

Ammonia Decomposition over Vanadium Carbide Catalysts

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Vanadium carbides were synthesized by the temperature-programmed carburization of vanadium oxide precursors (V_2O_5) with pure CH_4 or a mixture of 49.9% CH_4 in H_2 . It was found that the structural properties of these materials were strong functions of the heating rate and space velocity employed. The vanadium carbides with high surface areas could be prepared using high space velocities or low heating rates. The vanadium carbides proved to be active NH_3 decomposition catalysts. Since the activity varied with changes in the surface area and particle size, ammonia decomposition over the vanadium carbides appeared to be structure-sensitive. This response was considered to be due to variations in the surface stoichiometry with particle size. In general, the activities of the vanadium carbides were about 2 times less than those of Mo_2C catalyst while vanadium carbides had higher activities by a factor of 1 or 2 than those of Pt/C catalyst. The difference in activities of the vanadium and molybdenum carbides might be related to the degree of electron transfer between metals and carbon. A similarity between the catalytic behaviors of vanadium carbides and platinum metal appeared to be due to the similar electronic and magnetic properties of these materials. © 1999 Academic Press

Key Words: ammonia decomposition; vanadium carbides.

INTRODUCTION

Although previous investigations have reported that there are remarkable similarities between the catalytic properties of tungsten carbides and platinum-group metals for hydrocarbon conversion reactions including dehydrogenation (1–3), isomerization (3–5), and hydrogenolysis (2, 3, 5), not many studies have, thus far, been published using other early transition metal carbides. Moreover, there are very few investigations that were particularly focused on the reasons for the presence of similarities between the catalytic properties of these materials and platinum-group metals. It was considered that these catalytic similarities between the tungsten carbides and platinum metal were associated with the electronic properties of these materials. Additionally,

the catalytic and electronic properties of tungsten carbides were reported to be related to the carbon stoichiometry in the metal lattice and near the surface (6–8).

Ross and Stonehart (9) reported that nonstoichiometric carbides were active for the dehydrogenation of cyclohexane and hydrogenation of propene, implying that there are relationships between the catalyst stoichiometry and activity. A similar relationship has been reported by Choi (10) for the molybdenum nitride catalysts. Using a series of molybdenum nitrides, the catalytic properties of these materials were found to be related to the electronic properties at the near surface (10). For pyridine hydrodenitrogenation, the most active catalyst had the surface compositional N/Mo of 1.0 with the largest particle size. While there is some information available concerning the structure-function relationships for tungsten and molybdenum carbides, the detailed relationships between the structure, stoichiometry, and catalytic properties of other early transition metal carbides have not yet been systematically presented. Therefore, a detailed understanding of these properties of early transition metal carbides is of practical importance for designing a new generation of catalysts which might replace the expensive platinum-group metals that are currently used in commercial processes.

In the present study, the structural, compositional, and catalytic properties of a series of vanadium carbides will be described. The possible relationships between these properties of vanadium carbides will also be discussed, and these properties will be compared to those of other transition metal carbides and nitrides, and platinum catalyst. For this purpose, the vanadium carbides were prepared by the temperature-programmed carburization (TPC) of vanadium oxide precursors (V_2O_5) with pure CH_4 or a mixture of 49.9% CH_4 in H_2 . Characterization techniques including X-ray diffraction (XRD), BET total surface area measurements, and chemisorption were employed to evaluate the structural and sorptive properties of these materials. The catalytic properties for NH_3 decomposition were also evaluated. Finally, the electronic properties of vanadium carbides have been elucidated using X-ray photoelectron spectroscopy (XPS). For reference, the vanadium oxide precursors (V_2O_5) were also used for XPS studies.

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EXPERIMENTAL

The vanadium carbides were synthesized using a temperature-programmed reaction of V_2O_5 (99.95%, Junsei Chemical Co., Ltd.) with pure CH_4 or a mixture of 49.9% CH_4 in H_2 (Taedug Gas Co.). It was necessary to use different heating rates and molar hourly space velocities in order to obtain the final products with different structural and compositional properties. Therefore, for the preparation of vanadium carbides, two heating rates of 120 and 240 K/h, and two CH_4 molar hourly space velocities of 20.4 and 10.2 h^{-1} were used. Here, in this study the molar hourly space velocity was defined as the reactive gas molar flow rate (CH_4) divided by the molar amount of precursor (V_2O_5). Table 1 shows a summary of the synthesis conditions and BET surface areas of the vanadium carbides. For the synthesis of carbides, the reaction temperature was quickly increased from room temperature to 763 K in 1 h. The temperature was then increased from 763 to 1323 K at 120 and 240 K/h and held at 1323 K for 1 h. These synthesis conditions are similar to those employed previously to prepare vanadium carbides (11). After synthesis was finished, the final product was quenched to room temperature and passivated in a mixture of 0.5% O_2 in He (Taedug Gas Co.) flowing at 20 cm^3/min to prevent bulk oxidation. This passivation was continued for 2 h. After passivation, the

product was removed from the reactor for subsequent analysis.

The BET surface areas were measured by the flow method using a Quantasorb Model Chembet 3000 sorption analyzer. The standard pretreatment consisted of heating the sample in H_2 (99.99%, Taedug Gas Co.) flowing (20 cm^3/min) at 673 K for 3 h in order to remove the passivation layer and other impurities. The temperatures and times were varied for selected samples to evaluate the effects of the pretreatment conditions on the surface area. The amount of nitrogen removed from the flowing gas mixture (30.1% N_2 in He, Taedug Gas Co.) and physisorbed on the surface was determined using a thermal conductivity detector. Accurately measured pulses ($\pm 2\%$) of purified N_2 (99.998%, Taedug Gas Co.) were used to calibrate the amount of adsorbed N_2 . The average size of particles at the surface, d_p , was estimated using the equation $d_p = 6/S_g\rho$, where S_g is the BET surface area and ρ is the density of the primary bulk phase ($\rho = 3.36$ and 5.64 g/cm^3 for V_2O_5 and V_8C_7 , respectively).

Using the same Quantasorb sorption analyzer, oxygen chemisorption uptakes were measured by the pulsed method. Oxygen chemisorption proved to be a useful method to determine the number of active sites in Mo carbide and nitride hydrotreating catalysts (12, 13). The pretreatment conditions were basically the same as those used to determine the BET surface areas. After pretreatment, the catalysts were purged with flowing He at room temperature. Calibrated volumes of 10.1% O_2 in He (Taedug Gas Co.) were then injected into the He carrier gas entering the catalyst bed. The amount of oxygen adsorbed was easily calculated from the number of pulses and the peak areas.

The bulk structures and compositions of the materials were evaluated using a computer controlled Rigaku Rotaflex DMAX-B rotating anode X-ray diffractometer with a $CuK\alpha$ radiation source and a Perkin-Elmer 2400 CHN analyzer with an autosampler, respectively.

For catalytic activity measurements, roughly 0.2 g of catalyst was loaded over a plug of glass wool packed into the reaction zone of a 9 mm O.D. pyrex glass flow reactor. A chromel-alumel (K type) thermocouple was used to monitor the temperature. The catalyst was heated in H_2 from room temperature to 673 K at a rate of 120 K/h, held at 673 K for at least 14 h, and then cooled to the reaction temperature. After reduction, NH_3 (99.995%) was passed over the catalyst at atmospheric pressure with the same inlet space velocity based on the bed volume of 7500 h^{-1} for NH_3 decomposition reaction. The activities were measured at temperatures between 633 and 843 K. All of these measurements were in agreement with an estimated experimental error of $\pm 10\%$. External mass transport limitations were absent under the present reaction conditions since negligible changes in the reaction rate were observed with the variation of reactant flow rate. The catalytic properties

TABLE 1
Effect of Synthesis Conditions on BET Surface Areas
of Vanadium Carbides

Catalyst code	Heating rate (K/h) ^a	H_2/CH_4	Space velocity (h^{-1}) ^b		Surface area (m^2/g) ^c	
			Total	CH_4	Fresh	Used ^d
VaC-1	240	1.004	20.4	10.2	7.8 9.4 ^e	10.3 —
VaC-2	120	1.004	20.4	10.2	10.7	9.3
VaC-3	240	0	20.4	20.4	7.1	—
VaC-4	120	0	20.4	20.4	6.1	—
VaC-5	240	1.004	10.2	5.1	7.2 7.5 ^f	5.0 —
VaC-6	120	1.004	10.2	5.1	8.5	8.4
VaC-7	240	0	10.2	10.2	4.2	—
VaC-8	120	0	10.2	10.2	8.4	—
VaC-9	101	1.004	61.2	30.6	31.4	—
V_2O_5	—	—	—	—	3.9	—
VC^g	0.030	5	67,000	13,400	60	—

^a Heating rates indicate the linear temperature increases from 763 to 1323 K.

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

^c Measured after pretreatment in H_2 flow at 673 K for 3 h.

^d Used for NH_3 decomposition.

^e Measured after H_2 treatment at 673 K for 6 h.

^f Measured after H_2 treatment at 673 K for 4 h.

^g Kapoor and Oyama, who used a precursor of V_2O_5 with 19 m^2/g (see Ref. (43)).

of vanadium carbides were compared to those of VN, Mo₂N, Mo₂C, and 0.5 wt% Pt/C (Engelhard) that were pretreated under similar 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' × 1/8", CRS) connected to a gas chromatography detector.

The XPS was carried out using a VG ESCA LAB 220 I spectrometer using the MgK α X-ray source. The XPS spectra of the samples were collected before and after Ar ion sputtering at 3 kV for 1 h. For some selected samples, different Ar ion sputtering conditions were used to determine the influence of sputtering on the electronic structure of the samples. Vacuum in the test chamber during the collection of spectra was typically less than 4×10^{-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 nonlinear least-squares algorithm. The atomic compositions were estimated based on comparisons of the integrated peak areas normalized by the atomic sensitivity factors. Errors in the composition were expected to be $\pm 15\%$ (14).

RESULTS

Sorption Analysis

Table 1 shows the BET surface areas of the vanadium carbides ranging from 4.2 to 31.4 m²/g. It is clear that the surface areas depended on the synthesis conditions employed. Increasing space velocity resulted in the increase of surface areas of these materials; however, increasing the heating rate caused vanadium carbides to have low surface areas. For the relationship between space velocity and surface area, it was previously reported that high space velocities were necessary for the synthesis of high surface area carbides and nitrides (12, 13). For Mo carbides synthesized using Mo oxide (MoO₃) (12), the increase in surface area using high space velocities may be due to the removal of H₂O vapor from the reaction interface. Increasing the heating rate resulted in decrease in the surface areas of vanadium carbides. The reason for this is not yet clear. Nonetheless, Choi *et al.* [13] reported that this factor may influence the product selectivity of the solid-state reactions, and thereby, the surface areas may be changed with heating rate.

The effect of H₂ pretreatment condition on the surface areas of vanadium carbides is also shown in Table 1. The surface areas increased up to by 21% with increasing the treatment time from 3 to 4 or 6 h. It appears that this behavior was due to pore opening caused by the progressive conversion of the oxycarbide passivation layer into either the denser vanadium carbide or vanadium metal. Another reason might be ascribed to the removal of impurities (C and O) on the surface by H₂ treatment. For the synthesis of

vanadium carbides, the higher synthesis temperature used may expedite the formation of amorphous or graphitic carbon through the methane decomposition reaction. Therefore, the high surface area vanadium carbides may not be easily synthesized due to continual deposition of polymeric carbon on the product surface. However, it is possible to increase the surface area by removing polymeric carbon via H₂ treatment at high temperature. In this study, the pretreatment temperature of 673 K was used, which could possibly remove the polymeric carbon on the surface of vanadium carbides. This was confirmed by the findings that methane was produced during hydrogen treatment and the graphitic carbons were observed by XPS. The surface areas of fresh and used vanadium carbides for ammonia decomposition can also be seen in Table 1. Pretreatment conditions for used samples were the same as those for fresh samples. In general, the surface areas of the used vanadium carbides decreased except for VaC-1.

According to the V-C phase diagram, the vanadium carbides between $x = 0.5$ and 1 in VC_{*x*} are thermodynamically stable below 1900 K. Under our synthesis conditions, the crystalline phase of all the materials prepared in this study was observed to be one single phase of V₈C₇ using X-ray diffraction analysis (Fig. 1). V₈C₇ is simple cubic, while V₂O₅ is orthorhombic. During the carburization of V₂O₅ to V₈C₇, the specific volume (per gram of V) was decreased by 61%, resulting in the evolution of cracks and the exposure of significant amounts of internal surface area. One of the reasons for the increase in surface area is the increased shortest metal-metal distance of vanadium metal (2.62 → 4.16 Å) as a result of carbide formation. The insertion of carbon in the interstitial spaces of vanadium metal expands the metal lattice, resulting in an increase in the metal-metal bond distance. The increase in the metal-metal distance causes the variation in structure, leading to the creation of the final products with higher surface area.

Table 2 shows the oxygen chemisorptive properties of vanadium carbides measured at room temperature. A

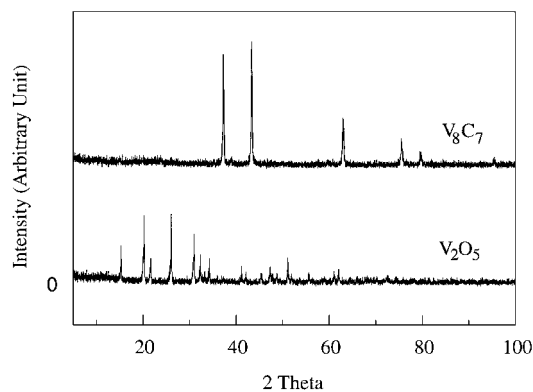


FIG. 1. Representative XRD patterns of vanadium oxide (V₂O₅) and vanadium carbide (V₈C₇).

TABLE 2
Oxygen Chemisorptive Properties of Vanadium and Other Metal Carbides

Catalyst code	Surface area (m ² /g)	Oxygen uptake (μmol O ₂ /g) ^a	Oxygen capacity × 10 ⁻¹³ (molecules O/cm ²)	Surface coverage (%)	References
VaC-1	7.8	1.09	1.68	1.5	Present study
VaC-2	10.7	2	2.25	2.1	Present study
VaC-2	10.7	1.77 ^b	1.99	1.9	Present study
VaC-3	7.1	0.72	1.22	1.1	Present study
VaC-4	6.1	1.15	2.26	2.1	Present study
VaC-5	7.2	0.80	1.34	1.2	Present study
VaC-6	8.5	0.97	1.37	1.3	Present study
VaC-7	4.2	0.79	2.25	2.1	Present study
VaC-8	8.4	0.47	0.67	0.6	Present study
VaC-9	31.4	3.1	1.14	1.0	Present study
Mo ₂ C	7	9	16	14.7	(12)
W ₂ C	37.3	2.9	0.94	0.9	(23)
W ₂ C	38.7	2.7	0.84	0.8	(23)

^a Measured at room temperature after 3 h hydrogen reduction.

^b Measured after 2 h hydrogen reduction.

nearly linear relationship between the oxygen uptake and the BET surface area was observed for the vanadium carbides. The average oxygen capacity was measured to be 1.81×10^{13} O/cm². Using an assumed surface vanadium number density (1.09×10^{15} V/cm²), the average oxygen uptake was equivalent to ~2% surface coverage by atomic oxygen. The values for vanadium carbides, while comparable to those for tungsten carbides, are significantly lower than those for molybdenum carbides. The low uptake values of vanadium carbides in the current study might be attributed to the surface blockage by polymeric carbon and/or residual oxygen at surface. This is supported by the observation that the oxygen uptake increased with increasing the pretreatment period, as shown in Table 2.

Catalytic Properties

The vanadium carbides have proved to be active for NH₃ decomposition. The freshly prepared vanadium carbides

exhibit the highest initial conversion, but then lose activity gradually over time (Fig. 2). The reaction rates decreased to the steady-state activities during the first 40 min on stream and remained constant for several hours on stream. Figures 3 and 4 show the catalytic behaviors of vanadium carbides for NH₃ decomposition as a function of the reaction temperature and the particle size, respectively. Arrhenius plots of the activities (Fig. 3) and the activity–particle size plots (Fig. 4) over vanadium carbides exhibit that the activities increased with decreasing the surface area. A similar relationship between activities and the surface areas was also observed for Mo carbides using pyridine hydrodenitrogenation (12).

Table 3 shows the comparison of the catalytic properties of the vanadium carbides with those of other materials. The catalytic reaction rate expressed on a gram basis was calculated using consumed, decomposed NH₃ moles and catalyst weight at steady state. Subsequently, areal rate and

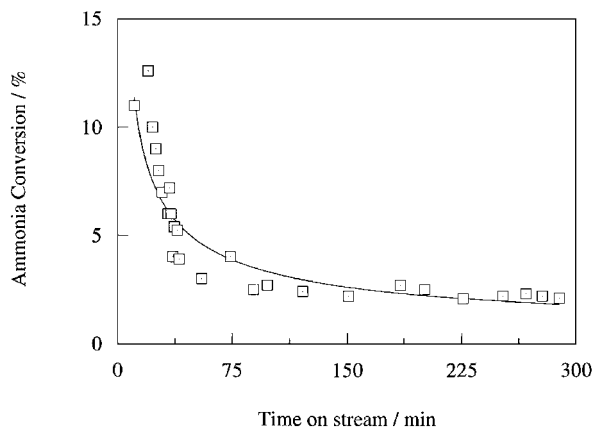


FIG. 2. A typical ammonia conversion versus time on stream over vanadium carbide at 653 K.

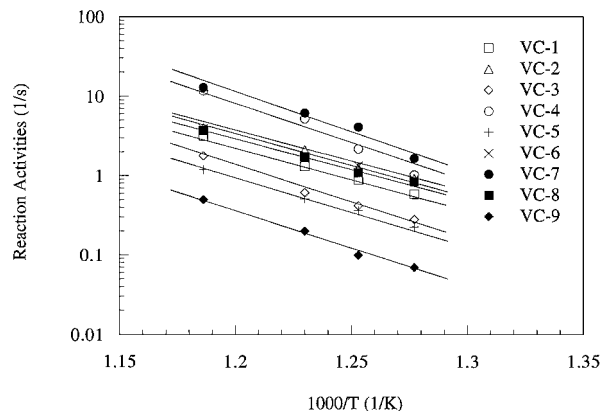


FIG. 3. Arrhenius plots of the NH₃ decomposition activities over vanadium carbides.

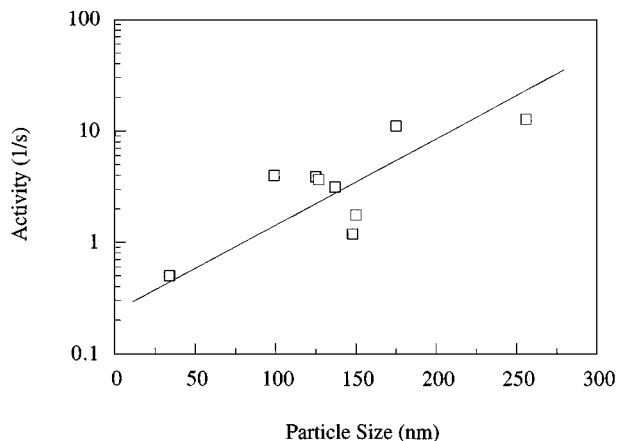


FIG. 4. Activities as a function of the particle sizes over vanadium carbides.

steady-state catalytic activity were estimated by dividing reaction rate by surface area and oxygen uptake, respectively. Even though vanadium carbides generally exhibited the lower reaction rates on a per gram basis, the activities for vanadium carbides bracketed those determined for the vanadium nitrides, molybdenum carbides, and platinum catalysts. On an oxygen uptake basis, the activities of the vanadium carbides were superior to that of vanadium nitride. These activity differences might be due to the electronic and structural differences of vanadium carbide and nitride prepared by the addition of carbon and nitrogen into vanadium lattice, respectively. A similar activity difference could be found for Mo carbides and nitrides in pyridine hydrodenitrogenation (12, 15). The activities of the vanadium carbides were about 2 times less than those of Mo carbide

catalyst, while vanadium carbides had activities that were higher by a factor of 1 or 2 than those of Pt/C catalyst. However, the areal rates of all vanadium carbides are lower than those of Mo nitride catalyst. The ammonia decomposition activation energies for all the vanadium carbides were similar with an average value of 35 kcal/mole, suggesting that ammonia decomposition over vanadium carbides proceeded via a common mechanism. However, these values are higher than those of platinum catalyst, indicating that the reaction rates over vanadium carbides were more temperature-sensitive. The activation energies of the vanadium carbide catalysts were similar to those reported in the literature for ammonia decomposition reaction (16, 17).

XPS Spectra

The typical survey of XPS spectra for the vanadium carbides is shown in Fig. 5. After Ar ion sputtering for 30 min, the species of V 2*p*, C 1*s*, O 1*s* could be clearly seen in the survey. To a first approximation, it can be seen that the peak size of O 1*s* between 530 and 532 eV is fairly large. This result indicates that the sputtering time of 30 min may not be sufficient for cleaning the surfaces of vanadium carbide. Since constant amounts (as expressed in area) of core levels of V 2*p*, C 1*s*, and O 1*s* were obtained after 1 h sputtering, a prolonged time of 1 h in Ar sputtering was used for the vanadium carbides used in this study. One might expect that this sputtering pretreatment would influence primarily on the light elements such as C and O, and have a relatively small effect on the heavy metal of vanadium. As will be discussed later, this can clearly be seen by the results in Table 4.

The V 2*p* spectra typically consisted of two envelopes. The relative intensities of spin-orbit doublet peaks are

TABLE 3

Catalytic Properties of Vanadium Carbides and Other Materials for NH₃ Decomposition

Catalyst code	Particle size (nm)	Reaction rate ($\mu\text{mol/g/s}$) ^a	Areal rate ($\mu\text{mol/m}^2/\text{s}$)	Activity (1/s)	ΔE_{act} (kcal/mol)	References
VaC-1	137	3.40	0.44	3.12	34	Present study
VaC-2	99	7.98	0.75	3.99	36	Present study
VaC-3	150	1.28	0.18	1.78	33	Present study
VaC-4	175	12.9	2.11	11.2	38	Present study
VaC-5	148	0.96	0.13	1.20	37	Present study
VaC-6	125	3.81	0.45	3.93	32	Present study
VaC-7	256	10.19	2.43	12.9	35	Present study
VaC-8	127	1.74	0.21	3.70	39	Present study
VaC-9	34	1.55	0.05	0.50	30	Present study
VN ^b	—	5.1	0.20	0.18	33	(17)
Mo ₂ N ^b	—	—	4.04	—	35	(16)
Mo ₂ C	—	24.6	3.23	28.3	36	Present study
Pt/C	—	0.74	6×10^{-4}	0.07	24	Present study

^a Measured at ~ 101 kPa and 843 K.

^b Measured at ~ 101 kPa and 800 K.

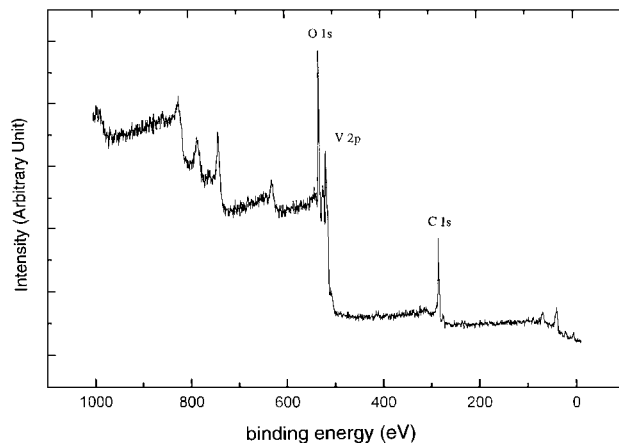


FIG. 5. A typical survey of XPS spectra for the vanadium carbide showing the core levels of V $2p$, C $1s$, and O $1s$.

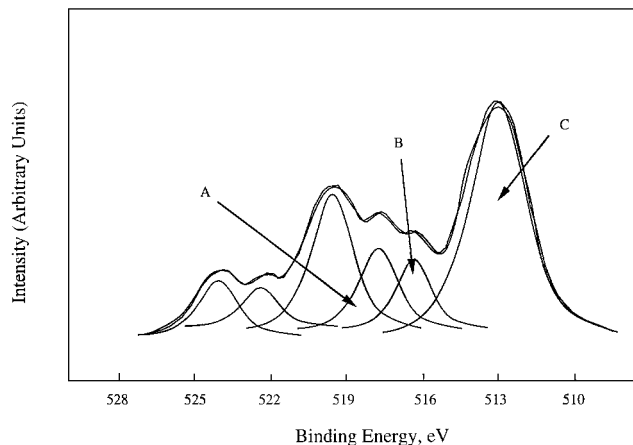


FIG. 6. The deconvoluted XPS spectrum of V $2p$ energy region for vanadium carbides. Peaks (A), (B), and (C) are due to V_2O_5 , VO_2 , and V_8C_7 , respectively.

given by the ratio of their respective degeneracies, and the intensity ratio for the V $2p_{3/2}$ -V $2p_{1/2}$ doublet should be $I(2p_{3/2})/I(2p_{1/2}) = 2/1$. A splitting energy of ~ 7.7 eV was expected for the V $2p_{3/2}$ -V $2p_{1/2}$ doublet. The binding energies of V $2p$ were shifted to lower ones ($517.3 \rightarrow 516.1 \rightarrow 513.2$ eV) as the carburization proceeded from oxides ($V^{5+} \rightarrow V^{4+} \rightarrow V^{\delta+}$). The distribution of vanadium oxidation states for vanadium carbides was estimated by the deconvolution of vanadium $2p$ spectra (Fig. 6). Peaks A, B, and C in Fig. 6 indicate the deconvoluted vanadium $2p_{3/2}$ species of V_2O_5 , VO_2 , and VC_x , respectively. A species with a V $2p_{3/2}$ binding energy of 513.2 ± 0.2 eV was newly identified by the deconvolution of V $2p$ spectra (Table 4). The

binding energy of this species is midway between those assigned to V^{4+} (516.0 ± 0.2 eV) and V^0 (511.9 ± 0.2 eV), and is about 1.3 eV higher than that for metallic V^0 . This species, then, was temporarily denoted as $V^{\delta+}$, where $0 < \delta < 4$. However, using V oxides the oxidation number was estimated by plotting the V $2p_{3/2}$ binding energies against the oxidation number (Fig. 7). The binding energy assignments for V^0 , V^{4+} , and V^{5+} states suggested that the binding energy of 513.2 eV might be due to $V^{1.3+}$. This value indicates that the absolute magnitude of charge transfer between vanadium and carbon is 1.3 electrons per vanadium in vanadium carbides, and suggests an actual ionic contribution to the bonding of vanadium carbides. Although there

TABLE 4

XPS Binding Energies (eV) of V $2p_{3/2}$, C $1s$, and O $1s$ Core Levels for Vanadium Carbides and Oxides

Catalyst code ^a	V $2p_{3/2}$			C $1s$			O $1s$		
	$V^{\delta+}$ (VC_x) ^b	V^{4+} (VO_2)	V^{5+} (V_2O_5)	C ₁ (carbide)	C ₂ (free)	C ₃ (ads)	O ₁ (VO_2)	O ₂ (V_2O_5)	O _{latt.} (lattice)
VaC-1	513.2(36) ^c	516.1(27)	517.3(37)	282.5(10)	284.3	285.8	530.2	530.9	532.1(31)
VaC-1s1	513.1(57)	516.2(18)	517.2(25)	282.4(14)	284.4	285.6	530.1	530.8	532.3(40)
VaC-1s2	513.2(76)	516.1(11)	517.3(13)	282.5(18)	284.3	285.8	530.2	530.9	532.1(42)
VaC-2	513.2(21)	516.1(44)	517.3(35)	282.5(7)	284.3	285.8	530.2	530.9	532.1(19)
VaC-2s2	513.3(50)	516.0(27)	517.2(23)	282.6(12)	284.4	285.7	530.1	530.8	532.2(47)
VaC-5	513.2(78)	516.2(14)	517.3(8)	282.6(13)	284.4	285.7	530.2	530.9	532.3(23)
VaC-5s2	513.2(81)	515.9(10)	517.1(9)	282.6(17)	284.5	285.6	530.3	530.8	532.1(46)
VaC-7	513.2(22)	516.1(23)	517.3(55)	282.5(4)	284.3	285.8	530.2	530.8	532.2(8)
VaC-7s1	513.1(34)	516.0(20)	517.1(46)	282.4(8)	284.4	285.6	530.1	530.9	532.2(24)
VaC-7s2	513.2(64)	516.1(14)	517.3(22)	282.5(15)	284.3	285.8	530.2	530.8	532.1(26)
VaC-9	513.3(42)	515.9(30)	517.2(28)	282.6(11)	284.5	285.6	530.2	530.9	532.3(12)
VaC-9s2	513.2(71)	516.1(13)	517.3(16)	282.5(16)	284.3	285.8	530.3	530.9	532.1(64)
V_2O_5	—	516.1(19)	517.3(81)	—	284.3	285.8	530.3	530.9	532.1(12)
V_2O_5 -s2	—	516.1(50)	517.3(50)	—	284.3	285.8	530.3	530.9	532.1(19)

^a The s1 and s2 indicate Ar sputtering time of 30 min and 1 h, respectively.

^b $0 < \delta < 4$ in oxidation number.

^c Area percentage is given in parentheses.

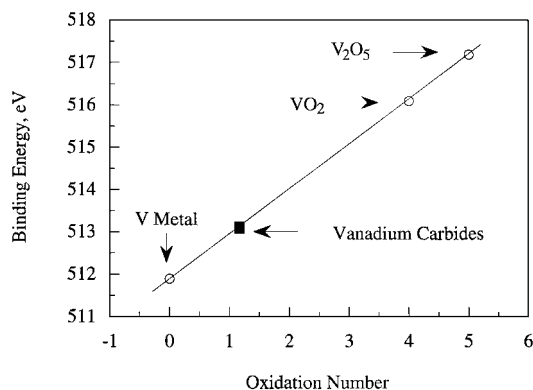


FIG. 7. Plot of V $2p_{3/2}$ binding energies versus the oxidation number.

is no reliable standard for the binding energy of $V^{1.3+}$, a similar $V^{1.2+}$ state has previously been suggested to exist for vanadium carbide films (18). It is noteworthy that with increasing Ar ion sputtering time, the area percentage of $V^{\delta+}$ is increased while those of V^{4+} and V^{5+} are decreased (Table 4). These results indicate that at the surface, the carbides are exposed as the oxide portions are decreased. This is supported by the calculation for the relative intensity of V_{VCx}/V_{VOt} , as shown in Table 5. The relative intensity of V_{VCx}/V_{VOt} is increased with increasing the sputtering time for vanadium carbides.

The binding energies of C $1s$ in the vanadium carbides are shown in Table 4. Figure 8 shows the C $1s$ spectra consisting of three deconvoluted components. The peak A in Fig. 8 indicates the C $1s$ peak with a binding energy of 285.6 ± 0.2 eV, which is associated with adsorbates on the surface such as

TABLE 5

Atomic Ratios and Relative Intensities of V $2p_{3/2}$, C $1s$, and O $1s$ Core Levels for Vanadium Carbides

Catalyst code	Atomic ratio ^a			Relative intensity ^b		
	$C_1/V^{\delta+}$ ^c	C_1/V_t	O_{1+2}/V_t	V_{VCx}/V_{VOt}	C_1/C_t	$O_{latt.}/O_{1+2}$
VaC-1	1.54	0.56	1.99	0.56	0.10	0.45
VaC-1s1	1.07	0.35	1.70	1.33	0.14	0.67
VaC-1s2	0.76	0.22	1.36	3.17	0.18	0.72
VaC-2	1.22	0.29	2.16	0.27	0.07	0.23
VaC-2s2	0.79	0.30	1.83	1.00	0.12	0.89
VaC-5	0.99	0.78	0.80	3.71	0.13	0.30
VaC-5s2	0.96	0.76	0.72	4.26	0.17	0.85
VaC-7	0.12	0.08	1.28	0.28	0.04	0.09
VaC-7s1	0.10	0.06	1.17	0.52	0.08	0.32
VaC-7s2	0.10	0.05	1.18	1.78	0.15	0.35
VaC-9	1.32	0.87	2.42	0.72	0.11	0.14
VaC-9s2	1.19	0.73	1.11	2.45	0.16	1.78

^a The C_1 , V_t , and O_{1+2} indicate the carbidic carbon, total vanadium, and total oxygen ($O_1 + O_2$), respectively.

^b The VO_t and C_t represent the total amount of vanadium oxides (VO_2 and V_2O_5) and the total carbon amount ($C_t = C_1 + C_2 + C_3$), respectively.

^c $0 < \delta < 4$ in oxidation number.

CO, CO_2 , and hydrocarbons. The carbon peak with a binding energy of 284.3 ± 0.2 eV corresponds to the free carbon contaminated on the surface of carbides (peak B in Fig. 8), suggesting that this free carbon is graphite-like. The peak C in Fig. 8 shows the carbidic carbon with 282.4 ± 0.2 eV, which is ascribed to the photoelectrons ejected from the carbon in vanadium carbide lattice. Thus, these carbidic carbon peaks were increased with increasing the sputtering time, as shown in Table 4. This can also be seen by the increase in the relative intensity of C_1/C_t in Table 5.

Table 4 also shows the O $1s$ energy region for vanadium carbides with the sputtering time. Peaks attributable to V^{4+} , V^{5+} , and chemisorbed or lattice oxygen can be identified with three different binding energies of 530.1 ± 0.2 , 530.8 ± 0.2 , and 532.1 ± 0.2 eV, respectively. Vanadium carbides used in this study had the same or very similar O $1s$ binding energies. Although the oxygen species is not yet well-assigned, it is generally agreed that peaks at ~ 530 eV are due to oxides and the peak at ~ 532 eV is attributed to oxygen species dissolved in the metal or to adsorbed oxygen. The relative intensity of the lattice oxygen inserted or dissolved into the vanadium carbides to the oxygen in vanadium oxides (VO_2 and V_2O_5) increased significantly after ion sputtering (Table 5), showing that there is a relationship between a relative intensity and a surface area of vanadium carbides. These results indicate that the oxygen extent inserted in high surface area vanadium carbide is larger than that in the low surface area carbide.

Atomic Ratios

Table 5 summarizes the XPS results, showing atomic ratios (C/V, O/V) and relative intensities of V $2p_{3/2}$, C $1s$, and O $1s$ core levels for vanadium carbides. The C/V ratios were calculated using the V $2p_{3/2}$ and C $1s$ peak areas, while the O/V ratios were estimated using the V $2p_{3/2}$ and O $1s$ peak areas. Quantitative relationships between C and V (C/V atomic ratio) were derived from calculation of peak area ratios of the respective states in the deconvoluted V $2p_{3/2}$ spectra (Fig. 6). These areas were normalized using the atomic sensitivity factors. The atomic sensitivity factors for the V $2p_{3/2}$, C $1s$, and O $1s$ peaks were 1.3, 0.25, and 0.66, respectively (14). Errors in the composition were expected to be less than $\pm 15\%$.

There are two different expressions for carbon–vanadium atomic ratios, $C_1/V^{\delta+}$ and C_1/V_t where C_1 and V_t indicate the carbidic carbon and the total vanadium, respectively. With increasing the sputtering time, the ratios of $C_1/V^{\delta+}$ and C_1/V_t generally decreased. This behavior was also observed for the atomic ratios of oxygen to vanadium, as shown in Table 5. These results again indicate that the effect of sputtering was larger on the light elements of C and O than on the heavy V metal. Similar results were also found for Mo $3p_{3/2}$, N $1s$, and O $1s$ in the molybdenum nitrides (19, 20).

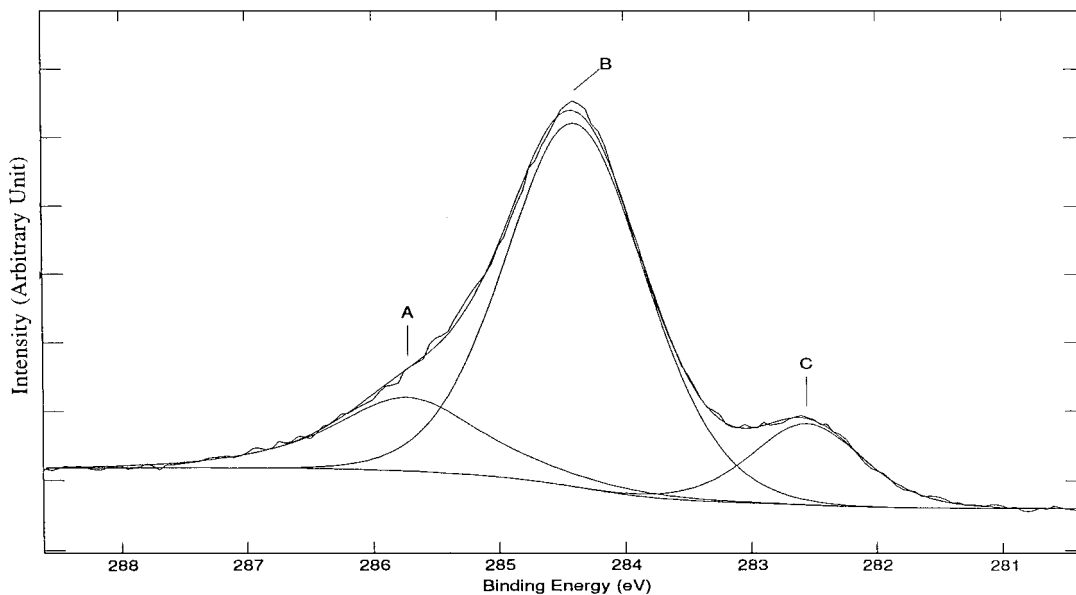


FIG. 8. The deconvoluted XPS spectrum of C 1s energy region for vanadium carbides. Peak (A) is associated with adsorbates on the surface such as CO, CO₂, and hydrocarbons. Peaks (B) and (C) indicate the free carbon and the carbidic carbon, respectively.

From the peak deconvolution of V $2p_{3/2}$ the binding energies for C 1s and V^{δ+} $2p_{3/2}$ were 282.4 ± 0.2 and 513.2 ± 0.2 eV, respectively. With reference energies for C 1s and V $2p$, the shifts in the binding energy of the C 1s and V $2p$ levels were unambiguously estimated. Taking reference energies of 511.9 eV for V $2p$ and 284.4 eV for C 1s, the V $2p$ peak tended to shift to higher energies while the C 1s peak shifted to lower energies. This result indicated that electron charge was transferred from the V $3d$ states to the C $2p$ states. The direction of charge transfer from vanadium to carbon was previously confirmed by the estimation of positive oxidation state of vanadium in the current study. Accordingly, it was considered that an ionic character of bonding was induced in the V-C lattice while the covalency of the V-C bonding has been reduced (21, 22). The expected binding energy separation between elemental V and adsorbed carbon is 227.5 eV. This result suggested that after carburizing, the increase of 3.3 eV in binding energy separation between the V^{δ+} $2p_{3/2}$ and C 1s peaks, and the binding energy separation of ~ 229.5 eV between V⁰ and C 1s, were attributed to the formation of vanadium carbides.

DISCUSSION

In the present study, the experimental data for NH₃ decomposition over vanadium carbide catalysts show that catalytic activities of vanadium carbides are similar or superior to those of platinum metal and other metal compounds. It is generally known that early transition metal carbides and nitrides exhibit catalytic properties similar to those of platinum-group metals (Group 8–10 metals in gen-

eral) (23, 24). By mixing early transition metals (Mo and W) with carbon or nitrogen, the surface reactivity of the host metals could be tempered, thereby causing their catalytic behaviors to resemble those of platinum-group metals (4, 25). For instance, the Mo metal was initially inactive for ethane hydrogenolysis but became catalytically active during carburization of the bulk metal (26). Levy and Boudart (4) reported the resemblance of WC to Pt using both the formation of water by hydrogen and oxygen at room temperature and the isomerization of 2,2-dimethylpropane to 2-methylbutane, but showing no catalytic behavior over W metal. Likewise, it was reported that vanadium films were not very active in ammonia decomposition but became activated after bulk nitridation (27). Therefore, from these previous results it appears that nitridation or carburization of the bulk metals might have caused catalytically inert parent metals to possess the catalytic behaviors similar to those of platinum-group metals. Notwithstanding that the early transition metal carbides and nitrides show catalytic properties similar to those of platinum-group metals, there is very little known concerning both the relationships between structural, stoichiometric, and catalytic properties of these materials, particularly for vanadium carbides, and the reasons that the catalytic similarities existed between these materials and platinum-group metals. Accordingly, these possible correlations and similarities for vanadium carbides are discussed in the following segments in more detail.

Relationship between Structure and Catalytic Function

Since the vanadium carbides exhibited the catalytic activity for NH₃ decomposition, the results indicated that there

is a relationship between the surface area and the reaction rates normalized by the surface area and oxygen uptake. The plot of vanadium carbide activities as a function of particle size shows that the activity decreased nearly linearly with increasing the surface area (Fig. 4). Therefore, it was concluded that NH_3 decomposition over the vanadium carbides was structure-sensitive. The ammonia decomposition has typically been found to be structure-sensitive over tungsten metal (28) and molybdenum nitrides (29). Lee *et al.* (29) reported that the ammonia decomposition rate of $\delta\text{-MoN}$ was greater than that of $\beta\text{-Mo}_{16}\text{N}_7$ or $\gamma\text{-Mo}_2\text{N}$, indicating the structure sensitivity for NH_3 decomposition on Mo nitrides. A similar result was observed for pyridine hydrodenitrogenation (HDN) over Mo carbides. Choi *et al.* (12) reported that the pyridine HDN activities over Mo carbides, which have different surface compositions but the same bulk composition, increased with decreasing the surface area. They concluded that the pyridine HDN over the Mo carbides was a structure-sensitive reaction. There are some examples of published structure-sensitive reactions over transition metal nitrides and carbides in Table 6.

For structure-sensitive reactions, the reaction rates expressed as turnover frequencies usually increase or decrease linearly with increasing the particle size, or vary convexly within the range of given particle sizes. At this time, variations in the reaction rates are again associated with the various crystallographic planes exposed at the catalyst surface. It is generally known that the structure sensitivity is typically manifested for metal particles smaller than ~ 10 nm (30). The reason for this is that within this range of particle size, the crystallographic planes or structures of metals are readily alterable as a function of particle size. However, for interstitial compounds like transition metal carbides and nitrides, the variation in the structure of materials could be possibly made within somewhat different ranges of particle size. In fact, for transition metal carbides and nitrides, the metal-metal atom distance may be increased when the nonmetal atoms such as carbon or nitrogen enter the interstices between the metal atoms (31). For vanadium carbides, the shortest metal-metal distance in vanadium metals (2.62 Å) has increased by 60% due to

vanadium carbide formation (4.16 Å). Subsequently, the physical, chemical, and electronic properties of the host metals can significantly be altered. For catalysts like metal carbides and nitrides, it is also believed that there are some differences between the activities of materials with different composition and structures that can coexist.

Given the observed variations in activity with the surface area, the near surface C/V stoichiometry was a function of the particle size, even for the relatively large particles in the metal carbides. Table 6 also shows the variations of the particle size of early transition metal carbides and nitrides for structure-sensitive reactions within a wide range. For example, it was reported that the significant variations in the near surface compositions and structures were observed for Mo nitrides with the particle sizes between 5.5 and 159.6 nm (19). All of these Mo nitrides were found to have the same bulk structure ($\gamma\text{-Mo}_2\text{N}$, fcc) with $\text{N/Mo} = 0.5$. However, the structure in the near surface was body-centered with different N/Mo ratios ranging from 0.48 to 1.3. In the same manner, for the structure sensitivity over vanadium carbides the different surface composition with particle size should also be considered, as demonstrated later in this study.

Relationship between Surface Composition and Catalytic Function

It is important to find out whether there is a correlation between the surface composition and the catalytic properties of vanadium carbides or not. Since catalysis is a surface phenomena, the surface properties should also be considered in entirely understanding the catalytic function of materials. Therefore, using XPS the electronic structures and the surface compositions were obtained for both the vanadium carbide catalysts in this study and the vanadium oxides for reference. While the surface stoichiometries of C/V for vanadium carbides are in the range of 0.1 and 1.19 after 1 h sputtering, the average bulk composition of C/V obtained from a CHN analyzer was found to be ~ 1.75 . Here, the larger average bulk composition for V_8C_7 was considered to be due primarily to the presence of polymeric carbon produced during the carburization of vanadium

TABLE 6

Published Structure-Sensitive Reactions over Transition Metal Nitride and Carbide Catalysts

Catalysts	Reaction type	Particle sizes (nm) ^a	Phases present	Reference
Mo nitrides	NH_3 synthesis	3, 12, 63	Mo_2N (FCC)	(44)
Mo nitrides	Pyridine hydrodenitrogenation	5, 15, 27, 53, 160	Mo_2N (FCC)	(15)
Mo carbides	Butane hydrogenolysis	3, 5, 11, 32	MoC_x (HCP)	(45)
W carbides	Butane dehydrogenation	10, 35, 55, 96	WC_x (HEX)	(32)
Mo carbides	Pyridine hydrodenitrogenation	58, 66, 74, 405	Mo_2C (HCP)	(12)
V nitrides	NH_3 decomposition	89, 101, 126, 145	VN (FCC)	(46)

^a Measured for all the unsupported materials.

oxide. Hence, these results indicate that for vanadium carbides, the properties of surface are different from those of bulk. Compared to the bulk composition, the smaller compositions suggest the carbon-deficient vanadium carbides while the larger values indicate the vanadium carbides containing excess carbon atoms located on other sites than lattice carbons in the cubic structure, such as interstitial or substitutional of vanadium atoms. These excess carbon atoms have a different bonding from V-C one in the cubic structure.

One might have questions concerning the reason for the observation that the surface properties for vanadium carbides were different from the bulk ones. In fact, it is not unusual to observe the compositional difference between the surface and the bulk in the early transition metal nitrides and carbides (19, 32). Choi *et al.* (15) found that using XPS, the surface compositions of N/Mo for molybdenum nitrides varied ranging from 0.48 to 1.3 while all the molybdenum nitrides had the same bulk composition of N/Mo = 0.5. They also observed that the structure in the near surface of molybdenum nitrides was body-centered, while the structure in the bulk was face-centered. Hakansson *et al.* (33) reported that using the vanadium carbide film with the fcc (100) crystal face, the carbon atoms in the bulk interstitial sites would be bonded to six metal atoms while those on the topmost surface layer would be coordinated to at most five metal atoms. However, for the vanadium carbides with the fcc (111) configuration, the surface would be terminated by vanadium atoms, with sequential layers of carbon and vanadium toward the bulk structure (34, 35). It was also reported that the C 1s energy level of the surface carbide is shifted from the bulk carbides for (100)- and (111)-terminated VC surfaces (33), and this shift is probably related to structural differences. Since these low-index surfaces of (100) and (111) are the most symmetric faces of fcc crystal, the similar structural difference is also expected to exist for other vanadium carbides with different crystal faces, for example, the polycrystalline vanadium carbides in the present study.

It was found that the variations in the surface properties of vanadium carbides correlated well with significant changes in the catalytic properties. Figure 9 shows the catalytic activities and the particle sizes as a function of surface stoichiometry (C/V), suggesting an almost linear relationship between the activities and the particle sizes, and the C/V values. These results indicate that the most active catalyst was carbon-deficient at surface and had a large particle size. Chen *et al.* (36) reported that using a VC/V(110) film, the fractions of decomposition of 1,3-butadiene, isobutene, and 1-butene decreased with increasing the C/V ratio. It was suggested that using HREELS, the interaction between the C=C bond of adsorbate and the substrate is much weaker on the carbide-modified surface. Some similar results have been previously reported for tungsten carbide catalysts (2,

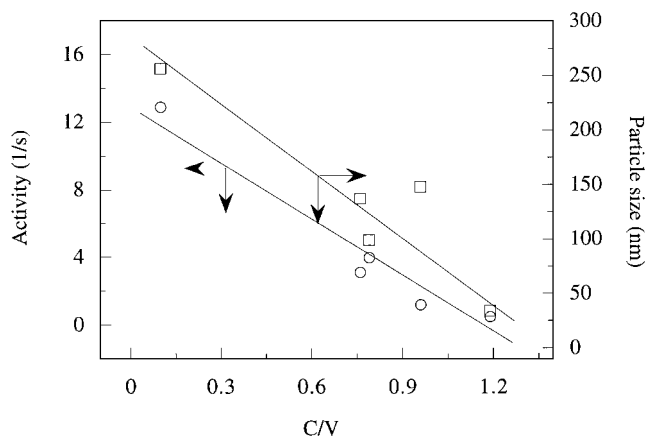


FIG. 9. The activities and the particle sizes as a function of the ratio of carbon atom/vanadium metal over vanadium carbides.

6, 7). Leclercq *et al.* (2) reported that WC and W₂C were active for cyclohexane dehydrogenation, and the most active catalyst was slightly carbon-deficient at the surface. It is well known that the properties of transition metal carbides depend on the amount of carbon present in the interstitial sites of the host metal lattice (6). Therefore, it is anticipated that the stoichiometry near the surface also affects the catalytic function. Ko and Madix (7) reported that the amount of carbon at the surface of W(100)-(5 × 1)C markedly affected the product distributions during the decomposition of acetaldehyde and ethanol.

Similarity between Structures of Vanadium Carbides and Platinum-Group Metals

As mentioned earlier, it is generally known that the early transition metal carbides and nitrides show catalytic properties similar to those of platinum-group metals. In the case of vanadium carbides, the catalytic properties can be generally described as similar to those of Pt-group metals, although the vanadium carbides may have a much higher activity for the activation of N-H bonds. Nevertheless, there are some questions to be addressed regarding why these materials contain those kinds of properties. One possible explanation is that the surface electronic structure of vanadium carbides is similar to that of platinum-group metals. As already discussed in this study, there is a strong interaction between metal 3d states of vanadium and 2p states of carbon as a result of the formation of vanadium carbides. This study, thereby, suggested that the electron charge in vanadium carbides was transferred from the V 3d states to the C 2p states, resulting in the change of density of states at the Fermi level, $N(E_F)$, the energy below which all the electronic states are filled up and above which they are empty. It is generally known that the electronic structure of early transition metal carbides is similar to that of

platinum-group metals (Ru, Os, Rh, Pd, Pt) (37). The theoretical and experimental calculations showed that the values of $N(E_F)$ for vanadium carbide were decreased by about 34 and 66%, respectively (38). These results suggest that the electronic structure of vanadium carbides became similar to that of platinum. Subsequently, it was assumed that the variation in the density of states might have caused vanadium carbides to contain the platinum-like catalytic behaviors in this study. A similar result has been observed by Chen *et al.* (37), showing that there was a resemblance between the surface reactivities of carbon-modified V(110) and platinum-group metals. They also reported that using dehydrogenation of isobutane, the vanadium carbide showed a better catalytic performance compared to vanadium metal, and exhibited the similar surface properties to that of platinum metal. They suggested that this similarity between vanadium carbides and platinum metal was due to the combined effects of (1) a charge donation from vanadium to carbon and (2) the narrowing of *d*-bands of vanadium as a result of vanadium carbide formation.

There are also some previous reports that show a similarity between the surface reactivities of other transition metal carbides and platinum-group metals, and thereby these catalytic behaviors were ascribed to semblance in the electronic structures of metal carbides and platinum-group metals (4, 38, 39). Levy and Boudart (4) reported that compared to tungsten metal, the catalytic activities of WC increased because the electron was donated from carbon to W metal. They also proposed that this electron transfer resulted in the production of electronic structure similar to that of Pt. Nakazawa *et al.* (39) showed that the coalition of C 2*p* with W 5*d* and W 6*s* bands increases the density of states near Fermi level, producing the platinum-like behavior of WC. One more similar result was reported by Gao and Qin (3), showing the charge transfer from tungsten to carbon and the platinum-like behavior of WC. Thus far, the direction of charge transfer between carbon and tungsten has been one of the most controversial issues in the tungsten carbides. Nevertheless, it is obvious that the density of states at the Fermi level has been changed as a result of metal carbide formation, which becomes similar to that of platinum metal.

Although there is a similarity between the electronic structures of early transition metal carbides and platinum-group metals, this explanation may not be sufficient for platinum-like catalytic behaviors of metal carbides. The reason for this is that some other transition metal such as Nb also has the density of states at Fermi level similar to that of platinum, but exhibit very little or no catalytic activities toward Pt-catalyzed reactions. While these transition metals do not demonstrate the exchange enhancement of the magnetic susceptibility, the platinum-group metals show strong susceptibility enhancement. Based on this difference another important condition for high catalytic activity might

be related to the magnetic properties of metals. Therefore, the relationship between the magnetic susceptibilities and catalytic properties of these materials should be the object of further studies.

Comparison between Catalytic Properties of Vanadium Carbides, Platinum, and Other Compounds

It is also important to compare the catalytic activities of vanadium carbides with those of platinum, vanadium nitride, and molybdenum carbide in terms of the electronic structure. On an oxygen uptake basis, the vanadium carbides were about 1 to 2 orders of magnitude more active than platinum catalyst. It was considered that the high activity of vanadium carbides was due to the broadening of the unfilled portion of the vanadium *d*-band as a result of carbide formation. Houston *et al.* (40) measured the density of states of the unfilled portion in the conduction bands of W, WC, and Pt, showing that the unfilled portion of the *d*-band of WC became broader than that of both W and Pt. Since it is generally believed that vanadium carbides have an electronic structure similar to that of tungsten carbides (23), one might expect a similar variation in the unfilled portion of the *d*-band of vanadium carbides. Subsequently, it appears that a broadening of the unfilled portion of the *d*-band would give vanadium carbides an opportunity to be better electron acceptors than both the host vanadium metals and the platinum-group metals. Because the reaction conditions used in this study were similar to those of Oyama (17) for vanadium nitrides, the kinetics of NH₃ decomposition could be described by two irreversible steps, the adsorption of ammonia and the desorption of dinitrogen (called the Tamaru mechanism). Therefore, since the activation of the N-H bond involves first the offering of bonding electrons to the unfilled portion of metal substrate (41), these vanadium carbides might be much more efficient catalysts than the platinum metal in the N-H bond activation, as shown in the present study.

Another comparison is that the activities of all the vanadium carbides are generally lower than those of molybdenum carbides. This difference in activities might be related to the degree of electron transfer between metals and carbon. According to comparative investigations of a series of early transition metal carbides, nitrides, and oxides (42), the magnitude of charge transfer should follow an order exhibiting Pauling's electronegativity scale, suggesting a larger degree of charge transfer in the vanadium carbides than that in the molybdenum carbide. This is supported by the results of Samsonov *et al.* (1), demonstrating that Group VIB, VB, and IVB carbides were active for ethylbenzene dehydrogenation. They also reported that the Group VIB carbides were more active than the Group IVB and VB carbides. In the same manner, one might expect a smaller degree of charge transfer of the vanadium carbides than that

in the vanadium nitrides since carbon is less electronegative than nitrogen. This is consistent with the observation of this study that the vanadium carbides were more active than the vanadium nitrides.

CONCLUSIONS

The properties of a series of vanadium carbides prepared using vanadium oxides (V_2O_5) by the temperature-programmed carburization depended significantly upon the synthesis conditions. Among them, the space velocity and heating rates were the most influential preparative parameters. The vanadium carbides with high surface areas were prepared using the higher space velocities. There was a nearly linear relationship between the O_2 uptake and the BET surface area for these materials.

The vanadium carbides were catalytically active for NH_3 decomposition. The ammonia decomposition activities normalized by the surface area and oxygen uptake varied with changes in the surface area and particle size, suggesting that NH_3 decomposition over the vanadium carbides appeared to be structure-sensitive. This response was considered to be due to variations in the surface stoichiometry with particle size. Using XPS, it was found that the activities and particle size decreased with increasing the surface stoichiometry (C/V) of vanadium carbides. These results suggested that the most active catalyst was carbon-deficient and had a large particle size. The activities of the vanadium carbides were about 2 times less than those of Mo_2C catalyst while vanadium carbides had higher activities by a factor of 1 or 2 than those of Pt/C catalyst. The difference in activities of the vanadium and molybdenum carbides might be related to the degree of electron transfer between metals and carbon. A similarity between the catalytic behaviors of vanadium carbides and platinum metal appeared to be due to the similar electronic and magnetic properties of these materials. Nevertheless, on a per oxygen uptake basis the vanadium carbides might be much more efficient catalysts than the platinum metal in the N-H bond activation. The high activity of vanadium carbides was considered to be attributed to the broadening of the unfilled portion of the vanadium *d*-band as a result of carbide formation.

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