresponds to a 31.03% conversion at the beginning of the reaction. Moreover, it was noted that rates of hydrogen formation for Pd/ZSM-5 (25) and Pd/ZSM-5 (140) after 90 min of TOS were somewhat similar. However, the deactivation of catalysts was observed with TOS. The experiments of methane decomposition were carried out at least two times to ensure the reproducibility of the results.

Table 1 shows the CHN analyses for the spent catalysts. The results show that the carbon amount deposited increased to 15.6, 17.1, and 34.3 wt% for Pd/ZSM-5(25), Pd/ZSM-5(140), Pd/ZSM-5 (750) catalysts, respectively. As displayed in Figure 1 and 2, the deposited amounts of carbon stay constant with reaction rates.

The SEM images of spent catalysts are presented in Figure 3. Most of the carbon produced over all of the catalyst samples were filamentous structure form with different diameters and lengths. The diameters of the resulting filamentous carbon varied in one sample, which also showed a variation from the other samples in its average diameter. The images revealed that the average diameter of the filamentous carbon on the samples was 189, 130, and 110 nm for Pd/ZSM-5(25), Pd/ZSM-5 (140) and Pd/ZSM-5 (750), respectively.

According to the reports, filamentous carbon is generated on metal particles of supported catalysts or polycrystalline metals [31–34]. In addition, it is supposed that the metal particle sizes play a significant role in determining the diameter of resultant filamentous carbon [35–38,42]. Cheung and co-workers [39] studied carbon nanotubes’ growth over different sizes of iron nanocluster catalysts; methane or ethylene was used as a source of carbon. The iron nanoparticle catalysts had mean diameters 3, 9, 13 nm, which had carbon nanotube growth over these catalysts with mean diameters.
Figure 3. SEM images of the spent catalysts showing filamentous structures of deposited carbon with different diameters.

3, 7, 12 nm, respectively. Chen et al. [40] showed the effects of crystal size of Ni during methane decomposition over Ni catalyst supported on hydrotalcite for the synthesis of carbon nanofibres. They demonstrated that Ni crystals with mean sizes of 12 and 24 nm obtained carbon nanofibres with mean diameters of 8 and 25 nm. Their results demonstrate that the synthesis of the size controlled of carbon nanofibres can be achieved by controlling the metal particle size.

It was also suggested that particles size can modify the catalyst activity. Ermakova and co-workers [41] studied the synthesis of filamentous carbon with the decomposition of methane reaction over nickel catalysts. They exhibited that the highest yield of carbon was noted with the system comprising average particles sizes of 10–40 nm, whereas an increase in particles size led to a sharp decrease in carbon deposited. Kutteri et al. [42] discussed the decomposition of methane over mono- and bimetallic metals (Fe, Ni, Co) on the SiO2 support. They found that compared to the catalysts of monometallic, the catalysts of bimetallic displayed highest activity levels. They revealed that the crystallite sizes of bimetallic catalysts were smaller than those with monometallic catalysts, which increases the active sites number in bimetallic catalysts. Pinilla et al. [43] studied the effect of nickel-crystal size on the performance of Ni and NiCu catalysts for the reaction of methane decompositions. They indicated that smaller nickel particle sizes resulted in better catalytic performance with the methane decomposition reaction. Kim et al. [44] investigated the effect of particles size with activated carbons as a catalyst for hydrogen production by the decomposition of methane. They mentioned that the catalyst activity increased with decreasing particle size, while increasing catalyst particle size led to the lowering of overall reaction rate.

From the above, it can be surmised that smaller particles sizes of the catalyst metal lead to increases in the active site numbers, which in turn, result in increasing catalyst activity and production of a filamentous carbon with a small diameter approximately equal to those of the metal catalyst particle size. Therefore, it can be deduced from the SEM images (Figure 3) that the palladium particle sizes in the catalysts of Pd/ZSM-5 were on the order of Pd/ZSM-5(750) < Pd/ZSM-5(140) < Pd/ZSM-5(25), respectively, which is identical to the catalyst performances shown in Figures 1 and 2 and Table 1. It means that the smallest palladium particles sizes were found with the Pd/ZSM-5 (750) catalyst, whereas the Pd/ZSM-5 (25) had the largest palladium particle sizes. This is a suggested reason for these catalysts’ performance and their relationship to the palladium particles size and the role of support types in the formation of these different sizes of particles.

Figure 4 shows the TGA oxidation analyses results, along with the corresponding derivative weight changes curves, under air for the spent catalysts. From Figure 4(A), it is apparent that the Pd/ZSM-5(25) catalyst displayed a degree of mass loss prior to 200°C, which can be attributed to the adsorbed water desorption; this behaviour was missing in the Pd/ZSM-5(140) and Pd/ZSM-5(750). Moreover, there was a significant mass loss in the area beyond 600°C which resulted from the combustion of formed carbon on the catalysts. However, a consistency should be observed between the TGA and CHN analyses results.
Figure 4. (A) TGA oxidation curves for the spent catalysts and (B) corresponding first derivative patterns.

Figure 5. (A) XRD patterns for fresh catalysts and (B) XRD pattern of the spent catalysts.

Figure 4(B) illustrates the curves of derivative weight changes for the spent catalysts. These curves can track the variations between the spent catalysts more obviously. Two peaks can be noted in the area of coke combustion at ca. 630 and 675°C, indicating that two kinds of carbonaceous species have been deposited. Carbon was said to have formed over time on catalysts used during the catalytic methane decomposition can comprise amorphous and filamentous carbons that contain single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [45]. In addition, it was found that the oxidation temperature with amorphous carbon, SWCNTs, and MWCNTs was 330, 500–600, and 600–700°C, respectively [45,46]. Carbon nanofibres (CNF) have been found to be oxidized at temperatures ranging from 500 to 600°C, whereas with graphitic carbon, it is beyond 700°C [46–48]. However, it should be mentioned that, generally, the complex nature of carbon is formed over the catalyst and its reactivity is determined by the conditions of formation, type of catalyst, and mechanism. Also, the residual metal that exists in the catalyst sample can catalyse the process of oxidation for the deposited carbon species, which could lead to decreases in the maximum temperature of the oxidation rate [46,49]. Hence, based on the SEM image in Figure 3 and the results of the TGA studies shown in Figure 4(B), it has been proposed that the filamentous carbon deposited over all catalysts took the form of SWCNTs and/or CNFs, taking into consideration that more investigation by transmission electron microscope (TEM) is required.

The powder X-ray diffraction patterns for the fresh and spent catalysts are displayed in Figure 5. The patterns show the distinctive reflections of ZSM-5 support, with the peaks at ranges of 2θ = 7°, 9°, and 23–25°. This confirms that the framework of zeolite remained intact during the process of catalyst preparation and at high reaction temperatures. The palladium-containing phase did not occur, which may indicate too-high palladium dispersion with a particle size below the XRD detection limit. However, it is obvious that the relative peak intensities at 7–9° and 23–25° 2θ in the fresh and spent catalysts were different. The peak intensities at 7–9° 2θ in the spent catalysts seem higher than those in fresh catalysts. It has been stated that peak intensities below 10° 2θ in the ZSM-5 pattern remain sensitive to existence situation of any species located inside the zeolite channels, and the peak intensities will be decreased when metals inhabit the channels [50]. Consequently, it can be proposed that palladium dispersion was low and remained outer surface of the zeolite during the reaction run. Moreover, it can be observed that the highest peak intensity of 7–9° 2θ was noted with the spent Pd/ZSM-5 (750) catalyst. Therefore, it can be suggested that particles of palladium in the spent Pd/ZSM-5 (750) catalyst were highly dispersed over the outer surface of zeolite, which facilitates the exposure
of palladium particles to methane molecules during the reaction time. This may be another explanation for the higher rates of activity with the Pd/ZSM-5 (750) catalyst in comparison to the other catalysts. However, there was a little decline in the intensity of the ZSM-5 distinctive peaks, between 20 of 23° and 25°, proposing a decline in the catalysts’ crystallinity due to the carbon deposited on them. Also, it was observed that the peaks at 26° 2θ have become slightly intense and wide, in the arrangement of Pd/ZSM-5(25) < Pd/ZSM-5(140) < Pd/ZSM-5(750). This is due to the deposition of graphitic carbon filamentous structures on catalysts. The widest peak, 26° 2θ, is clear with the spent Pd/ZSM-5(750) catalyst. This may suggest that the graphite carbon crystals are small, which is consistent with the images of SEM in Figure 3, where the smallest filamentous carbons are shown.

4. Conclusion

This study suggests that the type of support shows a significant function in catalyst activity. It seems that the Si/Al ratio difference in the support of ZSM-5 played a role in altering the properties of the ZSM-5. The increase of Si/Al ratio from 25 to 750 led to an enhancement in the palladium dispersion and its particle sizes on the surface of ZSM-5, which enhanced the efficiency of catalysts for methane decomposition. The catalysts’ performances in hydrogen formation rates were in the arrangement of Pd/ZSM-5(25) < Pd/ZSM-5(140) < Pd/ZSM-5(750). In addition, the amounts of carbon produced were 15.6, 17.1, and 34.3 wt% in the same order as the catalysts. The images of SEM for the spent catalyst showed the formation of filamentous carbon with different diameters. It suggests their growth on palladium particles and, therefore, their diameters represent the sizes of the palladium particles on the catalyst surface. Accordingly, it is concluded that the palladium particle sizes get smaller and their dispersion increases with increasing Si/Al ratios in ZSM-5 zeolite.

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