The Effect of Drying Technique of Silica Support on Properties and Catalytic Activity of Multi-Metal Catalyst for Oxidative Coupling of Methane

Nattawut Nintao[a], Yuttana Chuntalap[a], Noppadol Panchan[b], Anusorn Seubsai[a], Chalida Niamnuy[a],*

[a] Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, 50 Ngam Wong Wan Road, Chatuchak, Bangkok 10900, Thailand
[b] Department of Chemical Engineering, Faculty of Engineering, Mahanakorn University of Technology, 140 Chueam Samphan Road, Nong Chok, Bangkok 10530, Thailand
 fengcdni@ku.ac.th

Oxidative coupling of methane (OCM) is an alternative reaction for the direct conversion of methane into high-value hydrocarbons. Silica is more favoured for using as a catalyst support of metal catalyst used in OCM reaction. The affective catalyst used in OCM reaction is Na_2WO_4-Mn_2O_3/SiO_2 (NWM) catalyst. Drying is one of the processes directly effect on the characteristics and performance of catalysts. Microwave drying has been reported to be the effective drying method for catalyst preparation. The effect of microwave drying of silica support for multi-metal catalyst synthesis is very limited. The objective of this work was to investigate the effect of microwave (MW) drying with different power levels, compared to hot air (HA) drying for silica support preparation on the characteristics and performance of the Na_2WO_4-Mn_2O_3/SiO_2 catalyst for employing in OCM reaction. Silica support was prepared by the sol-gel method and the Na_2WO_4-Mn_2O_3/SiO_2 catalyst was prepared by incipient wetness impregnation method. The result showed that N_2-sorption isotherm of HA and MW dried silica support showed similar isotherm. These isotherms exhibited the type IV isotherm with H1 hysteresis loop, considered as the characteristic of mesopore structure and high uniform of pore size. MW dried silica support showed the high surface area and pore volume, while HA dried silica support showed densely packed particles with small pore volume. Moreover, the MW dried silica support exhibited greater dispersion and more uniform distribution of active Mn and W components after loading of Mn and W metal species, compared to HA dried silica support. NWM catalyst, which the silica support dried by microwave drying with the power of 1,000 W, displayed the highest methane conversion and the highest yield of C_{2+} hydrocarbon at a reaction temperature of 800 °C.

1. Introduction

Biogas is a clean source of energy, which is produced during the anaerobic digestion of sludge, animal manure, and organic waste. It is composed mostly of methane and carbon dioxide (CO_2) (Penteado et al., 2017). Methane is an important greenhouse gas with high climate change potential, produced by emission of heat energy during combustion reactions. In addition, methane is also oxidized to form several species of greenhouse gases such as carbon dioxide, ozone, carbon monoxide, among others. The oxidative coupling of methane (OCM) is an effective method for methane conversion, which involves the addition of oxygen into value-added chemicals for instance, ethane, ethylene, propane, propylene, and so on (C_{2+}). The OCM reaction is an exothermic one, and it normally occurs at high temperatures of around 600-1,000 °C. In the OCM reaction, methane is interacted with an atom of oxygen on the catalyst's surface to generate a hydroxyl (•OH) radical intermediate and a methyl radical (•CH_3). Subsequently, the generated methyl radical is interacted with another methyl radical to form ethane. Following this, the ethane is oxidized to generate a C_{2+} hydrocarbon (Kidamorn et al., 2020). Several previous research studies have looked at the development of a suitable catalyst for enhancing the selectivity in OCM reaction. Many reports demonstrated that 2 %Mn-5 %Na_2WO_4/SiO_2 catalysts

performed high activity for OCM (Li, 2003). Silica is an effective catalyst support for the OCM reaction due to its large pore size and pore volume, high surface area, and high dispersion of active metal components. An alternative catalyst for OCM is the Mn-Na$_2$WO$_4$/SiO$_2$ catalyst. It shows high activity in the ratio of 2 % Mn-5 % Na$_2$WO$_4$/SiO$_2$ (Li, 2003). Basically, the silica support is prepared using akyl orthosilicates as a silica source having several disadvantages such as high cost, flammability, and high toxicity to the environment. Sodium silicate is considered as an alternative source while chitosan is an effective template due to their lower prices and environmentally friendly properties. The textural properties of silica support are one of the most vital factors affecting the efficiency of catalyst support. The improvement of the textural properties of silica support is usually brought about through chemical techniques such as the use of decane for increasing the pore size of mesoporous silica (Blin et al., 2000). Nevertheless, the use of chemicals also resulted in high cost, toxicity to the environment, and a more complicated process of large-scale production.

Several previous research studies have proposed the use of drying, which is a physical process, for surface modification of silica support. The hot air drying process involves heat transfer by conduction from the external to the internal layers of the material (Niamnuy et al., 2020). Subsequently, the thermal gradient is used, which leads to the appearance of a moisture gradient between the external and internal layers of the material. This leads to low efficiency in water evaporation (Sarawade et al., 2011). In comparison, when using microwave drying techniques, the water molecules directly absorb heat energy, following which the vibration of molecules occurs due to the heat energy generated from the internal layer. This, in turn, leads to the rapid evaporation and reduction of the thermal gradient (Neves et al., 2002). The rapid evaporation of water can mitigate the problem of aggregation of particles. Thus, microwave drying is one of the promising techniques for improving catalyst properties due to its high heating rate, uniform heating, easy operation, and requirement of only a short time period.

As mentioned above, we are interested in the enhancement of the properties of silica support through the application of the drying process, which is a physical process rather than a chemical one. This study investigated the effect of microwave drying, at different power levels, on the properties of silica support that was to be utilized as a support for the Na$_2$WO$_4$-Mn$_2$O$_3$/SiO$_2$ (NWM) catalyst used in the OCM reaction.

2. Materials and methods

The silica supports were synthesized through the sol-gel method that has previously been reported (Panchan et al., 2019). After the filtration process, the wet obtained silica was dried by means of two different drying techniques such as hot air (HA) drying at 100 °C for 90 min by using a hot air dryer (Binder GmbH, Redline RF115, Tuttlingen, Germany) and microwave (MW) drying at the power of 600 and 1,000 W for 40 and 20 min, by using a microwave oven (Samsung, MS28H5125BK, Seoul, Korea). The studied power levels of microwave drying were chosen through the preliminary experiments for identification of parameter range. The synthesized silica, which were dried by hot air drying at 100 °C and microwave drying at 600 and 1,000 W, were implied as SiO$_2$-HA100, SiO$_2$-MW600, and SiO$_2$-MW1000. The 5 %wt-Na$_2$WO$_4$-2 %wt-MnO$_x$/SiO$_2$ (NWM) catalyst was prepared through the incipient wetness impregnation method onto 0.93 g of silica support using the mixture of 0.09 g of Na$_2$WO$_4$·2H$_2$O was mixed with 0.07 g of Mn(NO$_3$)$_2$·4H$_2$O and then dissolved with 4 mL of deionized water. The mixture was stirred at room temperature, until it formed a homogeneous solution, following which the mixed-metal solution was added dropwise onto 0.93 g of silica support. The mixture was then stirred at room temperature for 3 h. Subsequently, it was dried at 100 W for 5 min in a microwave oven and calcined at 800 °C for 8 h. The synthesized catalysts, with supports which were dried by hot air drying at 100 °C and microwave drying at its power of 600 and 1,000 W, were implied as NWM-HA100, NWM-MW600, and NWM-MW1000. The surface morphology of catalysts was examined by using a scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (SEM-EDS). The crystallographic features of the catalysts were monitored by an X-ray diffraction (XRD) using Cu Kα radiation. The textural characteristics of catalysts were investigated by N$_2$-sorption using a gas physisorption analyser (3Flex Physisorption, Micromeritics, Norcross, GA). The samples were degassed at 110 °C for 4 h before they were measured. The stretching and bending vibration of mixed oxide material was determined using Fourier-Transform Infrared spectroscopy (FTIR). The performance of NWM catalysts for usage in OCM was evaluated with a fixed bed reactor as presented in Figure 1. The reaction was carried out at 800 °C and methane and oxygen used in a volume ratio of 3.5:1 as a reactant gas, at a total feed rate of 50 mL/min. The reaction time was maintained for 1 h. The effluence gas was analyzed using gas chromatography (GC-14A, Shimadzu, Kyoto, Japan) with a flame ionization detector (FID) and a thermal conductivity detector (TCD).
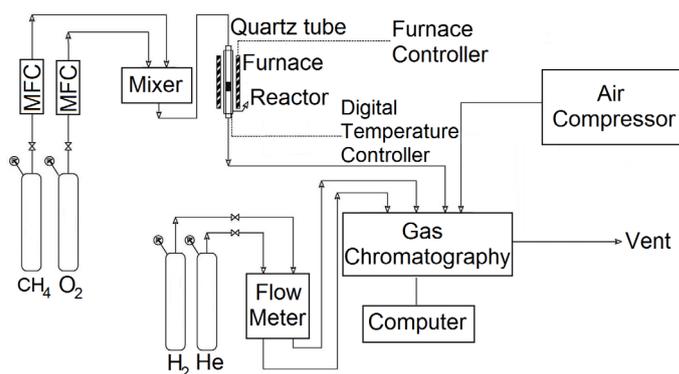
Figure 1: Schematic diagram of experimental test system.

3. Results and discussion

3.1 The influence of drying techniques on properties of SiO₂ support and NWM catalysts

The results of the textural properties of silica supports prepared by several drying techniques and NWM catalysts are presented in Table 1. The pore sizes of all silica support have a similar value of around 12–13 nm, with a mesoporous structure. All of the NWM catalysts also exhibited mesoporous structure with pore sizes of around 7–8 nm. The pore volume of hot-air dried silica support was lower than the microwave dried silica support. This was due to the hot air drying process, heat energy is transferred from the external to the internal layer of the wet gel silica via conduction, leading to the creation of a moisture gradient between the external and internal layers of wet gel silica (Niamnuy et al., 2020). It led to a slow and poor efficiency in water evaporation, resulting in the destruction of the pores of the hot-air dried silica support (Sarawade et al., 2011). On the contrary, the water molecules in the wet gel of silica were directly absorbed during the microwave radiation, and heat energy was generated from the interior of the water molecules, leading to the rapid evaporation of water and reduction of thermal gradient (Neves et al., 2002). The acute evaporation of water in wet gel silica reduced the aggregation of silica particles, which were the cause of higher pore volume and surface area (Liang et al., 2006). The surface areas of SiO2-MW600 and SiO2-MW1000 were higher than those of SiO2-HA100. After Na2WO4 and Mn2O3 were impregnated onto the silica supports, the amorphous silica was transformed into crystallization of α-cristobalite SiO2 owing to the available of Na and W (Elkins et al., 2015). It led to the lowering of the surface area, pore size, and pore volume. This result is corresponding to the finding of Sadjadi et al., 2014. The N2-sorption isotherms of silica supports and NWM catalysts are illustrated in Figures 2a-b. All of the silica supports exhibited mesoporous structure (type IV isotherm), and their hysteresis loops were found to be H1, which means that these silica supports had a relatively high uniformity of pore sizes and connectivity of facial pores. The NWM catalysts displayed a combination of micro- and mesoporous structures (type II isotherm), and their hysteresis loop was H3, which indicates an aggregation of particles and wide distribution of pore sizes (Kruk and Jaroniec, 2001).

Table 1: Textural characteristics of Silica Supports and NWM catalysts

Sample	Surface area[a] (m^2/g)	Average pore diameter[b] (nm)	Total Pore volume (cm^3/g)
SiO₂-HA100	401	12.6	1.2400
SiO₂-MW600	414	12.6	1.3000
SiO2-MW1000	413	12.5	1.3000
NWM-HA100	2.11	7.9	0.0042
NWM-MW600	2.32	7.8	0.0045
NWM-MW1000	2.30	7.7	0.0044

[a] Specific surface area calculated by Brunauer–Emmett–Teller (BET) method.
[b] Pore diameter measured by Barrett-Joyner-Halenda (BJH) desorption method.

The morphology of hot-air dried silica supports presents densely packed tiny particles with small pore volumes due to the poor efficiency in the removal of water (Sarawade et al., 2011), as shown in Figures 3a-c. In contrast, the microwave dried silica support had higher pore volume due to the better distribution of silica particles. After the silica support was impregnated with Na_2WO_4 and Mn_2O_3, the NWM catalysts were presented in a coral reef-like shape, as shown in Figures 3d-f. The elemental compositions of the NWM catalysts were examined using the

SEM-EDS analysis. Dot mapping was used to present the distribution of Mn and W in catalysts, as shown in Figures 3g-l. NWM-MW catalysts exhibited better uniformity of metal distribution on silica support compared to NWM-HA100 catalysts. Additionally, the NWM-MW catalysts presented higher concentration and dispersion of Mn and W active metal on the surface of the catalyst than NWM-HA catalysts, as shown in Table 2.
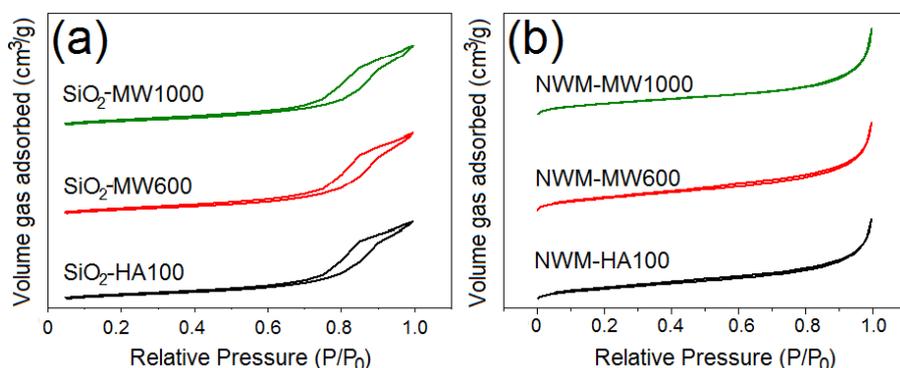

Figure 2: N_2-sorption isotherms of (a) Silica supports, and (b) NWM catalysts.
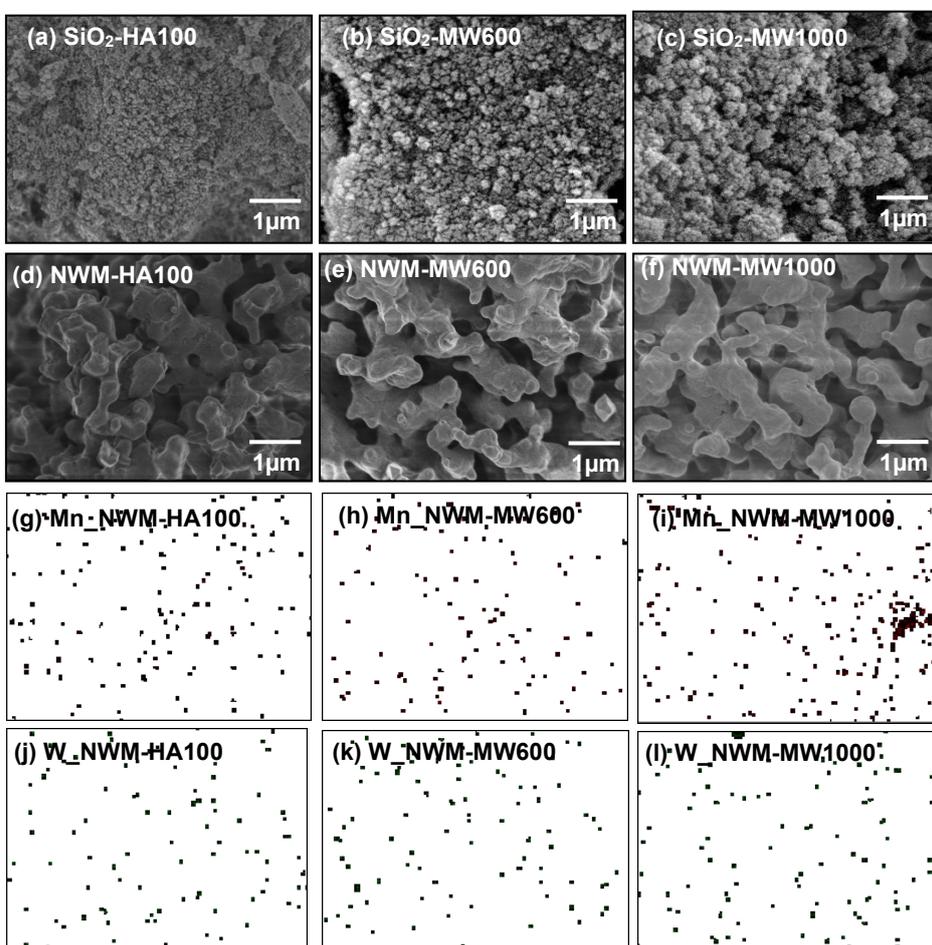

Figure 3: SEM images for silica support dried by different drying technique, and EDS mapping of Mn (g-i), and W (j-k) in NWM catalysts.

The x-ray diffraction (XRD) pattern of silica supports and NWM catalysts are shown in Figures 4a-b. The characteristic peaks of the XRD spectra of all silica supports were broad peaks at 2θ angle of $22.47°$, denoted as amorphous silica. The NWM catalysts exhibited the α-cristobalite crystalline phase [2θ = 22.1, 28.5, 31.5, 36.1, 42.9, 44.9, 46.9, 47.1, 48.8, 54.3, 57.1, and 62.0 (ICDD No. 00-001-0438)], Na_2WO_4 [2θ = 16.9, 27.6, 32.5, 48.8, 52.1, and 57.1 (ICDD No. 01-074-2369)], and Mn_2O_3 [2θ = 33.1, 38.1, and 44.8 (ICDD No.00-002-

0896)] (Nipan et al., 2016). The functional group of NWM catalysts was investigated using FT-IR, as illustrated in Figure 4c. All prepared NWM catalysts expressed the IR peak of crystalline Mn/SiO_2 (Mn-O-Si) and Na_2WO_4/SiO_2 (W-O-Si) at 465 and 797 cm^{-1}. Amorphous silica was detected by the IR band position at 1,080 cm^{-1}, and the additional peak at 631 cm^{-1} showed up due to the stretching of Si-O-Si bond in silica support (Karbowiak et al., 2010). NWM catalysts presented a broad peak at 3,354 cm^{-1}. This indicated that the surface of the prepared catalysts was rich in hydroxyl groups. It led to greater efficiency in the methane activation process on the surface of active oxygen species, in order to form methyl radicals (Kidamorn et al., 2020). Thus, it is evident that the activation of methane was the most important step in the OCM reaction (Kim et al., 2017).

Table 2: Elemental composition dispersed on the surface of NWM catalysts

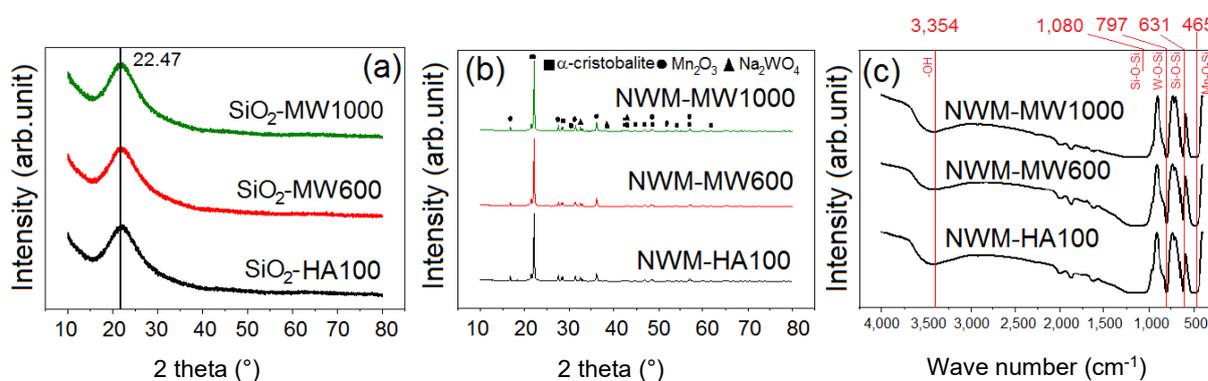| Sample	Weight %			
	Na	W	Mn	O
NWM-HA100	0.40	3.70	0.57	56.30
NWM-MW600	0.60	4.09	1.88	54.34
NWM-MW1000	1.02	4.33	0.84	53.73

Figure 4: XRD spectra plots of (a) Silica Supports, and (b) NWM catalysts and (c) FTIR spectrum of NWM catalysts.
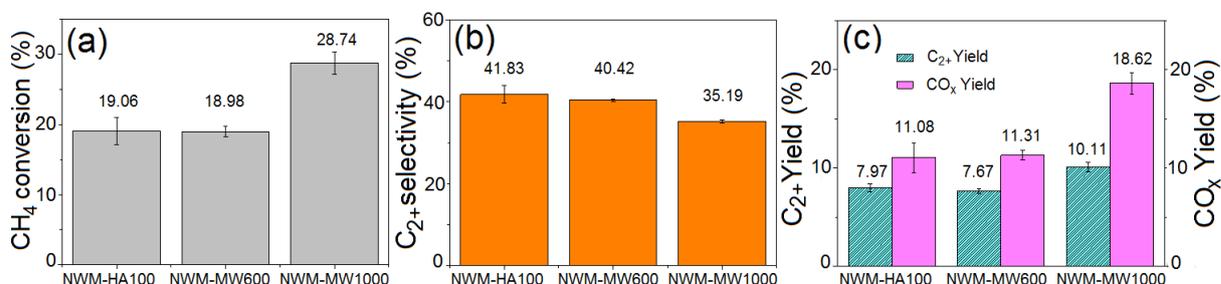

Figure 5: Activity test of Na_2WO_4-Mn_2O_3/SiO_2 (NWM Catalysts) in OCM reaction consists of (a) CH_4 conversion, (b) C_{2+} selectivity, and (c) C_{2+} yield.

3.2 Catalytic Activity of Na2WO4-Mn2O3/SiO2 catalysts

Figure 5a shows that the NWM-MW1000 catalyst displayed the highest CH_4 conversion with 28.74%, due to the high concentration of active metal species on the surface of silica supports. Figure 5b demonstrates that the NWM-HA100 has highest C_{2+} selectivity with 41.83%. While C_{2+} selectivity decreased with an increase the microwave power used for the drying of silica supports. As a result, there was greater oxygen concentration on the surface of the NWM-HA100 catalyst (table 2). This indicated that the presence of more oxygen resulted in the greater efficiency of the OCM reaction, as the oxygen component on the surface of NWM catalysts was vital for the activation of methane and C_{2+} condensation during OCM (Kim et al., 2017). The NWM-MW1000 exhibited the highest C_{2+} yield of 10.11 %, as shown in Figure 5c. This was due to the high dispersion of Mn and W active metal species on the silica supports of NWM catalysts. High amount of Mn which is a redox active exposed on NWM-MW1000 catalyst surface compared to other catalysts, may be too oxidizing leading to obtain oxidized products such as CO and CO_2, caused of the highest CO_x yield leading to be the lowest C_{2+} selectivity significantly (Elkins et al., 2015).

4. Conclusions

The effect of microwave drying to prepare silica supports for 5 %wt-Na_2WO_4-2 %wt-MnO_x/SiO_2 catalyst, to be used in the OCM reaction, was monitored. Microwave drying could generate heat energy from the internal layer of wet gel silica and cause rapid evaporation of water, which led to the reduction of thermal and moisture gradient, decreasing the particles aggregation. Moreover, microwave drying resulted in greater distribution of silica particles, on account of the higher surface area and pore volume in the structure of silica supports when compared to hot air drying. The large surface area and pore volume resulted in a higher dispersion of active metal species on the silica supports of NWM-MW catalysts. These results led to greater catalytic activity. The NWM-HA100 catalyst showed the highest C_{2+} selectivity of 41.83 % due to the high oxygen concentration on its surface. The NWM-MW1000 catalyst exhibited the highest CH_4 conversion and C_{2+} yield of 28.74 % and 10.11 %, due to the high dispersion of the Mn and W active metal species.

Acknowledgments

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