

전이금속 카바이드를 이용한 암모니아 분해 반응으로부터 수소생산

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Hydrogen Production from Ammonia Decomposition over Transition Metal Carbides

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Abstract >> The preparation and catalytic activities of various transition metal carbide crystallites (VC, MoC, WC) were examined in this study. In particular, the effect of different kinds of transition metal crystallites were scrutinized on the ammonia decomposition reaction. The experimental results showed that BET surface areas ranged from 8.3 m²/g to 36.3 m²/g and oxygen uptake values varied from 9.1 μmol/g to 25.4 μmol/g. Amongst prepared transition metal carbide crystallites, tungsten compounds (WC) were observed to be most active for ammonia decomposition reaction. The main reason for these results were considered to be related to the extent of electronegativity between these materials. Most of transition metal carbide crystallites were exceeded by Pt/C crystallite. However, the steady state reactivities for some of transition metal carbide crystallites (WC) were comparable to or even higher than that determined for the Pt/C crystallite.

Key words : Transition metal carbide crystallites(전이금속 탄화물 결정입자), BET surface area (BET 표면적), Oxygen uptake(산소흡착량), Ammonia decomposition reactivity(암모니아 분해 반응), Hydrogen production(수소생산)

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 tran-

sition metal carbide and nitride crystallites are some candidates for that purpose¹⁻¹⁰⁾, 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 oxidation¹¹⁾ and dehydrogenation reactions¹²⁾.

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 oxide⁴⁾.

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

We have used the reactor to prepare the transition metal carbide crystallites, which were made of a quartz tube with a cooling water jacket. The raw material of tungsten oxide was purchased from Alpha chemicals at a purity of 99.9985%.

Eight different transition metal carbide crystallites were synthesized according to the statistical method given in Table 1. These were prepared to examine the influence of the molar hourly space velocity, the heating rate, and the reaction gas composition on the synthesis of transition metal carbide crystallites.

Table 1. Synthesis conditions of catalysts

Sample	Heating rate (K/h)	H ₂ /CH ₄ ratio	MHSV CH ₄ (h ⁻¹)
WC-1	120	1.04	50
WC-2	60	1.04	50
WC-3	120	0	50
WC-4	60	0	50
WC-5	120	1.04	25
WC-6	60	1.04	25
WC-7	120	0	25
WC-8	60	0	25
VC	120	1.04	50
MoC	60	1.04	50

MHSV, molar hourly space velocity.

MHSV is the ratio of the CH₄ molar flow rate to the moles of corresponding transition metal oxides. For example, first glass wool was packed on the quartz frit in order to synthesize the tungsten carbide crystallites. Then, a measured amount of tungsten oxide was placed on top. The reactor was located in the furnace with air-tight seals on top and bottom to provide the gas inlet and outlet, respectively. Then, the gas flow was started. The furnace was heated to 1,073 K in 90 minutes. After heating, it was raised to 1,313 K and was held for 1 hour. 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 tungsten carbide crystallite was then collected and characterized. The other two transition metal carbides (VC and MoC) were also synthesized using the similar methods.

2.2 Materials characterization

We have utilized a Quantasorb[®] machine to measure of BET surface areas. Next, the attenuation of the Quantasorb[®] machine was set to give a peak height of approximately 60-90% of full scale. A peak height and count was then determined by the Quantasorb[®]

machine. Once again, a peak height and the count were determined. Finally, the catalyst sample was removed from the machine and weighed.

The oxygen uptake experiment was carried out using the Quantasorb[®] machine. The O₂ uptake experiment was then performed 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. The sample was then removed from the machine and weighed.

2.3 Activity measurements

Approximately, 0.2 g of transition metal carbide crystallites were loaded in the reactor to measure the reactivities of ammonia decomposition reaction. The sample was reduced using H₂ throughout the course of temperature rise, starting from room temperature to 673 K at a rate of 0.033 K/s. Then it was held at 673 K for 14 hours before being cooled to the reaction temperature before measuring reactivity. The reactivities were obtained at temperatures between 623 and 823 K. Reactor effluent was analyzed 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'×1/8", CRS) which was connected to a gas chromatography detector.

3. Results and Discussion

3.1 Physicochemical properties of materials

We have prepared eight tungsten carbides, vanadium carbide, and molybdenum carbide in this work. It appears that the most important trend in the synthesis of transition metal carbide crystallites is the gas

dispersion through the plug of solid material, particularly with slower heating rates. According to the principle of crystal growth, the solid crystallite growth proceeds simultaneously throughout the solid to smaller crystallite sizes while the gas is dispersed evenly through the reactor. In this case, if the gas is not fully dispersed, less crystallites begin and grow larger. Therefore, the materials with small crystallite size can be prepared using heating rates and low MHSV. This should be due to the fast temperature rise in order to overcome the crystallite growth trends. If the speed of temperature rising is enough, it will accelerate the reactions throughout the solid. Therefore, the reaction can spread starting from existing carbide. So as to synthesize carbides containing larger crystallite sizes, the opposite trends must be considered. Then, the aim would be to react the material before the gas penetration and saturation of solid reactant occurs.

We have synthesized, in the present study, the tungsten carbide crystallites using tungsten oxide and methane gas or methane-hydrogen mixture and their BET surface areas ranged from 9.3 m²/g to 36.3 m²/g. When the tungsten carbide crystallites were synthesized in pure CH₄, we have obtained the highest specific surface areas with the high heating rate of 120 K/h

Table 2. Surface properties of catalysts

Sample	Surface area (m ² /g)	Oxygen uptake (μmol O ₂ /g)	Site density* (m ⁻²)10 ⁻⁷	Surface coverage (%)
WC-1	32.3	19.4	17.4	18
WC-2	18.5	15.5	12.7	12
WC-3	11.3	11.6	9.8	9
WC-4	9.3	9.1	13.8	13
WC-5	21.8	14.6	15.8	14
WC-6	14.3	13.6	16.9	8
WC-7	36.3	25.4	22.8	23
WC-8	33.4	24.2	16.8	15
VC	8.3	8.6	9.3	8
MoC	12.4	10.3	11.3	9

*Based on O₂ uptake at 195 K.

and low space velocity of 25 hr^{-1} .

In the long run, we have produced the highest specific surface area tungsten carbide crystallites in pure CH_4 when the heating rate was 120 K/hr and the molar hourly space velocity was 25 hr^{-1} . As can be seen in Table 2, when the tungsten carbides were synthesized in an H_2/CH_4 mixture, the highest surface areas were observed when the heating rate and the MHSV were 120 K/hr and 25 hr^{-1} , respectively. It is believed that the effect of greater MHSV on specific surface area is due to the rapid removal of water vapor. Water vapor can trigger hydrothermal sintering which lowers the surface area¹⁻¹⁰. The effect of greater heating rate on surface area is that the reaction rate increased, as the conversion of tungsten oxide to tungsten carbide crystallites is increased. We have seen that similarities in the preparation of transition metal carbide crystallites including titanium and niobium carbide crystallites have been also found and previously published by the same group^{3,5,6}.

The sorption properties over tungsten carbide crystallites are seen in Table 2. Oxygen uptake was taken as a measure of the number of potential active sites on the tungsten carbide crystallites. These results could be also applied for other transition metal carbides (VC and MoC). Depending upon the different tungsten carbide crystallites, the different values of oxygen uptake were measured.

These results implied that the tungsten carbide has a potential of reactivity property as its property strongly depends on the synthesis conditions. As usual, oxygen site densities were determined from the O_2 uptakes and the BET surface areas. The O_2 site density averages and $16.7 \times 10^7 \text{ O}_2/\text{m}^2$. Assuming a 1:1 W:O stoichiometry, surface coverages averaged $\sim 14\%$. These values of site density and surface coverage for tungsten carbides are greater than those for vanadium and molybdenum carbides.

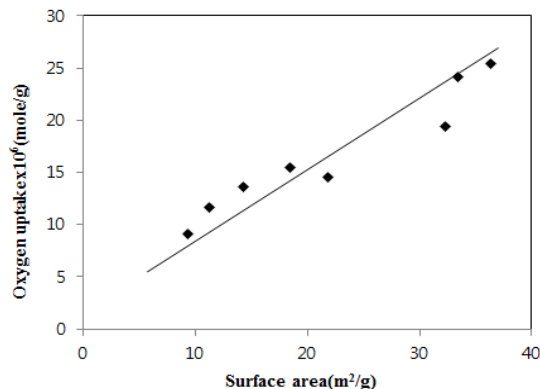


Fig. 1. Surface area and oxygen uptake for tungsten carbides

Fig. 1 shows that the oxygen uptake and BET surface area have a linear trend. This result suggests that oxygen was a nonselective adsorbate to the tungsten carbide crystallites. The linear relationship between oxygen uptake and BET surface area in tungsten carbide crystallites is similar to that in other transition metal crystallites⁴. These results indicated that for the same metal, tungsten-based carbide and nitride crystallites the capacity of adsorbate increases almost proportionally with the increase of surface area produced by insertion of carbon or nitrogen into the base metal of tungsten.

It is 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 with the high surface areas.

3.2 Catalytic properties of tungsten carbides

We have observed that all of the tungsten carbide crystallites synthesized in this study were active for ammonia decomposition reaction. The freshly prepared tungsten carbides exhibited the highest initial conversion, but gradually lost activity over time. Even though the clear graph is not shown in this article, the NH_3 decomposition reaction rates were decreased to

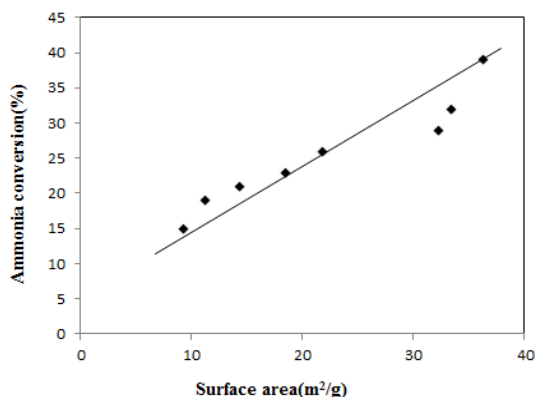


Fig. 2. Ammonia decomposition conversion as a function of surface area

Table 3. NH₃ decomposition conversion for various catalysts

Sample	Surface area (m ² /g)	Oxygen uptake (μmol O ₂ /g)	Coverion (%)
WC-1	32.3	19.4	29
WC-2	18.5	15.5	23
WC-3	11.3	11.6	19
WC-4	9.3	9.1	15
WC-5	21.8	14.6	26
WC-6	14.3	13.6	21
WC-7	36.3	25.4	39
WC-8	33.4	24.2	32
VC	8.3	8.6	11
MoC	12.4	10.3	14
Pt/C	-	-	28

*Based on O₂ uptake at 195 K.

the steady-state activities and remained constant for several hours. All of the tungsten carbide crystallites exhibited the linear relationship of surface area with reactivity of ammonia decomposition (Fig. 2).

In Table 3, we can see the steady state activities for all tungsten carbide crystallites. In the case of tungsten carbides, these results indicated that the surface area is linearly related to the reactive site of these crystallites for ammonia decomposition. Subsequently, these results suggested that the ammonia decomposition reaction was structure-sensitive for tungsten carbide crystallites. In the previous work, Choi and coworkers¹⁰⁾ reported that ammonia decomposition was

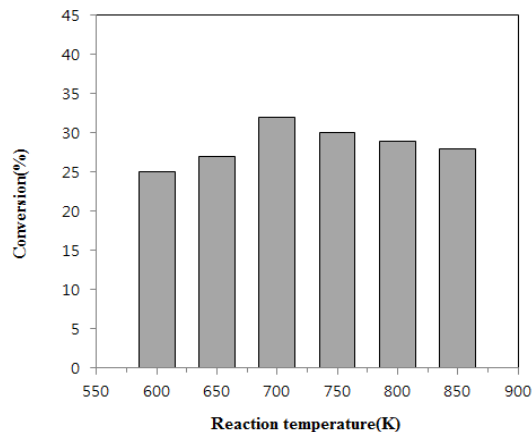


Fig. 3. Surface area and oxygen uptake for tungsten carbides

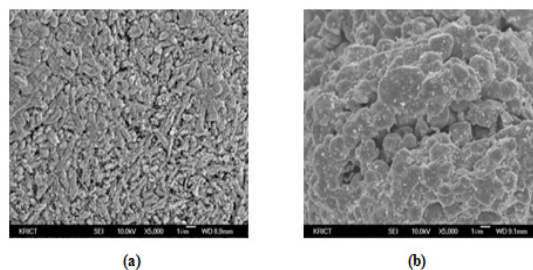


Fig. 4. SEM results for (a) fresh WC (×5,000) and (b) aged WC (×5,000)

structure-sensitive by vanadium and niobium carbide crystallites. Fig. 3 shows the influence of reaction temperature (at 600, 650, 750, 800, and 850 K) on the conversion, clearly indicating that the conversion increased with the increase of temperature. However, above 750 K no serious temperature effects were observed for tungsten carbide crystallites.

It can be seen that in the present study, from the tungsten carbide crystallites WC-7 had the highest steady state reactivity for NH₃ decomposition.

The WC-7 crystallites was ~2.6 times more reactive than WC-4, having the lowest activity. It is suggested that the reactive species in the WC-4 crystallites was different from that in the WC-7 crystallites. Similarly, Claridge et al.¹²⁾ observed that the molybdenum nitride crystallites which has high surface area exhibited the

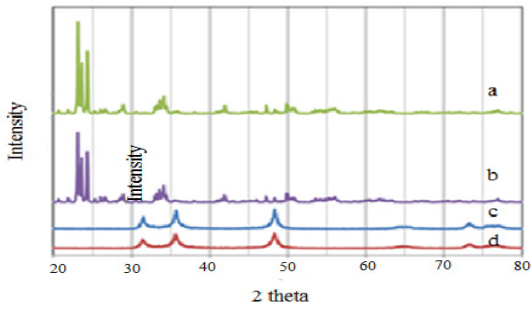


Fig. 5. XRD results for W oxides (a, b) and for W carbides (c, d)

highest activity over pyridine hydrodenitrogenation. Figs. 4 and 5 are also showing the SEM pictures of fresh (Fig. 4[a]) and aged (Fig. 4[b]) tungsten carbides, and XRD results of tungsten carbides (Fig. 5[c] and 5[d]) prepared from tungsten oxides (Fig. 5[a] and 5[b]). It is noted that these kinds of physicochemical properties of tungsten carbides should be related to the final reactivities for NH_3 decomposition.

3.3 Comparison between tungsten and other transition metal carbides

We have also compared the activities of tungsten carbide crystallites with vanadium and molybdenum carbides. It is generally seen that the activities of tungsten carbide crystallites are ~ 3 times higher than those of vanadium and molybdenum carbides. These results might be related to the difference in electronegativity between tungsten carbides ($\Delta=0.19$), and vanadium ($\Delta=0.92$) and molybdenum carbides ($\Delta=0.39$). It appeared that with the increase of the difference in electronegativity decreased the activities of ammonia decomposition.

By the way, the reactivity of Pt/C was obtained to be 28% and compared with other transition metal carbides. Although there are vanadium and molybdenum carbide crystallites that were exceeded by Pt/C sample, the steady state reaction activities for tungsten

carbides were comparable to or even higher than that of the Pt/C sample. Based on these results, we can figure out that the characteristics of reactive sites in the tungsten carbide crystallites were similar to those in the group 8-10 metal based materials. Moreover, it is suggested from these results that the tungsten carbide crystallites can be used for many petroleum industries as the substitutes of the precious metal crystallites.

4. Conclusions

We have synthesized the tungsten carbide crystallites using all eight preparation conditions. It is noted that the most important trend affecting the BET surface area in the synthesis of tungsten carbides is a combination of heating rate and space velocity. It is general that tungsten carbide crystallites produced under various synthesis conditions have relatively high surface areas when compared to other crystallites. The surface area of prepared tungsten carbide crystallites was increased by temperature programmed reduction of tungsten oxide in pure methane with a lower molar hourly space velocity and a higher heating rate. It was found that the tungsten carbide crystallites were reactive for ammonia decomposition reaction. Although vanadium and molybdenum carbide crystallites were exceeded by Pt/C sample, the steady state reaction activities for tungsten carbide crystallites were comparable to or even higher than that determined for the Pt/C sample. Based on these results, it is suggested that the tungsten carbides could be utilized for the precious metal materials.

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