

바나듐 탄화물 촉매를 이용한 수소생성용 암모니아 분해반응

김정수 · 최성신 · 최정길[†]

한남대학교 화학공학과

NH₃ Decomposition Reaction for Hydrogen Formation Using Vanadium Carbide Catalysts

JUNG-SU KIM, SEONG-SHIN CHOI, JEONG-GIL CHOI[†]

Department of Chemical Engineering, Hannam University, 1646 Yuseong-daero, Yuseong-gu, Daejeon 34054, Korea

[†]Corresponding author :
father8318@naver.com

Received 5 December, 2019
Revised 27 December, 2020
Accepted 28 February, 2020

Abstract >> The synthesis and catalytic activities over vanadium carbides were examined for ammonia decomposition reaction to produce the hydrogen. In particular, the comparison of vanadium nitrides were made on the ammonia decomposition reaction. The experimental data exhibited that BET surface areas ranged from 5.2 m²/g to 25.6 m²/g and oxygen uptake values varied from 3.8 μmol/g to 31.3 μmol/g. It is general that vanadium carbides (VC) were observed to be superior to vanadium nitrides for ammonia decomposition reaction. The primary reason for these differences were thought to be related to the extent of electronegativity between these materials. Most of vanadium carbide crystallites were exceeded by Pt/C crystallite. We assumed that the activities for vanadium carbide crystallites (VC) were comparable to or even higher than that determined for the Pt/C crystallite.

Key words : Vanadium metal carbide crystallites(바나듐 탄화물 결정입자), Ammonia decomposition reactivity(암모니아 분해반응), BET surface area (BET 표면적), Oxygen uptake(산소흡착량)

1. Introduction

Recently, several noble metals including Pt have been increasing in price due to the limited amount of reserves. Based on this background, many scientists have been attempting to find out the substitutes for Pt-based materials. Although it was reported that

transition metal carbide and nitride crystallites are some candidates for that purpose¹⁻⁶⁾, some of transition metal carbides crystallites (VC, MoC, WC) have been reported to contain similar surface and electronic properties to noble metal materials. For example, molybdenum carbide crystallites were reported to be used in the oxidation and dehydrogen-

ation reactions⁷⁻⁸⁾.

And tungsten carbides were also believed to contain some of similar characteristics to Pt-based materials. Another fascinating feature of some of transition metal carbide crystallites is that they can be produced with high surface areas. General preparation methods have given low surface area transition metal carbide crystallites. It has been demonstrated that high surface area transition metal carbide crystallites can be prepared through temperature-programmed reduction of molybdenum oxide⁹⁾.

This study examines the effect of synthesis parameters on the structural properties, including chemisorption uptake capacity of transition metal carbide crystallites, and evaluating the reactivity of ammonia decomposition. For this, the three experimental variables examined includes heating rates, molar hourly space velocity (MHSV), and gas composition. Here, the effects of synthesis conditions on the BET surface area and oxygen chemisorption uptake were given. Finally, in order to evaluate the reactivity of transition metal carbide crystallites the measurements of ammonia decomposition reaction were also utilized.

2. Experimental

2.1 Preparation of materials

The original material of vanadium oxide was obtained from Alpha chemicals at a purity of 99.99%. In order to prepare the vanadium metal carbide crystallites, the reactor used were made of a quartz tube with a cooling water jacket.

We have synthesized the eight different vanadium carbide crystallites based on the general statistical method as shown in Table 1. These vanadium carbide materials were prepared to scrutinize the influ-

ence of the molar hourly space velocity, the heating rate, and the reaction gas composition on the synthesis of vanadium carbide crystallites.

In this case, MHSV is the ratio of the methane molar flow rate to the moles of corresponding transition metal oxides (here, vanadium oxides in this study).

The experimental procedures are as follows. First of all, the furnace was heated to 1,073 K in 90 minutes. And then, it was raised to 1,313 K and was held for 1 hour. After this heating, the reactor was then cooled rapidly by removing it from the furnace. When it reached room temperature, the gas was switched to He for 30 minutes, then to 1% O₂/He for a 2 hour passivation period. The vanadium carbide crystallite was then collected and characterized. The other transition metal nitrides (VN) were also prepared using the similar methods.

2.2 Materials characterization

A Quantasorb[®] machine has been used to measure of BET surface areas. And then, the attenuation setting of the Quantasorb[®] machine was used to give a peak height of approximately 60-90% of full

Table 1. Preparation conditions of VCs

Sample	Heating rate (K/h)	H ₂ /CH ₄ ratio	MHSV CH ₄ (h ⁻¹)
VC-1	80	1.04	60
VC-2	40	1.04	60
VC-3	80	0	60
VC-4	40	0	60
VC-5	80	1.04	30
VC-6	40	1.04	30
VC-7	80	0	30
VC-8	40	0	30
VN	80	1.04	60

MHSV, molar hourly space velocity.

scale. A peak height and count were determined by the Quantasorb[®] machine. Using these procedures, the peak height and the count were determined. Finally, the catalyst sample was removed from the machine and weighed.

We have also performed the oxygen uptake experiment by using the same Quantasorb[®] machine. These O₂ uptake experiments were then carried out at 351 K. The Quantasorb[®] machine attenuation was set at 2 and 0.5 cc injections of 9.98%, then O₂/He gas were made. The injections were repeated until the machine exhibited a constant count for about 5 straight injections. And then, we removed the sample from the machine and weighed.

2.3 Activity measurements

Usually, we have loaded 0.2 g of vanadium carbide crystallites in the reactor to measure the reactivities of ammonia decomposition reaction. The reduction of the given sample was performed using H₂ throughout the course of temperature rise, starting from room temperature to 673 K at a rate of 0.033 K/s. After this, it was held at 673 K for 14 hours before being cooled to the reaction temperature before measuring reactivity. In most cases, the reactivities were obtained at temperatures between 623 and 823 K. We have analyzed the reactor effluent using an on-line gas chromatograph (SD6200) equipped with both flame ionization and thermal conductivity detectors. The products were separated with Porapak Q packed columns (80/100,8'x1/8", CRS) which was connected to a gas chromatography detector.

3. Results and discussion

3.1 Physicochemical properties of materials

In the present work, the eight vanadium carbides, vanadium nitride, and platinum supported on carbon have been synthesized for comparison. It is generally known that in the synthesis of transition metal carbide crystallites, the most important factor is the gas dispersion through the plug of solid material and heating rate. Therefore, we can prepare the materials with small crystallite size using large heating rates and low MHSV. These might be related to the fast temperature rise. If we want to prepare carbides which have larger crystallite sizes, the opposite trends must be considered. As shown in Table 1, our goal is to react the material before the gas penetration and saturation of solid reactant occurs at the same time.

Here, in this study we have synthesized, the vanadium carbide crystallites using vanadium oxide and CH₄ gas or methane-hydrogen mixture and their BET surface areas ranged from 5.2 m²/g to 29.9 m²/g. For the case of the vanadium carbide crystallites synthesized in pure CH₄, we have obtained the highest specific surface areas (29.9 m²/g) with the low heating rate of 30 K/h and high space velocity of 80 hr⁻¹.

As we can see the sorption properties in Table 2, the highest surface areas were observed for the vanadium carbides synthesized in an CH₄ gas only. The influence of greater heating rate on surface area is that the reaction rate increased, as the conversion of vanadium oxide to vanadium carbide crystallites is increased. There are several similarities in the preparation of transition metal carbide crystallites including titanium and niobium carbide crystallites and previously published by the other research group^{3,5,6}.

We can also see the sorption properties over vanadium carbide crystallites in Table 2. It is generally accepted that the oxygen uptake was taken as a measure of the number of potential active sites on the vanadium carbide crystallites. We can also apply these results for other transition metal carbides (WC and MoC). As the different vanadium carbide crystallites vary, the different values of oxygen uptake were obtained in this case.

These results implied that the vanadium carbide has a properties that the reactivities is totally dependent on the synthesis conditions. By the same token, in the case of vanadium carbides the sorption properties of BET surface areas and oxygen uptakes are strongly relying on preparation conditions. It is general that the oxygen site densities were determined from the O₂ uptakes and the BET surface areas. For the case of vanadium carbides, the O₂ site density averages and 18.3×10^7 O₂/m². Assuming a 1:1 V:O stoichiometry, surface coverages averaged ~16%. These values of site density and surface coverage for vanadium carbides are greater than those for tantalum and titanium carbides.

Table 2. Sorption properties and NH₃ decomposition conversion for various catalysts

Sample	Surface area (m ² /g)	Oxygen uptake ^a (μmol O ₂ /g)	Conversion (%)
VC-1	21.3	16.6	26
VC-2	12.4	12.5	17
VC-3	7.1	8.6	14
VC-4	5.2	9.1	19
VC-5	18.1	10.9	13
VC-6	9.5	9.8	12
VC-7	29.9	25.9	31
VC-8	25.4	23.1	24
VN	8.7	6.2	10
Pt/C	-	-	21

^aBased on O₂ uptake at 195 K.

Fig. 1 also shows that there is a linear relationship between the oxygen uptake and BET surface area of vanadium carbides.

This result suggests that oxygen was a nonselective adsorbate to the vanadium carbide crystallites. The linear relationship between oxygen uptake and BET surface area in vanadium carbide crystallites is similar to that in other transition metal crystallites¹⁰. We have considered that these kinds of findings are very important since the reaction properties of the transition metal carbide and nitride are related to their preparation conditions with the different sorption properties.

3.2 Catalytic properties of vanadium carbides

It has been shown that all of the vanadium carbide crystallites prepared in the present work were active for ammonia decomposition reaction. For the most of cases, the freshly prepared vanadium carbides exhibited the highest initial conversion. However, their activities were gradually decreased as times went by.

Here, as shown in Fig. 2, the NH₃ decomposition reaction rates for vanadium carbides were rapidly

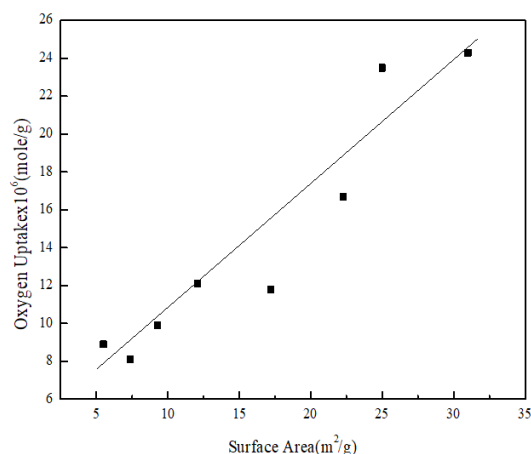


Fig. 1. Surface area and oxygen uptake for vanadium carbides

decreased to the steady-state activities and remained constant for several hours. Fig. 3 shows the influence of reaction temperature (at 600, 650, 750, 800, and 850 K) on the conversion. These results show clearly that the conversion increased with the increase of temperature. The maximum conversion was obtained at 700 K. However, no serious temperature effects were found after 750 K for vanadium carbide crystallites.

In Table 2, the steady state activities for all vanadium carbide crystallites were described. We can see that all of the vanadium carbide crystallites exhibited

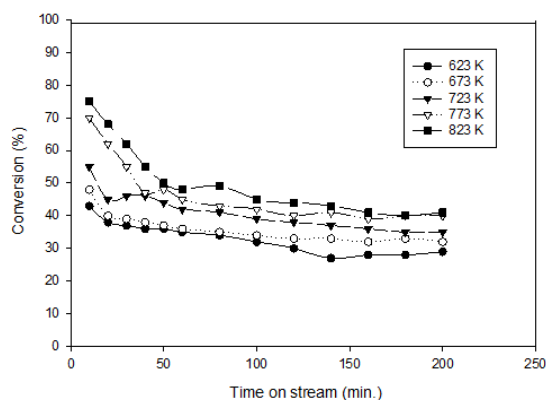


Fig. 2. NH_3 decomposition conversion vs. reaction temperature of VC

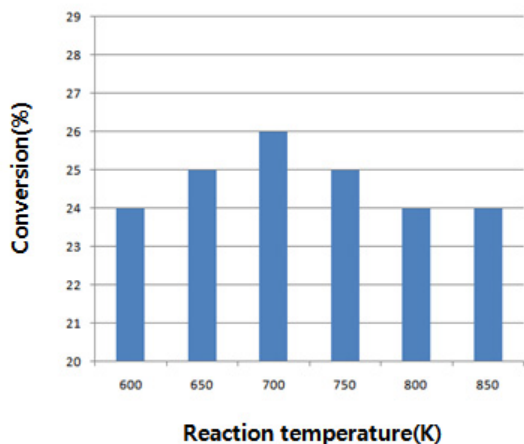


Fig. 3. NH_3 decomposition conversion vs. reaction temperature of VC

the linear relationship of surface area with reactivity of ammonia decomposition. Based on these results, it is believed that the surface area is linearly related to the reactive site of these vanadium carbide crystallites for ammonia decomposition.

These kinds of linear relationship between the surface area and the reactivity suggested the existence of structure sensitivity for the ammonia decomposition reaction in vanadium carbide crystallites.

In transition metal carbide crystallites, it was known that the concept of structure sensitivity frequently appeared in several catalytic reactions. Previous experimental results suggested that ammonia decomposition reaction was structure-sensitive by molybdenum and titanium carbide crystallites^{11,12}.

In the present study, amongst all the prepared vanadium carbide crystallites VC-7 had the highest steady state reactivity for NH_3 decomposition. From all of the synthesized vanadium carbides, the VC-7 crystallites was ~ 2.58 times more reactive than VC-6 which had the lowest activity. These results indicated that the reactive species in the VC-6 crystallites were different from that in the VC-7 crystallites. The similar results were observed that the molybdenum nitride crystallites which has high surface area exhibited the highest activity over pyridine hydro-

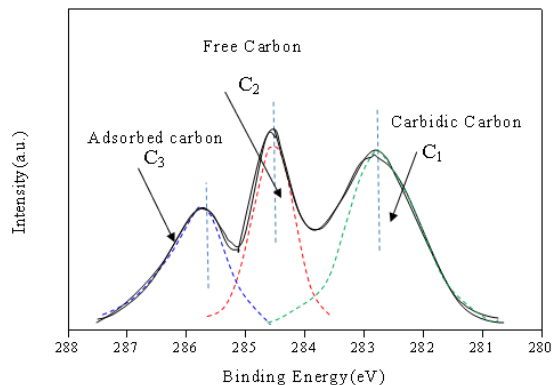


Fig. 4. XPS pictures of carbon species in the vanadium carbides

denitrogenation¹³⁾.

Fig. 4 shows the XPS pictures of carbon species in the vanadium carbides. The C1 peak of carbidic carbon in Fig. 4 indicates that vanadium carbides prepared from vanadium oxides. The other two carbon peaks of C2 and C3 shows the free carbon and adsorbed carbon in the vanadium carbides surface, respectively. Therefore, depending upon the kinds of carbidic carbons, the final ammonia decomposition reactivity would be different.

Fig. 5 shows the XRD results of vanadium oxide (Fig. 4[a]) and carbides (Fig. 4[b]), respectively. Similarly, it is clear that vanadium oxides and carbides exhibit the different pictures of XRD, indicating the differences of bulk structure in these materials.

In summary, it is noted that for vanadium oxides and carbides, these kinds of physico-chemical properties should be related to the final reactivities for NH_3 decomposition.

3.3 Comparison between vanadium carbides and nitrides

The reactivities of all of the vanadium carbides are more active than that of vanadium nitrides as shown in Table 2. The reason for these differences might be ascribed to the electronic and structural

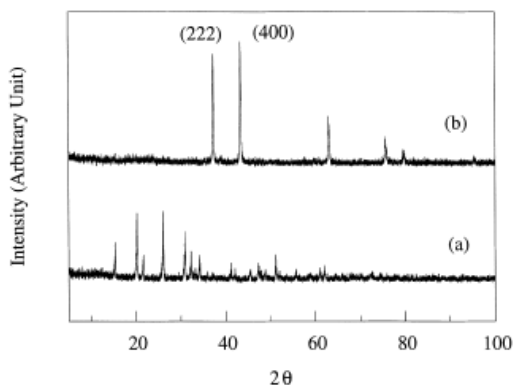


Fig. 5. XRD results for (a) vanadium oxides and (b) carbides

differences. Because of the differences of electronegativities, it was assumed that the vanadium carbides contained a different electron character at the surface from the vanadium nitrides. Since the nitrogen is more electronegative than carbon, vanadium carbides should be less acidic than vanadium nitrides. For ammonia decomposition reaction, the ammonia as a base adsorb more strongly on nitrides than on carbides. Based on this scenario, this difference might be allowing vanadium carbides to contain the higher activities. And also, as shown in Fig. 5, the crystallographic structure of vanadium carbides is different from that of vanadium oxides and nitrides. This structural difference also appeared to be involved in reactivity difference.

By the way, we also compared the reactivity of Pt/C with those of vanadium carbides. In the current study, the steady state reaction activities for vanadium carbides were comparable to or even higher than that of the Pt/C sample. According to these results, it was assumed that the characteristics of reactive sites in the vanadium carbide crystallites were similar to those in the group 8-10 metal based materials¹⁴⁾. Moreover, it is suggested based on these results that the vanadium carbide crystallites¹⁵⁻¹⁷⁾ can be utilized for various areas including many petroleum industries as the substitutes of the precious metal crystallites including Pt and Pd.

4. Conclusions

It was concluded that the vanadium carbide crystallites have been synthesized using all eight different preparation conditions. We found that the surface area of prepared vanadium carbide crystallites was increased by temperature programmed reduction of vanadium oxide. It was observed that the vanadium carbide crystallites were reactive for ammonia

decomposition reaction. In general, the vanadium carbide crystallites were exceeded by Pt/C sample. However, for ammonia decomposition reaction, the steady state reaction activities for vanadium carbide crystallites were comparable to or even higher than that determined for the Pt/C sample. According to all of these results, we have suggested that the vanadium carbides crystallites could be utilized for the precious metal materials in the petroleum fields.

Acknowledgement

This paper has been supported by 2019 Hannam University Research Fund (starting from April 1, 2019 through March 31, 2020).

References

1. J. G. Choi, "Influence of surface composition on HDN activities of molybdenum nitrides", *J. Ind. Eng. Chem.*, Vol. 8, No. 1, 2002, pp. 1-11. Retrieved from <https://www.cheric.or.kr/research/tech/periodicals/view.php?seq=362649>.
2. D. J. Sajkowski and S. T. Oyama, "Symposium on the chemistry of W/Mo catalysis", *Prep. Petrol. Chem. Div.*, 199th ACS Nat. Meeting, Vol. 35, No. 2, 1990, pp. 233.
3. N. I. Il'chenko, "Oxidative catalysis on transition-metal carbides", *Kinetics and Catalysis*, Vol. 18, No. 1, 1977, pp. 153-163, doi: <https://doi.org/10.6111/JKCGCT.2010.20.2.074>.
4. L. leclercq, K. Imura, S. Yoshida, T. Barbee, and M. Boudart, "Preparation of catalysts II", Elsevier, USA, 1978, pp. 627.
5. L. Volpe and M. Boudart, "Ammonia synthesis on molybdenum nitrides", *J. Phys. Chem.*, Vol. 90, 2015, pp. 4874, doi: <https://doi.org/10.1021/j100411a031>.
6. R. B. Levy and M. Boudart, "Platinum-like behavior of tungsten carbide in surface catalysis", *Science*, Vol. 181, No. 4099, 2013, pp. 547-549, doi: <https://doi.org/10.1126/science.181.4099.547>.
7. L. H. Bennett, J. R. Cuthill, A. J. McAlister, N. E. Erickson, and R. E. Watson, "Electronic structure and catalytic behavior of tungsten carbide", *Science*, Vol. 184, No. 4136, 2014, pp. 563-565, doi: <https://doi.org/10.1126/science.184.4136.563>.
8. J. G. Choi, J. Ha, and J. W. Hong, "Synthesis and catalytic properties of vanadium interstitial compounds", *Applied Catalysis*, Vol. 168, No. 1, 1998, pp. 47-56, doi: [https://doi.org/10.1016/S0926-860X\(97\)00332-3](https://doi.org/10.1016/S0926-860X(97)00332-3).
9. J. H. Sinfelt and D. J. C. Yates, "Effect of carburizing on the hydrogenolysis activity of molybdenum", *Nature Phys. Sci.*, Vol. 229, 1971, pp. 27-28, doi: <https://doi.org/10.1038/physci229027b0>.
10. P. A. Armstrong, A. T. Bell, and J. A. Reimer, "Comparison of the dynamics and orientation of chemisorbed benzene and pyridine on molybdenum nitride (γ -Mo₂N)", *J. Phys. Chem.*, Vol. 97, No. 9, 2013, pp. 1952-1960, doi: <https://doi.org/10.1021/j100111a037>.
11. L. E. Toth, "Transition metal carbides and nitrides", Academic Press, USA, 1971, pp. 234.
12. J. B. Claridge, A. P. E. York, A. J. Brungs, and M. L. H. Green, "Study of the temperature-programmed reaction synthesis of early transition metal carbide and nitride catalyst materials from oxide precursors", *Chem. Mater.*, Vol. 12, No. 1, 2000, pp. 132-142, doi: <https://doi.org/10.1021/cm9911060>.
13. J. G. Choi, "Ammonia decomposition over titanium carbides", *J. Korean Crystal Growth and Crystal Technology*, Vol. 22, No. 6, 2012, pp. 269-273, doi: <https://doi.org/10.6111/JKCGCT.2012.22.6.269>.
14. J. G. Choi, "Preparation and characterization over niobium carbide crystallites", *J. Korean Crystal Growth and Crystal Technology*, Vol. 19, No. 3, 2009, pp. 125-129. Retrieved from <http://www.koreascience.or.kr/article/JAKO200922951806937.page>.
15. J. Yu, X. Gao, G. Chen, and X. Yuan, "Electrocatalytic performance of commercial vanadium carbide for oxygen reduction reaction", *Int. J. Hydrogen Energy*, Vol. 41, No. 7, 2016, pp. 4150-4158, doi: <https://doi.org/10.1016/j.ijhydene.2016.01.008>.
16. W. Fu, Y. Wang, H. Zhang, M. He, L. Fang, X. Yang, Z. Huang, J. Li, X. Gu, and Y. Wang, "Epitaxial growth of graphene on V₈C₇ nanomeshes for highly efficient and stable hydrogen evolution reaction", *J. Catal.*, Vol. 369, 2019, pp. 47-53, doi: <https://doi.org/10.1016/j.jcat.2018.10.033>.
17. L. Peng, J. Shen, L. Zhang, Y. Wang, R. Xiang, J. Li, L. Li, and Z. Wei, "Graphitized carbon-coated vanadium carbide nanoboscages modified by nickel with enhanced electrocatalytic activity for hydrogen evolution in both acid and alkaline solutions", *J. Mater. Chem. A Mater.*, Vol. 44, 2017, pp. 23028-23034, doi: <https://doi.org/10.1039/C7TA07275A>.