

## Effects of experimental conditions on synthesis of titanium carbide crystallites

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**Abstract** The temperature-programmed reduction of titanium oxide ( $\text{TiO}_2$ ) with pure  $\text{CH}_4$  was used for the preparation of titanium carbide crystallites. The synthesized materials had the different surface areas, indicating that the structural properties of these materials were strong functions of two different heating rates and space velocity employed. The titanium carbide crystallites were active for  $\text{NH}_3$  decomposition. Since the reactivity varied with changes in the particle size, ammonia decomposition reactivity over the titanium carbides crystallites appeared to be related to the different active species. The reactivities of titanium carbide crystallites were two and three times lower than those of the vanadium and molybdenum carbide crystallites, respectively. These results suggested that the difference in activities might be related to the degree of electron transfer between metals and carbon.

**Key words** Titanium carbide crystallites, BET surface area, Oxygen uptake, Reactivity for ammonia decomposition

### 1. Introduction

It has been known that titanium carbide crystallites ( $\text{TiC}$ ) is one of the transition metal carbides which have been reported to be very active for reaction including hydrodenitrogenation [1, 2], CO hydrogenation [3], and  $\text{NH}_3$  synthesis [4]. Additionally, transition metal carbide crystallites such as W and Mo carbides crystallites, exhibited resemblances of platinum-based crystallites in the reactivities of dehydrogenation, hydrogenolysis and isomerization reactions [5-7]. For the case of transition metal carbide crystallites, the reactive properties are generally known to be controlled by their structure and stoichiometry near the surface. For example, Choi *et al.* [8] and Toth [9] have reported that the reactive properties of molybdenum and tungsten carbide crystallites varied with the amount of carbon present in the interstitial sites of the host metal lattice. Choi *et al.* [8] have showed that the pyridine HDN reactivities over the molybdenum carbide crystallites increased with increasing particle size, suggesting a structure sensitive reaction. From these results, they drew a conclusion that the surface stoichiometry was related to the particle size, producing the different reactivities. In the case of vanadium carbide crystallites and tantalum carbide crystallites which were reactive for ammonia decomposition, it was reported that the reactivity of these materials was explicitly related

to the amount of carbon at the surface [10, 11]. As shown in the above examples, it is very important to note that the reactive function of transition metal carbide crystallites could be possibly influenced by the stoichiometry near the surface. Furthermore, although transition metal carbide crystallites have a great possibility as promising materials, not many materials including titanium carbide crystallites have been studied, particularly for reactivity.

Based on the above background, here in the current paper the surface and bulk and reactive properties of titanium carbide crystallites were described. These carbide crystallites were prepared by the temperature-programmed reaction of titanium oxide precursor ( $\text{TiO}_2$ ) with  $\text{CH}_4$ . Characterization techniques including BET total surface area measurements, and oxygen chemisorption were employed to evaluate the sorptive properties of these materials. Besides the reactive properties of these materials for  $\text{NH}_3$  decomposition were evaluated, and compared to those of other transition metal carbide crystallites [10, 11].

### 2. Experimental

Titanium carbide crystallites used in this study were synthesized via the TPR (temperature-programmed reduction) of  $\text{TiO}_4$  (99.95 %, Junsei Chemical Co. Ltd) with pure  $\text{CH}_4$ . Different heating rates and molar hourly space velocities gave rise to the production of various kinds of titanium carbide crystallites with different structures and composition. For titanium carbide crystallites,

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two CH<sub>4</sub>, molar hourly space velocities of 15 and 30 h<sup>-1</sup> were used for the synthesis. Here the space velocity is defined as the CH<sub>4</sub> molar flow rate divided by the molar amount of TiO<sub>2</sub>. And two different heating ramps ( $\beta_1$ ,  $\beta_2$ ) were also used for the temperature increase in this study. The reaction temperature for the synthesis of titanium carbide crystallites was increased from room temperature to 900 K at 200 or 400 K/h during the first heating ramp ( $\beta_1$ ). During the second heating ramp, the temperature was then increased from 900 to 1400 K at 25 or 50 K/h ( $\beta_2$ ), and held at 1400 K for an additional hour. These synthesis conditions are similar to those employed previously to prepare vanadium carbide crystallites and tantalum carbide crystallites [10, 11]. After synthesis, the product was quenched to room temperature for passivation and a mixture of 0.5 % O<sub>2</sub> in He (Taedug Gas Co.) flowing at 20 cm<sup>3</sup>/min was used to passivate the sample. This passivation process was continued for another 2 hours, and the product was then removed from the reactor for subsequent analysis. Table 1 shows a summary of the experimental conditions for the preparation of the titanium carbide crystallites.

Measurements of BET surface areas and oxygen uptakes for titanium carbide crystallites were similar to those previously used for other transition metal crystallites [10, 11]. Nitrogen BET surface areas and oxygen uptakes were measured using a Quantasorb model Chembet 3000 sorption analyzer. Prior to N<sub>2</sub> BET surface area measurements, the pretreatment of material was needed so that the sample was isothermally reduced in H<sub>2</sub> (20 cm<sup>3</sup>/min) at 673 K for 3 hours, purged in flowing He (20 cm<sup>3</sup>/min) for 10 minutes then cooled to room temperature. Standard single point BET measurements were made at 77 K using a 30.1 % N<sub>2</sub> in He mixture

(Hanmi Gas Co.). Pulses of purified N<sub>2</sub> (99.998 %, Hanmi Gas Co.) were used to calibrate the amount of adsorbed N<sub>2</sub>. The similar pretreatment conditions were used for oxygen chemisorption measurements. Calibrated volumes of 9.98 % O<sub>2</sub> in He (Hanmi Gas Co.) were injected into the He carrier gas entering the crystallite bed at room temperature until the surface was saturated. The volume of O<sub>2</sub> that was not adsorbed, was measured and used to determine the chemisorbed volume.

Approximately 0.2 g of crystallite was used for ammonia decomposition reaction. Before measuring reactivity, the sample was reduced using H<sub>2</sub> from room temperature to 673 K at a rate of 0.033 K/s, held at 673 K for at least 14 hours then cooled to the reaction temperature. After reduction, atmospheric pressure of NH<sub>3</sub> (99.995 %) was used for NH<sub>3</sub> decomposition reaction where the same inlet space velocity based on the bed volume was 7,500 h<sup>-1</sup>. The reactivities were measured at temperatures between 633 and 843 K. Due to little changes in the reaction rate observed with the variation of reactant flow rate the external mass transport were considered to be neglected at the present reaction conditions. The reactor effluent was analyzed using an on-line Donam gas chromatograph (DS 6200) equipped with both flame ionization and thermal conductivity detectors. The products were separated using Porapak Q packed columns (80/100, 8x1/8", CRS) connected to a gas chromatography detector.

### 3. Results and Discussion

Depending on the synthesis conditions employed, the titanium carbide crystallites were prepared with the BET

Table 1  
Experimental conditions for the synthesis of titanium carbide crystallites

Sample	Heating rate ( $\beta_1$ ) <sup>a</sup> (K/h)	Heating rate ( $\beta_2$ ) <sup>b</sup> (K/h)	Space velocity <sup>c</sup> (h <sup>-1</sup> )
TiC-2	200	25	30
TiC-3	400	50	30
TiC-4	200	25	30
TiC-5	400	50	15
TiC-6	200	25	15
TiC-7	400	50	15
TiC-8	200	25	15

<sup>a,b</sup>Heating rates  $\beta_1$  and  $\beta_2$  indicates the linear temperature increases from room temperature to 900 K, and from 900 K to 1400 K, respectively.

<sup>c</sup>Ratio of molar flow rate of gas to moles of precursor.

Table 2  
Sorptive properties of titanium carbide crystallites<sup>a</sup>

Sample	Surface area (m <sup>2</sup> /g)		O <sub>2</sub> uptake ( $\mu$ mol/g)	Site density (m <sup>-2</sup> )10 <sup>-7</sup>	Surface coverage (%)
	Fresh	Used <sup>b</sup>			
TiC-1	15.2	13.8	2.0	3.2	1.1
TiC-2	11.2	10.3	1.4	1.5	0.6
TiC-3	16.4	15	2.3	3.9	0.8
TiC-4	18.7	17	2.8	4.1	1.5
TiC-5	8.5	8.1	0.9	1.9	0.4
TiC-6	15.8	14.9	2.5	3.9	1.3
TiC-7	13.4	12.6	1.6	3.3	1.0
TiC-8	14.5	14.2	1.7	3.8	1.2
TiO <sub>2</sub>	2.2	-	-	-	-

<sup>a</sup>Based on O<sub>2</sub> uptake at 195 K.

<sup>b</sup>Samples were used for NH<sub>3</sub> decomposition.

surface areas ranging from 8.5 to 18.7 m<sup>2</sup>/g (Table 2). These results indicated that there were significant influences of preparative conditions on the resultant BET surface area of titanium carbide crystallites. It was observed that the heating rates employed during the first and second heating ramps ( $\beta_1$  and  $\beta_2$ ) had a similar effect on the surface areas. Irrespective of space velocity used, decreasing the heating rate produced titanium carbide crystallites with higher surface areas. The relationship between the heating rate and surface area is not uncommon to observe in the synthesis of transition metal carbide crystallites. A negative effect of high heating rate on surface area was also found for the synthesis of vanadium and tantalum carbide crystallites via TPR of their corresponding oxides [10, 11]. It was considered that the changes of surface area with the heating rate were associated with the product process of the solid-state reactions. In addition to the effect of heating rate, the molar hourly space velocities were also observed to have influenced the resulting surface area. It is generally reported that the higher space velocity resulted in the production of high surface area in the preparation of transition metal carbide crystallites [10, 11]. The reason for the plausible effect of space velocity on surface area may be related to the removal of water vapor from the reaction interface during the titanium oxide reduction.

Table 2 also shows the surface areas of fresh and used titanium carbide crystallites for ammonia decomposition reaction. Prior to measurements of the BET surface area, the same pretreatment conditions for used materials were used as those for fresh materials. The deviation of the surface area was estimated to be in the minimal range of ~15%. Subsequently, the comparison between surface areas of the fresh and used titanium carbide crystallites exhibited that these materials were reasonably stable in the structure. As can be also seen in Table 2, the surface area of titanium carbide crystallites synthesized in this study was 4 or 9 times as high as that of a titanium oxide of the starting material. This result implied that some variations in the structural formation might have occurred during the reduction process of precursor oxide.

The oxygen chemisorptive properties of titanium carbide crystallites were measured at room temperature. These oxygen uptakes are described in Table 2. Fig. 1 shows that there was a nearly linear relationship between the O<sub>2</sub> uptake and the BET surface area of titanium carbides. It is not unusual to observe these relationship between the O<sub>2</sub> uptake and the BET surface area in the area of transition metal carbide crystallites. Table 2 also shows that an average oxygen capacity was calculated

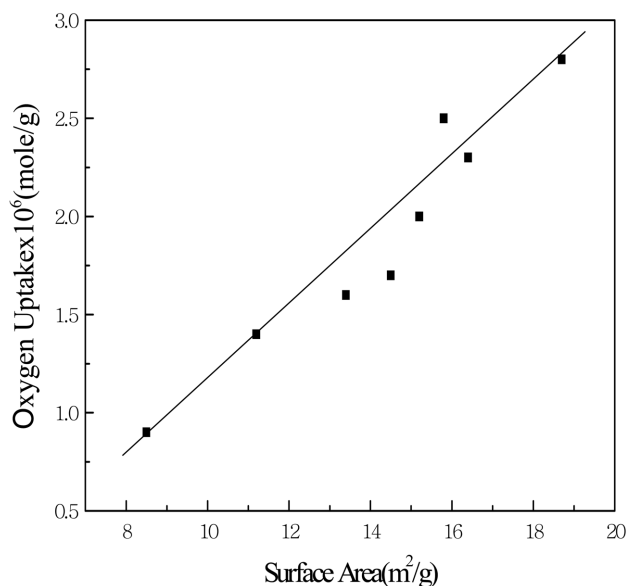


Fig. 1. Oxygen uptake versus surface area for titanium carbide crystallites.

to be  $3.2 \times 10^7$  O/m<sup>2</sup>. An assumed surface titanium number density ( $1.09 \times 10^{15}$  Ti/cm<sup>2</sup>) gave the average oxygen uptake being equivalent to ~0.9% surface coverage by atomic oxygen. Comparison between the oxygen uptakes for titanium carbide crystallites and other transition metal carbide crystallites exhibited that the oxygen uptakes for titanium carbide crystallites were one or two orders of magnitude lower than those for other carbide crystallites [9-11]. The low uptake values of titanium carbide crystallites in the current study might have been

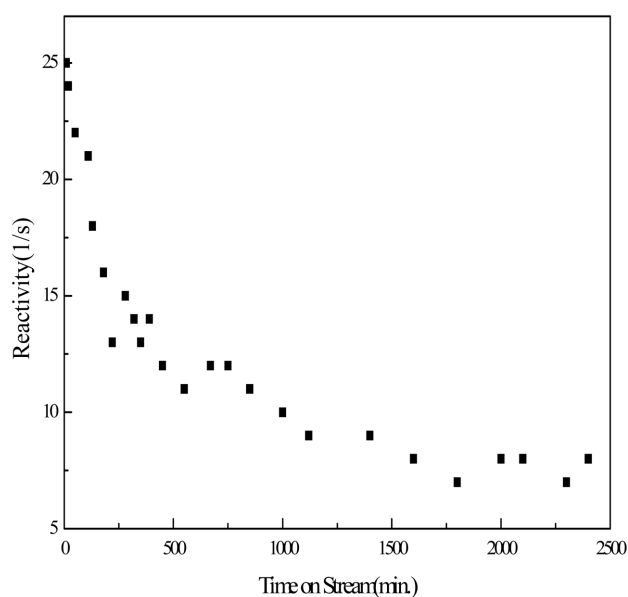


Fig. 2. Typical reactivity for ammonia decomposition (1/s) as a function of time on stream.

related to the surface blockage originating from the formation of polymeric carbon and/or residual oxygen at surface. In particular, the deposition of polymeric carbon on the product surface may impede the preparation of titanium carbide crystallites with high surface area. This can be supported by the observation the formation of amorphous or graphitic carbon during the methane decomposition reaction  $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$  [12].

Titanium carbide crystallites in the current study have proved to be active for ammonia decomposition. Fig. 2 shows typical reactive behavior of titanium carbide crystallites with time on stream for the decomposition of ammonia. When the reactivity is expressed in terms of turnover frequency (1/s), the fresh samples exhibited the highest initial conversion and then gradually lost activ-

Table 3  
Reactivities of titanium carbide and other metal carbide crystallites for ammonia decomposition

Sample	Particle size (nm)	Reactivity (1/s)
TiC-1	80	8.1
TiC-2	105	9.2
TiC-3	74	5.9
TiC-4	65	6.2
TiC-5	143	11.8
TiC-6	77	6.9
TiC-7	91	9.3
TiC-8	84	8.5
VC	-	16
Mo <sub>2</sub> C	-	31

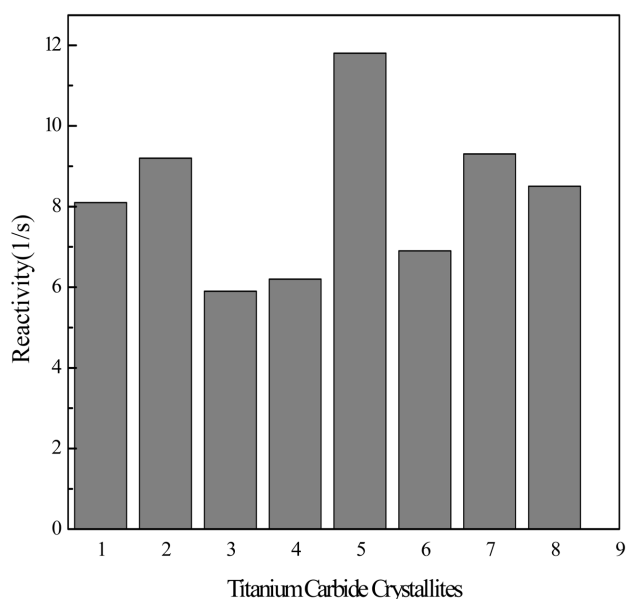


Fig. 3. Reactivity of ammonia decomposition for different titanium carbide crystallites. Number 1, 2, 3, 4, 5, 6, 7, and 8 indicate TiC-1, TiC-2, TiC-3, TiC-4, TiC-5, TiC-6, TiC-7, and TiC-8, respectively.

ity with time. After the reactivity decreased to the steady-state reactivities, it remained constant for several hours. Consequently, a steady state reactivities are described in Table 3 for all the titanium carbide crystallites. Amongst the titanium carbide crystallites, TiC-5 had the highest steady state activity for  $\text{NH}_3$  decomposition. This sample contained almost twice higher activity than TiC-4, exhibiting the lowest activity (Fig. 3). In general, even though there was no remarkable difference in the reactivity of titanium carbide crystallites prepared in this study, these results suggested that reactivity deviation might have been attributed to the reactive species at surface in the titanium carbide crystallites. In fact, the most reactive titanium carbide crystallite showed the largest particle size, while the lowest active sample was synthesized with a smallest particle size. Fig. 4 showed that the reactivity increased with increasing the particle size, indicating that there is a linear relationship between the activity and the particle size. This relationship between the reactivity and the particle size can be also seen in other carbide crystallites such as vanadium carbide crystallites. Choi reported that the vanadium carbide crystallites showed the positive linear relationship between the  $\text{NH}_3$  decomposition reactivity and the particle size [10]. This result was also explained by the fact that the particle size was related to the carbon/vanadium metal ratio at surface. In other words, the particle size increased with the decrease of the carbon/vanadium metal ratio. Unfortunately, notwithstanding the fact that the surface properties of titanium carbide crystallites were not obtained

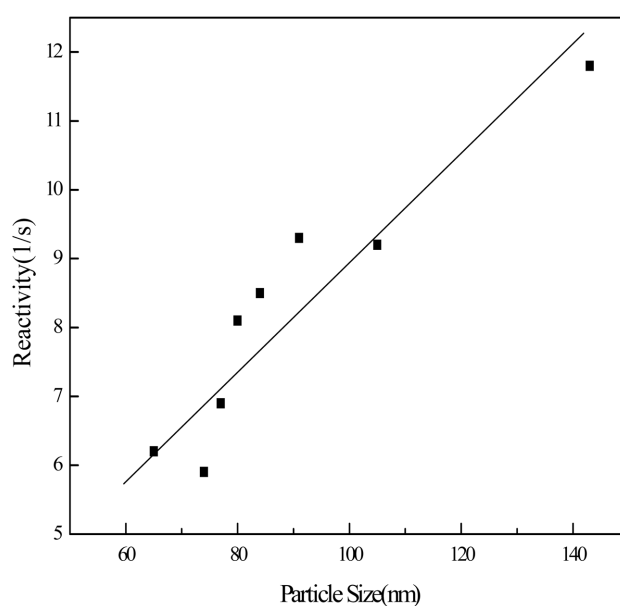


Fig. 4. The reactivity versus particle size of titanium carbide crystallites.

in this study, a similar interpretation could be applied for the reactivity results of titanium carbide crystallites.

Table 3 also exhibits a comparison between the reactivities of titanium, vanadium and molybdenum carbide crystallites. On the basis of turnover number, the reactivities of titanium carbide crystallites were three and five times lower than those of the vanadium and molybdenum carbide crystallites, respectively. These results suggested that the difference in reactivities might be related to the degree of electron transfer between metals and carbon. Since the electronegativities of Ti, V, and Mo are 1.54, 1.63, and 2.16, respectively, it was considered that a larger degree of charge transfer in the titanium carbide crystallites might be ascribed to the lower activity. This explanation is supported by the previous results in the literature that the Group VIB carbide crystallites were more active than the Group IVB and VB carbide crystallites.

#### 4. Conclusions

The titanium carbide crystallites was prepared by using temperature-programmed reduction of titanium oxide ( $\text{TiO}_2$ ) with pure  $\text{CH}_4$ . The resulting materials had the different surface areas, indicating that the structural properties of these materials were strong functions of two different heating rates and space velocity employed. The higher space velocity resulted in the production of high surface area. There was a nearly linear relationship between the  $\text{O}_2$  uptake and the BET surface area of titanium carbides. The titanium carbide crystallites were active for  $\text{NH}_3$  decomposition, showing that the reactivity varied with changes in the particle size. The reactivity comparison showed that the reactivities of titanium carbide crystallites were two and three times lower than those of the vanadium and molybdenum carbide crystallites, respectively.

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