

수소연료전지용 탄탈륨 탄화물에 대한 암모니아 분해반응

최정길*

Ammonia Decomposition Over Tantalum Carbides of Hydrogen Fuel Cell

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Abstract Tantalum carbide crystallites which is to be used for H₂ fuel cell has been synthesized via a temperature-programmed reduction of Ta₂O₅ with pure CH₄. The resultant Ta carbide crystallites prepared using two different heating rates and space velocity exhibit the different surface areas. The O₂ uptake has a linear relation with surface area, corresponding to an oxygen capacity of 1.36×10⁻¹³ O cm². Tantalum carbide crystallites are very active for hydrogen production form ammonia decomposition reaction. Tantalum carbides are as much as two orders of magnitude more active than Pt/C catalyst (Engelhard). The highest activity has been observed at a ratio of C₁/Ta^{δ+}=0.85, suggesting the presence of electron transfer between metals and carbon in metal carbides.

Key words

Tantalum Carbides(탄탈륨 탄화물), Ammonia Decomposition Activity(암모니아 분해반응), Temperature-programmed Reduction Synthesis Method(TPR제조방법), Relation between particle size and activity(입자크기와 반응성과의 관계)

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Nomenclature

β_1, β_2 : heating rate (°C/h)
 S_g : surface area (m²/g)
 D_p : particle size (nm)
 ρ : density of material (g/cm³)

1. Introduction

Transition metal carbide and nitride crystallites have contained many of the attractive catalytic properties of noble metals (such as Pt, Pd, and Rh), there has been a growing interest in utilizing these materials as catalysts or catalytic supports for various petroleum reactions including ammonia decomposition and hydrodenitrogenation (HDN)⁽¹⁻⁶⁾. For example, tungsten and molybdenum carbides

crystallites have exhibited activities similar to those of platinum-based crystallites for dehydrogenation, hydro-genolysis and oxidation reactions^(1,7,8). In particular, it is known that for transition metal carbides and nitrides, the structure and stoichiometry of these materials near the surface have influenced the catalytic properties. The catalytic activities of Mo and W carbides varied with the amount of carbon present in the interstitial sites of the host metal lattice^(2,9). Choi et al. reported that there is a linear relationship between the pyridine HDN activities over the molybdenum carbide crystallites and particle size⁽²⁾. These results suggested a structure sensitive reaction for pyridine HDN reaction over Mo carbides. Therefore, they found that the surface stoichiometry might have been correlated with the particle size, showing the different activities. Similar results have been observed for other transition metal carbide crystallites. For instance, the reactivity of vanadium carbides for ammonia decom-position was found to be explicitly related to the amount of carbon at the surface⁽³⁾. Based on the above-mentioned results, it should be noted that the surface stoichiometry is one of the important functions in determining the catalytic activity of transition metal carbide crystallites.

Tantalum carbide is one of the promising candidates which might be able to substitute for platinum group metals (Pt, Pd, Rh). However, very little is known concerning the catalytic properties of the tantalum carbide crystallites compared to other metal carbides such as V, Mo, and W^(1~3). Furthermore, not much information is available for the fundamental relationship between catalytic activity and surface stoichiometry for Ta carbide crystallites⁽¹⁰⁾.

Eight different tantalum carbides were prepared by using the temperature-programmed reaction of tantalum oxide precursor (Ta_2O_5) with CH_4 . BET total surface area measurements and oxygen chemisorptions were used for obtaining the sorptive properties of these materials. We also evaluated the catalytic properties of these materials for hydrogen production from ammonia decomposition reaction, and compared these results to that of 0.5 wt%

Pt/C (Engelhard) catalyst. Finally, x-ray photoelectron spectroscopy (XPS) was used to have the information about surface structure and stoichiometry of these materials.

2. Experimental

2.1 Ta carbide Preparation

The conventional methods were used to prepare and characterize tantalum carbide crystallites which were very similar to other transition metal carbides^(2,3). Tantalum carbides used in this study were synthesized via the TPR (temperature-programmed reduction) of Ta_2O_5 (99.99%, Aldrich Chemical Co. Ltd) with pure CH_4 . Previous studies already showed that different heating rates and molar hourly space velocities could produce various kinds of transition metal carbides with different structures and composition^(2,3). For tantalum carbides, two CH_4 , molar hourly space velocities of 50 and 25 h^{-1} were used for the synthesis. Here the space velocity is defined as the CH_4 molar flow rate divided by the molar amount of Ta_2O_5 . And two different heating ramps (β_1 , β_2) were also used for the temperature increase in this study. The reaction temperature for the synthesis of tantalum carbides was increased from room temperature to 527°C at 200 or 400°C h^{-1} during the first heating ramp (β_1). During the second heating ramp, the temperature was then increased from 527°C to 1027°C at 40 or 80°C h^{-1} (β_2), and held at 1027°C for an additional hour. After synthesis, the product was quenched to room temperature for passivation. A mixture of 0.5% O_2 in He (Taedug Gas Co.) flowing at 20 $cm^3 min^{-1}$ 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.

2.2 Materials Characterization

Quantasorb model Chembet 3000 sorption analyzer was used to measure BET surface areas and oxygen uptakes of tantalum carbide crystallites prepared in this study. Prior to N₂ BET surface area measurements, the pretreatment of materials were performed by a isothermal reduction in H₂ (20 cm³min⁻¹) at 480°C for 3 hours, purged in flowing He (20 cm³min⁻¹) for 10 minutes then cooled to room temperature. Standard single point BET measurements were made at -196°C using a 30.1% N₂ in He mixture (Hanmi Gas Co.). Pulses of purified N₂ (99.998%, Hanmi Gas Co.) were used to calibrate the amount of adsorbed N₂. The similar pretreatment conditions were used for oxygen chemisorption measurements. Calibrated volumes of 9.98% O₂ in He (Hanmi Gas Co.) were injected into the He carrier gas entering the catalyst bed at room temperature until the surface was saturated. The volume of O₂ that was not adsorbed, was measured and used to determine the chemisorbed volume.

2.3 Reactivity of Ta Carbides

Ta carbide crystallites were reduced using H₂ from room temperature to 480°C at a rate of 0.033°C s⁻¹, held at 480°C for at least 14 hours then cooled to the reaction temperature. After reduction, atmospheric pressure of NH₃ (99.995%) was used for NH₃ decomposition reaction where the same inlet space velocity based on the bed volume was 7,500 h⁻¹. The activities were measured at temperatures between 350 and 550°C. 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, 8'x1/8", CRS) connected to a gas chromatography detector. The catalytic properties of tantalum carbide crystallites in this study were compared to those of 0.5 wt% Pt/C (purchased from Engelhard) that were pretreated under similar conditions. Particularly, the tantalum carbides (named as TaC-a, TaC-b, TaC-c) purchased from Aldrich chemical corporation were also evaluated using conditions similar to those of tantalum carbide crystallites in this study. These commercial crystallites of TaC-a, TaC-b, and TaC-c were pretreated in H₂ flow for the duration of 3, 6, and 9 h before the measurements of activity, respectively.

2.4 X-ray photoelectron spectroscopy (XPS)

We have used A VG ESCA LAB 220 I spectrometer and the Mg K α X-ray source to obtain the XPS spectra for tantalum carbide crystallites synthesized in this study. Before and after argon ion sputtering at 3 kV for 1h, the XPS experiments were performed and then XPS spectra of tantalum carbides were collected for further analysis. We have also utilized different argon ion sputtering conditions for some selected samples for checking the influence of sputtering on the electronic structure of the samples. The vacuum state in the test chamber during the collection of spectra was typically less than 3.9x10⁻⁹ Torr. The spectrometer energies were calibrated using the Au 4f_{1/2} peak at 84.0 eV and the Cu 2p_{3/2} peak at 932.6 eV. Gaussian and/or Lorentzian peaks were deconvoluted using a non-linear least squares algorithm. The atomic compositions were estimated based on comparisons of the integrated peak areas normalized by the atomic sensitivity factors. In order to deconvolute the collected XPS spectra of Ta carbide crystallites the Ta metal and oxides were also used before and after Ar ion sputtering. The expected errors in the composition were to be ~15% in this study⁽¹¹⁾.

3. Results and Discussion

3.1 Ta carbide Surface Areas

Table 1 shows a summary of the synthesis conditions and surface areas of the tantalum carbides. Using a 2³ method of synthesis conditions various tantalum carbide crystallites were prepared with different BET surface areas. The BET surface areas of fresh Ta carbide crystallites ranged from 1.88 to 6.21 m²g⁻¹ depending on the preparative conditions employed in this study. These surface areas are similar to or higher than those reported in the literature⁽¹⁰⁾. From these results we can see that the BET surface area of tantalum carbides have been explicitly influenced by preparative conditions. As shown in Table 1, two different heating rates (β_1 and β_2) employed in this study had a similar effect on the surface areas. As the heating rates decreased, the surface area of tantalum carbides increased. This behavior of heating rate on surface area was identical to all the eight samples regardless of space velocity used.

It was reported that the heating rate could influence

the surface area in the synthesis of transition metal carbides^(2,3). It was considered that the variations of surface area with the heating rate were associated with the solid-state reactions. Accordingly, depending on the synthesis conditions the solid-state reduction process could finally produce the resultant carbides with different surface areas. For the production of tantalum carbides, a molar hourly space velocity was shown to be one more significant synthesis condition to produce different surface areas. The high surface area tantalum carbides were obtained using higher space velocities. It was thought that the positive effect of space velocity on surface area might be associated with the removal of water vapor produced from the reaction of the tantalum oxide with methane. For reference, we also measured the surface areas for commercial Ta carbides, tantalum oxide (Ta₂O₅), and Ta metal. Our materials showed 9 times higher surface area as a maximum than commercial ones. As the H₂ treatment time for three commercial Ta carbides (TaC-a, TaC-b, and TaC-c) increased from 3 to 6 h or 9 h, the surface areas also increased by 19%. The surface area of TaC-4 showing the highest value is 14 and 69

Table 1. Experimental conditions for the synthesis of tantalum carbide crystallites

Sample	Heating rate (β_1) ^a (°C/h)	Heating rate (β_2) ^b (°C/h)	Space velocity ^c (h ⁻¹)	Surface area (m ² /g)
TC-1	300	60	40	2.61
TC-2	300	30	40	3.32
TC-3	100	60	40	4.23
TC-4	100	30	40	6.01
TC-5	300	60	20	1.28
TC-6	300	30	20	2.30
TC-7	100	60	20	2.23
TC-8	100	30	20	3.32
TC-a	-	-	-	0.61
TC-b	-	-	-	0.67
TC-c	-	-	-	0.76
Ta ₂ O ₅	-	-	-	0.42
Ta	-	-	-	0.09

^{a,b} Heating rates β_1 and β_2 indicates the linear temperature increases from room temperature to 527°C, and from 527°C to 1027°C, respectively.

^c Ratio of molar flow rate of gas to moles of precursor.

times higher than those of Ta₂O₅ and Ta metal, respectively. It is noted that the difference between the surface areas of tantalum carbide crystallites prepared in this study and reference materials indicated that the present preparative conditions have positively affected the solid-state reaction product selectivities⁽²⁾, resulting in production of Ta carbides with high surface areas.

3.2 BET Surface Areas and Oxygen Uptakes

In Table 2 it is shown that the sorptive properties of eight tantalum carbides in this study and three tantalum carbides purchased from Aldrich. As a durability test of sample, the surface areas of fresh and used tantalum carbides for ammonia decomposition reaction were measured. For the purpose of obtaining the precise comparison, the pretreatment conditions for used materials were identical with those for fresh materials. Since the difference in the surface area was not significant within the minimal range of ~10%, it was considered that the tantalum carbides synthesized in this study were reasonably stable in terms of structure. The surface area of tantalum carbides was 4 or 14 times higher than that of a tantalum oxide of the starting material. This result

suggested that the structural variation might have been involved in formation of final carbides in the course of reducing process of precursor oxide.

O₂ chemisorption technique was used for measuring the accessibility of the active surface. Since atomic oxygen can diffuse into the subsurface layers of tantalum carbides^(2,4), the measurements of oxygen chemisorption uptake were made at -77°C. The oxygen uptakes for eight samples are shown in Table 2.

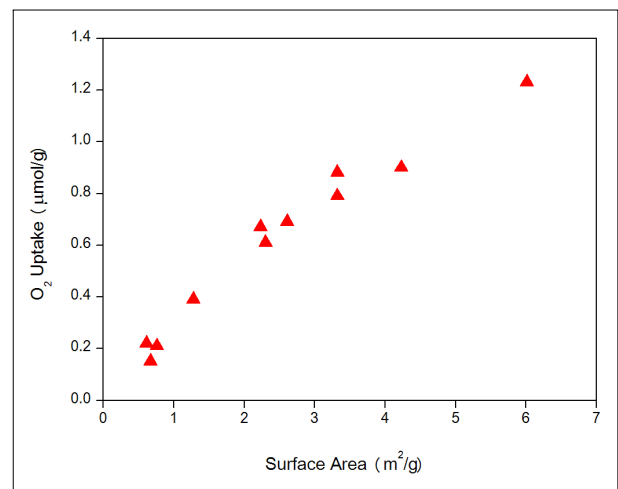


Fig. 1 Oxygen uptakes as a function of surface area for tantalum carbides

Table 2. Sorption properties of tantalum carbide crystallites^a

Sample	Surface area (m ² /g)		O ₂ uptake (μmol O ₂ /g)	Oxygen capacity (x10 ¹³ molecules O/cm ²)	Surface Coverage (%)
	Fresh	Used ^b			
TC-1	2,61	2,62	0,69	3,35	2,9
TC-2	3,32	3,37	0,88	3,34	2,4
TC-3	4,23	4,61	0,90	2,81	2,5
TC-4	6,01	6,60	1,23	2,34	2,1
TC-5	1,28	1,39	0,39	2,59	2,3
TC-6	2,30	2,32	0,61	3,38	3,0
TC-7	2,23	2,41	0,67	3,45	3,1
TC-8	3,32	3,34	0,79	3,12	2,9
TC-a	0,61	0,60	0,22	3,34	2,7
TC-b	0,67	0,71	0,15	3,20	3,0
TC-c	0,76	0,77	0,21	3,29	3,1

^a Based on O₂ uptake at -77°C.

^b Samples were used for NH₃ decomposition.

Fig. 1 shows that the O₂ uptake has a linear relation with the BET surface area of tantalum carbides. It is general to observe the linear relationship between the O₂ uptake and the BET surface area in the area of transition metal carbides^(3,6). The slope of the straight line corresponds to a site density, showing that an oxygen capacity was averaged to be 1.36×10¹³ O cm⁻². Assuming equal proportions of the low-index planes at surface, the density of the metal atoms on a clean carbide surface can be 1.09 × 10¹⁵ Ta cm⁻². Therefore, the surface tantalum number density (1.09 × 10¹⁵ Ta cm⁻²) gave the average oxygen uptake being equivalent to 2.78% surface coverage by atomic oxygen. It was considered that the low uptake values of tantalum carbides might be ascribed to (1) the surface blockage originating from the presence of graphitic carbon and/or (2) oxygen residue from the synthesis at surface. It is generally known that oxygen, hydrogen, and CO do not chemisorb on graphitic carbon at -77°C^(2,5). Especially, in the synthesis of transition metal carbides the deposition of polymeric carbon on the product surface may hinder the preparation of metal carbides with high surface area. This phenomena can be supported by the fact that the amorphous or graphitic carbon during the methane decomposition reaction CH₄ → C + 2H₂ could be formed on the surface⁽¹²⁾. It is generally known that there are three different kinds of carbonaceous surface species produced from methane decomposition^(6,10). They can be hydrogenated via H₂

treatment at different temperatures; (1) carbidic surface carbon below 130°C, (2) a less reactive amorphous carbonaceous layer around 230°C, and (3) unreactive graphitic carbon at higher temperatures than ~380°C. In this study from the separate experiments we observed the peak of methane production at 430°C during H₂ TPR. The CH₄ peak obtained from temperature programmed reaction (TPR) between H₂ and Ta carbide suggests the existence of graphitic carbon formed at carbide surface. Since tantalum carbide crystallites were synthesized at a high temperature, a high reduction temperature may be needed to get rid of the polymeric carbon from the sample. The presence of these three carbonaceous species was also confirmed by independent XPS (X-ray photoelectron spectroscopy) experiment.

The XPS results exhibit that the graphitic free carbon peak appears at a binding energy of 284.3 eV, and the carbidic and adsorbed carbon species are shown at 282.6 eV and 285.7 eV, respectively (Table 3).

3.3 Ta Carbide Crystallite Reactivities

We can see that the tantalum carbides synthesized in this study proved to be active for ammonia decomposition reaction. Fig. 2 shows typical activities of ammonia decomposition over four tantalum carbides (TaC-1, TaC-4, TaC-5, and TaC-8) as a function of time on stream at 350°C. Here, these four tantalum carbides were selected

Table 3. The C 1s core levels and relative intensity for tantalum carbide crystallites

Sample	C 1s			Relative intensity
	C ₁ (carbidic)	C ₂ (graphitic)	C ₃ (adsorbed)	C ₁ /(C ₂ +C ₃)
TC-1	282.6(21)	284.3	285.7	0.25
TC-2	282.7(25)	284.4	285.6	0.36
TC-3	282.5(30)	284.5	285.7	0.41
TC-4	282.6(19)	284.4	285.6	0.30
TC-5	282.6(15)	284.3	285.6	0.19
TC-6	282.7(18)	284.4	285.8	0.21
TC-7	282.6(22)	284.3	285.7	0.20
TC-8	282.5(30)	284.3	285.6	0.49

for representing the lowest, medium, and highest surface area materials, which spanned the entire range of surface areas produced. It was observed that the fresh crystallites exhibited the highest initial conversion and then gradually and significantly lost their activities with time prior to reaching steady states. After the conversion reached the steady-state activities, it remained constant for a long time.

Fig. 3 exhibits typical activity vs. time on stream over tantalum carbide (TaC-1) at different temperatures. As the reaction temperature increased, the steady state

activities increased.

Table 4 shows the steady state activities for all the tantalum carbide crystallites which are nano-sized materials. Average particle sizes of Ta carbides (D_p) were estimated using the following relation⁽²⁾

$$D_p = 6/S_g \rho$$

where S_g is the BET surface area and ρ is the density of the primary bulk phase of tantalum carbide crystallites (here, it is taken to be 14.3 g cm^{-3}). The particle sizes

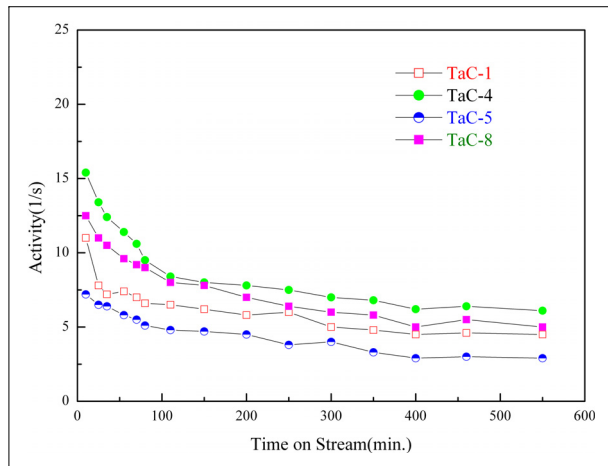


Fig. 2 Typical activities of ammonia decomposition over four tantalum carbides

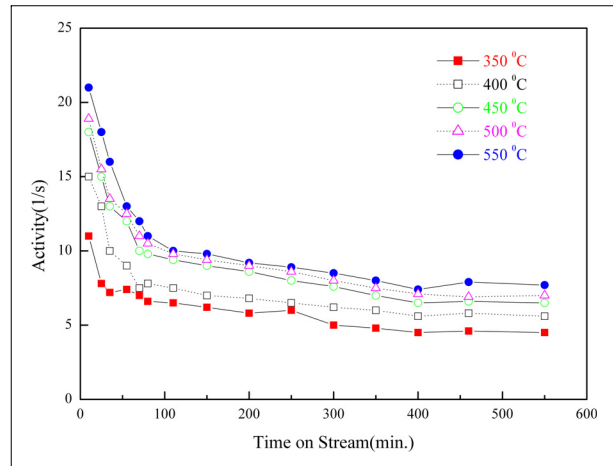


Fig. 3 Typical activities vs. time on stream over tantalum carbide (TaC-1) at different temperatures

Table 4. Catalytic activities as a function of particle size and $C_1/\text{Ta}^{\delta+}$ for tantalum carbide crystallites

Sample	Activity (1/s)	Particle size (nm)	ΔE_{act} (kcal/mol)	$C_1/\text{Ta}^{\delta+}$
TC-1	4.2	23	36	0.61
TC-2	4.6	22	35	0.63
TC-3	5.2	18	36	1.21
TC-4	6.0	13	33	0.92
TC-5	2.7	38	40	0.29
TC-6	4.2	33	41	0.49
TC-7	4.0	25	35	0.48
TC-8	5.2	21	35	1.19
TC-a	1.4	95	37	–
TC-b	1.8	86	40	–
TC-c	2.3	81	42	–
Pt/C	0.07	–	25	–

of Ta carbides ranged from 11 to 37 nm. Among the tantalum carbide

crystallites, TaC-4 had the highest steady state activity for NH_3 decomposition, while TaC-5 shows the lowest one. The catalyst TaC-4 contained about 2 times higher activity than TaC-5. Although all the eight samples prepared in this study have the same bulk structure (TaC, cubic), the different activity values suggested the formation of different active species at surface in the tantalum carbide catalysts. In fact, the most active tantalum carbide catalyst showed the smallest particle size. In the meantime, the sample produced with the largest particle size exhibited the least activity. The relationship between the activity and the particle size indicates that the activity decreased with the particle size. This kind of linear relationship between the activity and the surface area is not uncommon. It was reported that the vanadium carbide catalysts showed the linear relationship between the ammonia decomposition activity and the particle size⁽⁶⁾, suggesting the presence of structure-sensitivity for ammonia decomposition. Based on the previous results, it was concluded that the NH_3 decomposition over tantalum carbides was structure-sensitive.

One might compare the activity of tantalum carbides with those of commercial carbides and Pt catalyst. The activities of Ta carbides in this study were similar or higher than those of commercial ones. This might be due to (i) the different pretreatment time in H_2 before activity measurements and (ii) the difference at surface structure with the same bulk structure. On the contrary, our Ta carbides had activities that were higher by a factor of 32 or 87 than Pt/C catalyst. It was considered that the surface of these Ta carbides has been advantageously restructured and tamed to be active for ammonia decomposition reaction by carburization of raw materials. The activation energies of ammonia decomposition over all the tantalum carbide crystallites were shown to be very similar and averaged $37.5 \text{ kcal mol}^{-1}$. These results suggested that ammonia decomposition for tantalum

carbides proceeded via a common reaction mechanism which is to be discussed later. Our Ta carbide activation energy is similar to commercial ones but higher than that of Pt/C catalyst, indicating that compared to platinum catalyst the reaction rates over our materials were more temperature-sensitive. The activation energies of tantalum carbide crystallites were similar to those published in the literature for ammonia decomposition reaction^(6,13).

4. Conclusions

8 tantalum carbides were prepared via TPR (temperature-programmed reduction) of tantalum oxide (Ti_2O_5) with pure CH_4 . The prepared crystallites contained the different surface areas, indicating that the structural properties of these carbide materials were strong functions of two different heating rates and space velocity employed in the current study. When the space velocity increased, the higher surface area was produced. For tantalum carbides, the O_2 uptake increases linearly with the increase of BET surface area. The slope of the straight line corresponds to a site density, showing that an oxygen capacity was averaged to be $1.36 \times 10^{13} \text{ O cm}^{-2}$. The surface tantalum number density ($1.09 \times 10^{15} \text{ Ti cm}^{-2}$) gave the average oxygen uptake being equivalent to 2.78% surface coverage by atomic oxygen. The tantalum carbide crystallites have proved to be active for hydrogen production from ammonia decomposition reaction with catalytic properties that were similar or superior to those of commercial Ta carbide catalysts. It was also observed that the activities of tantalum carbide crystallites were higher by a factor of 32 or 87 than that of Pt/C catalyst. The activity decreased with increasing the particle size, indicating that ammonia decomposition over Ta carbides is structure-sensitive. From eight samples, the most active catalyst showed the carbon/tantalum ratio ($\text{C}_1/\text{Ta}^{8+}$) of 0.85, suggesting that there is a correlation between the activity and the degree of electron transfer between

metals and carbon in metal carbides. The XPS results indicated that the electron charge was transferred from the Ta $5d$ states to the C $2p$ states, resulting in the production of platinum-like catalytic properties in tantalum carbide crystallites in the current study.

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