Metal Carbide as A Light-Harvesting and Anticoking Catalysis Support for Dry Reforming of Methane

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Dry reforming of methane (DRM) is one of the most attractive chemical reactions, since it converts global-warming gases into valuable syngas including hydrogen and carbon monoxide. Numerous previous studies used metal oxides catalysis supports, such as Al₂O₃, but their operating temperature was very high and severe coking occurred and deteriorated their catalytic activities. The present study reports that a metal carbide like tantalum carbide (TaC) acts as a multifunctional catalyst support for the DRM reaction, including light-harvesting properties for saving energy operation as well as an anticoking property for long-term stability. Nickel nanoparticles loaded on tantalum carbide (Ni/TaC) are prepared by impregnation and reductive hydrogen treatment. TaC particles act as a light-harvesting support to promote the DRM reaction by photon irradiation through plasmonic photothermal energy conversion in TaC. Furthermore, Ni/TaC exhibits an excellent long-term anticoking property, as compared to Ni loaded on conventional metal oxide supports such as Al₂O₃ or Ta₂O₅. According to the sole gas condition’s experiment, and secondary ion mass spectroscopy, the oxy-carbide layer near the interface between TaC and Ni plays an essential role in imparting the efficient anticoking property of Ni/TaC.

Methane (CH₄) has recently become an attractive energy resource, since shale gas has been found to be stored as an abundant natural resource ideal for practical use. However, its combustion emits carbon dioxide (CO₂), which causes global warming. Thus, the need for technologies that allow CO₂ capturing and its utilization are urgent for sustainable energy and environmental management.[1] Among various CO₂ utilization methods, dry reforming of methane (DRM) is one of the most attractive chemical reactions, since it converts global-warming gases into valuable syngas including hydrogen (H₂) and carbon monoxide (CO) as follows

\[
\text{CH}_4 + \text{CO}_2 = 2\text{H}_2 + 2\text{CO} \quad \Delta H_{\text{drxn}} = 247 \text{ kJ/mol}
\]

(1)

However, DRM is an endothermic reaction, thus requiring a high operating temperature, more than 1073 K, to achieve an efficient conversion or yield.[3] Furthermore, intermediate carbon is deposited onto the catalyst during the DRM reaction, so-called “coking,” which deteriorates catalytic activity.[4] From a practical point of view, nickel (Ni)[5] or cobalt (Co) catalysts are preferable promoters compared to noble metal catalysts,[6] but their catalytic activities and anticoking properties for the DRM reaction are limited. Besides the development of metal catalysts, various catalysis supporting materials including metal oxides have been studied to solve the coking problem. For example, metal oxides consisting of alkaline-earth elements such as magnesium oxide (MgO) were reported to suppress coking due to their strong CO₂ adsorption property.[7] Also, cerium oxide (CeO₂) was studied as an anticoking catalysis support, owing to its efficient redox property at the interface between the metal catalyst and metal oxide.[8]

To lower the operating temperature of DRM, high-quality photon energy can potentially assist the reaction using bandgap excitation of semiconductor photocatalysts,[9] mid-gap excitation of defective TiO₂,[10] and hot carrier generation in noble metal nanoparticles.[11] In addition to these techniques, our group recently reported that tantalum carbide (TaC) promoted the DRM reaction involving a cobalt catalyst by using photon energy on the basis of photothermal conversion induced by surface-localized plasmon resonance (SLPR) in TaC.[12] Nagao and co-workers investigated the plasmonic photothermal effect in various metal carbides and metal nitrides including TiC, ZrC, HfC, TaC, WC, TiN, ZrN, HfN, TaN, and WN by their theoretical approach.[13] Then, the absorption efficiency (Q_{abs}) of TaC was broadly ranged in visible light region,
and its integral $Q_{abs}$ value was higher than that of plasmonic silver (Ag) metal. This unique feature of TaC is owing to its strong and broad resonance, which makes it as a good sunlight harvester.

Herein, we have focused on a metal carbide that can be used as an anticoking catalysis support, as well as for its light-harvesting property. Nickel nanoparticles loaded on tantalum carbide (Ni/TaC) were prepared and their catalytic properties were compared with those loaded on alumina and tantalum oxide (Ni/Al$_2$O$_3$ and Ni/Ta$_2$O$_5$) supports. In this study, we discuss anticoking properties of these catalysts with respect to their interface chemical structure between Ni particles and support materials.

Commercial TaC, γ-Al$_2$O$_3$, and Ta$_2$O$_5$ powders were used as catalyst supports. Ni nanoparticles were loaded on these supports by impregnation in aqueous nickel nitrate solution and subsequent annealing treatment under hydrogen (H$_2$) flow. Detailed experimental procedures are described in the Supporting Information.

Figure 1 shows the characterization results of Ni/TaC particles. The X-ray diffraction (XRD) pattern indicates the formation of crystalline metal Ni in addition to the strong diffraction peaks of TaC. According to the scanning electron microscope (SEM) image, pristine TaC particles exhibited smooth surface (Figure 1b), whereas small particles, less than 100 nm, appeared in Ni/TaC (Figure 1c). The transmission electron microscope (TEM) image revealed that the Ni nanoparticle with the size about 50 nm was attached onto TaC support (Figure 1d). The same structural analyses were conducted for Ni/Al$_2$O$_3$ and Ni/Ta$_2$O$_5$ and shown in Figures S1 and S2 in the Supporting Information, and Ni nanoparticles were successfully loaded onto these catalyst supports. X-ray photoelectron spectroscopy (XPS) analysis also indicated that the chemical state of Ni nanoparticles was identical on various support materials (Figure S8b, Supporting Information).

A catalytic test for the DRM reaction was performed, using a fixed bed reactor under flow of 1% of CH$_4$ and CO$_2$ mixture in argon (Ar) balance gas, where photons can be irradiated onto catalyst surface through a quartz window (Figure S3, Supporting Information). Figure 2 shows the H$_2$ and CO yields at 773 K under light-on or light-off conditions. H$_2$ production yield was relatively less than that of CO generation over all of the catalysts because of reverse water gas shift reaction. The H$_2$ production yield of Ni/Al$_2$O$_3$ under dark condition was higher than the other catalysts, because its surface area (117.6 m$^2$ g$^{-1}$) was much higher than that of Ni/TaC (1.0 m$^2$ g$^{-1}$). It is noted that the light irradiation effect is the most significant in Ni/TaC among these catalysts. Panel (d) in Figure 2 shows UV–visible absorption spectra of these catalysts and spectrum of a xenon light source, which is close to the solar light spectrum. Ni/TaC has strong visible light absorption, which overlapped with the light irradiation. In this study, the photon-driven DRM reaction is not simply explained by the bandgap excitation of catalysis supports, since both Al$_2$O$_3$ and Ta$_2$O$_5$ are ultra-widegap semiconductors while TaC is a conductive material.[14] Hot carriers generation in Ni nanoparticles is not dominant for this catalysis reaction, since Ni nanoparticles are identically loaded onto these support materials as shown in the Supporting Information (Figures S1 and S2, Supporting Information). According to the previous studies, some of the metal carbides can be excited through SLPR, and the visible light absorption in TaC is superior to those in early-d-metal carbides such as TiC, ZrC, HfC, or WC.[13] Strong visible light absorption in Ni/TaC in this study...
is due to SLPR of TaC particles. The previous report indicated that the electric field near TaC involves a dipolar distribution and the temperature is considerably increased due to the SLPR excitation. These results indicate that TaC functioned as a light-harvesting catalysis support for the DRM reaction. We have conducted the catalysis test under the specific diluted gas condition. However, our system uses photothermal effect, thus the catalytic behavior under high reactant pressures most likely depends on thermodynamical equilibrium, i.e., higher partial pressure causes a lower conversion and/or yield of DRM reaction.

Next, we evaluated the catalyst durability for the DRM reaction in the same reactor. Figure 3a shows the time course of CH₄ conversion using Ni catalysts on various catalyst supports for 24 h under dark condition. CH₄ conversion on Ni/Al₂O₃ was drastically decreased after 500 min catalysis running, and the flow line of the reactor was plugged by coking. The DRM conversion activity in the presence of Ni/Ta₂O₅ was lower than that of the other catalysts. Interestingly, Ni/TaC exhibited stable DRM conversion activity. Similar trends were seen for CO₂ conversion as well as H₂ and CO production yields (Figure S4, Supporting Information). Figure 3b–d shows the SEM images of these catalysts after 24 h DRM reaction. It is noted that numerous carbon fibers appeared in either Ni/Al₂O₃ (Figure 3c) or Ni/Ta₂O₅ (Figure 3d), but fibrous carbon could not be seen in Ni/TaC (Figure 3b). Panel (e) in Figure 3 shows the amount of carbon of these catalysts after the DRM reaction analyzed by thermogravimetry and differential thermal analysis (TG-DTA). Coking was significantly suppressed in the Ni/TaC catalyst. The turnover number after 24 h DRM reaction of Ni/TaC was 119. We also investigated the catalyst durability of Ni/TaC under Xe light irradiation at 773 K for 50 h, and DRM conversion and yield were sustained for a long term (Figure S5, Supporting Information). Conversions and/or yields under light irradiation were similar to those under dark condition. In our system, the light absorber is metallic carbide unlike semiconductor photocatalysts, thus photon energy can be converted into thermal energy. Therefore, it is reasonable that the trend under dark condition was similar to that under light irradiation. The previous study suggested that the C–H dissociation in CH₄ is the rate-determining step as was widely accepted for DRM on Ni thermal catalysts. It is also known that coking proceeds after the cracking of the CH₄ molecule, thus the oxidation process of residual carbon is very important for an efficient anticoking function.

Here, we discuss the mass transport process of oxygen species in the Ni/TaC catalyst under the DRM reaction. First, we evaluated the catalytic activity under sole CH₄ or CO₂ conditions and analyzed the change of the oxygen amount in the catalysts by energy dispersive X-ray spectrometry (EDS), as shown in Figure 4. In this experiment, 1% CH₄ in Ar gas was flowed and the temperature was increased from room temperature (295 K) to 973 K. After that, EDS analysis was performed, then the catalyst was re-introduced into a reactor for the test under CO₂ gas without CH₄ condition. Regarding the Ni/TaC catalyst under sole CH₄ condition (Figure 4a), H₂ generation was about twice of the CO concentration, indicating these products originated from CH₄. Interestingly, CO was produced even under sole CH₄ condition, where no oxygen species were introduced in the gas phase. The chemical composition of the oxygen/tantalum (O/Ta) ratio was also investigated by EDS before and after CH₄ flow condition plotted as red circles in Figure 4a. The
O/Ta ratio before the test was 0.8, which decreased to 0.3 after sole CH$_4$ treatment. These results strongly imply that oxygen in the produced CO molecules originated from some oxygen species in the Ni/TaC catalyst. When the catalyst was exposed under sole CO$_2$ condition, the O/Ta ratio was recovered to 0.45 and the produced CO was equivalent to CO$_2$ conversion. These oxygen amount changes in the Ni/TaC catalyst and the CO production trend were seen in neither Ni/Al$_2$O$_3$ (Figure 4b) nor Ni/Ta$_2$O$_5$ (Figure S6, Supporting Information). These results strongly imply that oxygen species in Ni/TaC play an important role for its anticoking property. Previous studies also suggested that the oxygen species in molybdenum carbide participated in the redox reaction of DRM.\cite{17} In this study, we expected that some oxygen species would be formed at the interface between Ni and TaC, since the catalyst was prepared by an H$_2$ reduction treatment of amorphous nickel oxide nanoparticles, where oxygen species in these nanoparticles would partially oxidize TaC near their interface, as speculated in Figure S7a in the Supporting Information.

We investigated the interface structure between Ni and TaC by secondary ion mass spectrometry (SIMS) using the thin film model of the catalyst structure. The thin film of NiO was coated on a bulk TaC pellet by a DC magnetron sputtering with the thickness of 50 nm, which was close to the particles size of Ni as shown in Figures 1d or 3b. The NiO film on the TaC substrate was annealed under the same H$_2$ flow condition with particle preparation. XRD patterns of this film before and after H$_2$ treatment, shown in Figure S7b in the Supporting Information, indicate that the metallic Ni film was successfully coated on a TaC pellet. Figure 4c shows the depth profile of this film for each mass fragment by SIMS analysis. The blue line shows the profile of the Ta$_2$O$_5$ fragment in a bare TaC pellet as a control.

Figure 3. Durability test under DRM condition at 973 K. a) Change in CH$_4$ conversion of Ni catalysts on various support materials. SEM images after the DRM reaction of b) Ni/TaC, c) Ni/Al$_2$O$_3$, d) Ni/Ta$_2$O$_5$. Panel e) demonstrates carbon amount of these samples after the DRM reaction analyzed by TC-DTA.
group. By comparing the fragment profile of Ta$_2$O$_5$ in the Ni/TaC film (red line) with that in the pristine TaC film (blue line), the oxygen species were found to diffuse deeper from the surface in the Ni/TaC film sample. The black line shows the profile of the metal Ni fragment, and it ended at the sputtering time of 180 s, corresponding to its thickness of 50 nm. These results revealed that oxygen species were diffused into the TaC side. These oxygen species would be formed during the annealing treatment under H$_2$ to reduce nickel oxide. These oxy-carbide species near the interface would play an important role in the efficient and stable DRM reaction reported in this study.

Although oxygen atoms in metal oxides would be more abundant than those in TaC, Al$_2$O$_3$ and Ta$_2$O$_5$ supports did not contribute to their anticoking property. We suppose that the chemical state of oxygen species at the interfacial oxy-carbide in the Ni/TaC catalyst is different from those in densely packed metal oxides. Therefore, we conducted the X-ray photoelectron spectroscopy analysis on Ni/TaC and Ni/Ta$_2$O$_5$ samples to discuss their oxygen ions states (Figure S8, Supporting Information). The O-1s peak of Ni/TaC was shifted toward higher binding energy as compared to that of Ta$_2$O$_5$. Previous studies also reported the similar chemical shift of the O-1s peak in defective metal oxides. These oxygen defects are known to be active sites for the reduction of CO$_2$ or nitro-compounds. According to our XPS analysis on the Ta-4f core level (Figure S8c, Supporting Information), the Ni/TaC catalyst contains Ta$^{4+}$ species and Ta−C bonding after sole CH$_4$ gas exposure condition. Also, the mass signal for the TaO$_2$ fragment was detected in Ni/TaC by SIMS analysis in addition to that of the Ta$_2$O$_5$ fragment. These Ta$^{5+}$ species would be formed by the release of oxygen ions from the oxy-carbide layer to CH$_4$, then residual carbon species were formed near the interface of the catalyst. Figure 4d shows the schematic diagram to depict the reaction scheme of the present Ni/TaC catalyst. Oxygen species at the interfacial oxy-carbide layer (O$_{in}$) act as a redox mediator for CO$_2$ reduction into CO (CO$_2$ $\rightarrow$ CO + O$_{in}$) and CH$_4$ oxidation (CH$_4$ + O$_{in}$ $\rightarrow$ 2H$_2$ + CO). CH$_4$ oxidation and CO$_2$ reduction would be balanced on our Ni/TaC; thus, the long-term efficiency of the DRM reaction was sustained, as shown in Figure 3 and Figure S5 in the Supporting Information. A similar redox cycle for the DRM reaction was reported in the cerium and/or lanthanum oxide support.

In conclusion, the TaC catalysis support is multifunctional due to its light-harvesting property for saving energy operation as well as an anticoking property for long-term stability of CH$_4$ conversion reaction. The light-harvesting property is driven by the SLPR in TaC under visible light irradiation. The anticoking property is imparted to Ni/TaC by the interfacial oxygen species between the Ni catalyst and TaC support. The interfacial oxy-carbide layer in TaC act as a redox mediator for CO$_2$ reduction and CH$_4$ oxidation, thus the residual carbon atoms were efficiently oxidized into CO in the Ni/TaC catalyst. The findings of this study demonstrate that metal carbide can be used as an efficient catalyst support for not only dry reforming but also for partial oxidation or steam reforming of CH$_4$ reactions.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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[1] B. Li, Y. Duan, D. Luebke, B. Morreale, Appl. Energy 2013, 102, 1439.
[2] a) C. B. Roberts, N. O. Elbashir, Fuel Process. Technol. 2003, 83, 1; b) M. Stelmachowski, L. Nowicki, Appl. Energy 2003, 74, 85.
[3] a) W.-C. Chung, M.-B. Chang, Renewable Sustainable Energy Rev. 2016, 62, 13; b) D. Pakhare, J. Spivey, Chem. Soc. Rev. 2014, 43, 7813.
[4] O. Muraza, A. Galadima, Int. J. Energy Res. 2015, 39, 1196.
[5] Z. Bian, S. Das, M. H. Wai, P. Hongmanorom, S. Kawi, ChemPhysChem 2017, 18, 3117.
[6] a) S. Kawi, Y. Kathiraser, J. Ni, U. Oemar, Z. Li, E. T. Saw, ChemSusChem 2015, 8, 3556; b) S. Li, J. Gong, Chem. Soc. Rev. 2014, 43, 7245; c) S. De, J. Zhang, R. Luque, N. Yan, Energy Environ. Sci. 2016, 9, 3314.
[7] a) F. Meshkani, M. Rezaei, Catal. Commun. 2011, 12, 1046; b) M.-S. Fan, A. Z. Abdullah, S. Bhatia, Appl. Catal., B 2010, 100, 365.
[8] a) S. Das, J. Ashok, Z. Bian, N. Dewangan, M. H. Wai, Y. Du, A. Borgna, K. Hidajat, S. Kawi, Appl. Catal., B 2018, 230, 220; b) N. Laosiripojana, S. Assabumrungrat, Appl. Catal., B 2005, 60, 107; c) Z. Liu, P. Lustemberg, R. A. Gutiérrez, J. J. Carey, R. M. Palomino, M. Vorokhta, D. C. Griner, P. J. Ramirez, V. Matolin, M. Nolan, M. V. Ganduglia-Pirovano, S. D. Senanayake, J. A. Rodriguez, Angew. Chem., Int. Ed. 2017, 56, 13041.
[9] a) L. Yuliati, H. Itoh, H. Yoshida, Chem. Phys. Lett. 2008, 452, 178; b) S. Wibowo, A. Yamaguchi, S. Shoji, T. Fujita, H. Abe, M. Miyauchi, Chem. Lett. 2018, 47, 935.
[10] B. Han, W. Wei, L. Chang, P. Cheng, Y. H. Hu, ACS Catal. 2016, 6, 494.
[11] H. Song, X. Meng, Z.-j. Wang, Z. Wang, H. Chen, Y. Weng, F. Ichihara, M. Oshikiri, T. Kako, J. Ye, ACS Catal. 2018, 8, 7556.
[12] O. Anjaneyulu, K. Takeda, S. Ishii, S. Ueda, T. Nagao, P. Xiaobo, T. Fujita, M. Miyauchi, H. Abe, Mater. Chem. Front. 2018, 2, 580.
[13] M. Kumar, N. Umezawa, S. Ishii, T. Nagao, ACS Photonics 2016, 3, 43.
[14] T. Jang, L. M. Porter, G. W. M. Rutsch, B. Odekirk, Appl. Phys. Lett. 1999, 75, 3956.
[15] S.-G. Wang, X.-Y. Liao, J. Hu, D.-B. Cao, Y.-W. Li, J. Wang, H. Jiao, Surf. Sci. 2007, 601, 1271.
[16] S. Wang, G. Q. Lu, G. J. Millar, Energy Fuels 1996, 10, 896.
[17] a) A. Zhang, A. Zhu, B. Chen, S. Zhang, C. Au, C. Shi, Catal. Commun. 2011, 12, 803; b) C. Shi, A. Zhang, X. Li, S. Zhang, A. Zhu, Y. Ma, C. Au, Appl. Catal., A 2012, 431–432, 164.
[18] a) S.-J. Jeon, J.-W. Chang, K.-S. Choi, J. P. Kar, T.-I. Lee, J.-M. Myoung, Mater. Sci. Semicond. Process. 2010, 13, 320; b) H. Tan, Z. Wang, W.-b. Zhu, E. N. Coker, B. Li, M. Zheng, W. Yu, H. Fan, Z. Sun, ACS Appl. Mater. Interfaces 2014, 6, 19184.
[19] a) B. Chen, Y. Ma, L. Ding, L. Xu, Z. Wu, Q. Yuan, W. Huang, J. Phys. Chem. C 2013, 117, 5800; b) Y. Su, J. Lang, L. Li, K. Guan, C. Du, L. Peng, D. Han, X. Wang, J. Am. Chem. Soc. 2013, 135, 11433; c) A. L. Sauvet, J. Foulquier, F. Gaillard, M. Primet, J. Catal. 2002, 209, 25.
[20] V. A. Tsipouriari, X. E. Verykios, Catal. Today 2001, 64, 83.