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Synthesis and Catalytic Properties of Vanadium Nitrides

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Vanadium nitride catalysts were synthesized by the temperature-programmed reduction of vanadium oxide (V_2O_5) with pure NH_3. The resulting materials contained VN or VN with a negligible amount of vanadium sesquioxide (V_2O_3) in the bulk after the nitrization of V oxides, indicating that the structural properties of these materials were strong functions of the heating rate and space velocity employed. The V nitrides 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 V nitrides appeared to be structure-sensitive. While detailed relationships between the catalytic activity and surface composition could not be ascertained, there was a direct correlation between the activity, and the surface area and grain-boundary length. The most active catalyst, VN-c, which contained the δ-phase, had the greatest grain-boundary length. The catalytic properties of V nitrides were comparable or superior to those of a $Ni/SiO_2{\cdot}Al_2O_3$ catalyst. These results suggested that the characteristics of the active sites in the vanadium nitrides were similar to those in the Group 8—10 metal-based catalysts.

Vanadium nitride is one of the transition-metal nitrides which possess unique physical and chemical properties, due to the presence of nitrogen atoms in the interstitial sites of the parent metal lattice. In catalysis, transition-metal nitrides have been reported to be very active for reactions including hydrodenitrogenation,[1,2] CO hydrogenation,[3] and NH_3 synthesis.[4] Furthermore, their function as catalysts for dehydrogenation, hydrogenolysis and isomerization reactions resembles that of platinum-based catalysts.[5—7] Since ammonia is a product of the hydrodenitrogenation of most organonitrogen compounds, and can influence the activity and selectivity of the catalyst, the interaction of NH_3 with the catalyst surface is of particular importance. For instance, ammonia suppressed the hydrogenolysis and dealkylation rates during quinoline hydrodenitrogenation over Mo nitrides,[8] and poisoned a number of other catalytic reactions.[9]

Recently, Oyama reported that vanadium nitride is active for the decomposition of ammonia.[10] He also found that from a kinetic study, the rate parameters of vanadium nitride are similar to those of iron and platinum. Even though vanadium nitride is one of the promising candidates for catalytic reactions as substitute for Pt group metals, very little is currently known about its catalytic properties. This paper describes the surface, bulk, and catalytic properties of vanadium nitrides. Vanadium nitrides were prepared by a temperature-programmed reduction of vanadium(V) oxide precursor (V_2O_5) with pure NH_3. X-ray diffraction and BET surface-area measurements were employed to characterize these materials. The catalytic properties were evaluated using the NH_3 decomposition, and compared to the $Ni/SiO_2{\cdot}Al_2O_3$ catalyst.

Experimental

Vanadium nitrides were synthesized via the TPR (temperature-programmed reduction) of V_2O_5 (99.95%, Junsei Chemical Co. Ltd.) with pure NH_3. To obtain various kinds of vanadium nitrides with different structures and compositions, different heating rates and molar hourly space velocities were utilized. For the vanadium nitrides, two heating ramps (β_1 and β_2) and two NH_3 molar hourly space velocities of 12.5 and 25 h^{-1} were used for the synthesis. The space velocity is defined as the NH_3 molar flow rate divided by the molar amount of V_2O_5. A summary of the synthesis conditions and surface areas of the vanadium nitrides is given in Table 1. The reaction temperature for the synthesis of nitrides was quickly increased from room temperature to 573 K in half an hour. The temperature was increased from 573 to 873 K at 75 or 150 K h^{-1} during the first heating ramp (β_1). The temperature was then increased from 873 to 1123 K at 150 or 300 K h^{-1} during the second heating ramp (β_2), and held at 1123 K for an additional hour. These synthesis conditions are similar to those employed previously to prepare vanadium nitride.[10] 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 was continued for 2 h, and the product was then removed from the reactor for subsequent analysis.

The Quantasorb model Chembet 3000 sorption analyzer was used to measure the BET surface areas of the materials. Prior to N_2 BET surface area measurements, the material was reduced isothermally in H_2 (20 $cm^3\,min^{-1}$) at 673 K for 3 h, purged in flowing He (20 $cm^3\,min^{-1}$) for 10 min, and then cooled to room temperature. Standard single-point BET measurements were made at 77 K using a 30.1% N_2 in a He mixture (Taedug Gas Co.). Pulses of purified

Table 1. Synthesis Conditions and Bulk Structural Properties of Vanadium Nitrides and Precursor

Catalyst code	Heating rate (β_1) $\mathrm{K\,h^{-1}}$	Heating rate (β_2) $\mathrm{K\,h^{-1}}$	Space velocity[a)] $\mathrm{h^{-1}}$	Surface area[b)] $\mathrm{m^2/g^{-1}}$	Particle size Å	Crystallite size[c)] Å	$D_p/D_c)^2$ ($\times 10^2$)
VN-a	150	300	25	6.8	1450	331	1.32
VN-b	75	300	25	7.8	1261	236	2.27
VN-c	150	150	25	11.0	890	153	3.46
VN-d	150	300	12.5	9.7	1011	219	2.09
VN-d	150	300	12.5	10.0[d)]	981	219	2.05
V_2O_5	—	—	—	3.9	4356	—	—

a) Ratio of molar flow rate of gas to moles of precursor. b) Measured after pretreatment in H_2 flow at 673 K for 3 h. c) Based on the most intense peak in the patterns. d) Measured after pretreatment in H_2 flow at 673 K for 5 h.

N_2 (99.998%, Taedug Gas Co.) were used to calibrate the amount of adsorbed N_2. The average particle size (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 6.13 $\mathrm{g\,cm^{-3}}$ for V_2O_5 and VN, respectively). A computer-controlled Rigaku Rotaflex DMAX-B (Cu $K\alpha$ source) was used to evaluate the bulk structure of the materials. The average crystallite size (D_c) was estimated using the Scherrer equation,[11)] $D_c = 0.9\lambda/(\beta \cos\theta)$, where λ is the wavelength of the Cu $K\alpha$ radiation (1.5405 Å), θ is the Bragg angle, and β is the peak full width at half-maximum intensity of the most intense peak in the pattern.

For ammonia decomposition a catalyst weight of ca. 0.2 g was used and 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 2K $\mathrm{min^{-1}}$, held at 673 K for at least 14 h then cooled to the reaction temperature. After a H_2 pretreatment, NH_3 (99.995%) was passed over the catalyst at atmospheric pressure with the same inlet space velocity based on a bed volume of 7500 $\mathrm{h^{-1}}$ for NH_3 decomposition. Activity measurements were performed at temperatures of between 593 and 653 K. The activities were reproducible to within $\pm 15\%$. The catalytic properties of nitrides were compared to those of 65.5 wt% $Ni/SiO_2\cdot Al_2O_3$ (Aldrich) that was pretreated under similar conditions. The reactor effluent was analyzed using an on-line 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.

Results and Discussion

Table 1 shows that the BET surface areas of the vanadium nitrides ranging from 6.8 to 11.0 $\mathrm{m^2\,g^{-1}}$, depended on the synthesis conditions employed. In general, it appeared that the heating rate employed during the first and second heating ramps (β_1 and β_2) had a significant effect on the resulting surface areas. Increasing the heating rate resulted in the production of materials with lower surface areas, regardless of space velocity used. A similar result was observed for the synthesis of molybdenum nitrides via TPR of molybdenum oxides.[12)] Variations in the surface area with the heating rate are not unusual, since one would expect these factors to influence the product selectivity of the solid-state reactions. It was not anticipated that the higher space velocity would result in the production of materials with a lower surface area. This is contrary to previous studies which indicated that high space velocities were necessary for the synthesis of high surface-area nitrides and carbides.[12,13)] The reason for that difference is not yet clear, but may be related to other synthesis conditions over the range studied, such as the heating rates. Choi et al. reported similar behavior during the preparation of Mo_2C.[14)] Table 1 also shows the effect of the H_2-treatment condition on the surface area of vanadium nitride. As the treatment time increased from 3 to 5 h, the surface area of VN-d remained almost constant. XRD results indicated that while VaN-c contained only the VN phase, the resultant product for VN-a, VN-b, and VN-d was VN with a negligible amount of V_2O_3 (vanadium sesquioxide). VN possesses the mononitride δ-phase with the NaCl (cubic close-packed) structure. Since we estimated the crystallite size using the most intense peak in the patterns, a comparison of the crystallite and particle sizes suggested the presence of polycrystalline aggregates in vanadium nitrides. There was a nearly linear correlation between the crystallite and particle sizes, indicating that the particle size increased with increasing the crystallite size (Table 1). Increasing the first or second heating ramp caused the sizes of the particle and crystallite to increase.

Vanadium nitrides were active for ammonia decomposition. Figure 1 shows typical catalytic behavior of vanadium nitride with time on stream for the decomposition of ammonia. The freshly prepared vanadium nitride exhibited

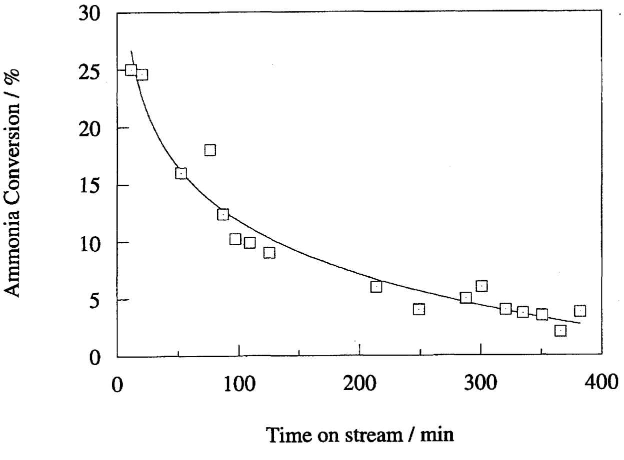

Fig. 1. NH_3 conversion versus time on stream over vanadium nitride at 653 K.

the highest initial conversion, but then gradually lost activity with time. The NH_3 decomposition reaction rates decreased to the steady-state activities during the first 100 min on stream, and then remained constant for several hours. Table 2 shows a steady state activity for all vanadium nitrides. Among the vanadium nitride catalysts, VN-c had the highest steady state activity for NH_3 decomposition. The VN-c catalyst was ca. 13 times more active than VN-a, having the lowest activity. This suggested that the active species in the VN-c catalyst was different from that in the VN-a catalyst. In fact, the most active VN-c catalyst contained the mononitride VN with the δ-phase, while the other samples had a VN phase with a negligible amount of V_2O_3 (vanadium sesquioxide). The finding that the nitride with δ-phase exhibited the highest activity was not remarkable. Choi et al. reported that the molybdenum nitride catalyst having the δ-phase at the surface showed the highest activity over pyridine hydrodenitrogenation.[2] Table 2 also exhibits a catalytic activity of $Ni/SiO_2{\cdot}Al_2O_3$ to compare with those of vanadium nitrides on a per gram or surface-area basis. Even though vanadium nitride catalysts were exceeded by $Ni/SiO_2{\cdot}Al_2O_3$ catalyst in initial activity, the steady state reaction rates and activities for vanadium nitrides were comparable to those determined for the $Ni/SiO_2{\cdot}Al_2O_3$ catalyst. On a per gram basis, the most active catalyst of VN-c was more active than $Ni/SiO_2{\cdot}Al_2O_3$ catalyst. Furthermore, on a surface-area basis the activity of VN-c was an order of magnitude higher than that of the $Ni/SiO_2{\cdot}Al_2O_3$ catalyst. These results suggested that the characteristics of active sites in the vanadium nitrides were similar to those in the Group 8—10 metal based catalysts. The reaction rates and activities of the vanadium nitrides used in this study were similar to or an order of magnitude higher than those reported for vanadium nitride in the literature for an ammonia-decomposition reaction.[10]

It is generally known that the vanadium films is relatively inert in NH_3 decomposition but become catalytically active after nitrization.[15] Similar results were reported for tungsten and molybdenum metals which were initially inactive, but became active in catalytic reactions during nitriding.[6,7] The nitrization of these metals caused their catalytic behaviors to resemble those of Pt and Ru, respectively.[6,16] Recently it was reported that from a kinetic study vanadium nitride showed rate parameters similar to those of iron and platinum.[10] Similarly, vanadium nitrides synthesized in this study exhibited catalytic activity for NH_3 decomposition. The results indicated that the activities normalized by the surface area increased with increasing surface area. Figure 2 shows plots of the vanadium nitride activities as a function of the surface area, indicating a linear relationship between the activity and the surface area. The linear relationship suggested that NH_3 decomposition over the vanadium nitrides was structure-sensitive. Similar conclusions have been drawn for ammonia synthesis over molybdenum nitride catalysts.[4,17] Choi et al. have reported that the pyridine HDN (Hydrodenitrogenation) activities increased with decreasing surface area over the molybdenum carbides.[14] They concluded that the pyridine HDN over the molybdenum carbides was a structure-sensitive reaction.

In general, structure-sensitivity over metal catalysts is associated with variations in the reaction rates with the crystallographic places of the catalyst surface. However, the concept of structure-sensitivity for vanadium nitrides must also include variations in the activities of surfaces with differing V : N stoichiometries. Therefore, the character of the clean surface was expected to be affected by the size of the nitride particles. We also noticed that the activity normalized by the surface area increased as the deviation between the particle and crystallite sizes increased. This result suggested that the catalytic activity was influenced by characteristics

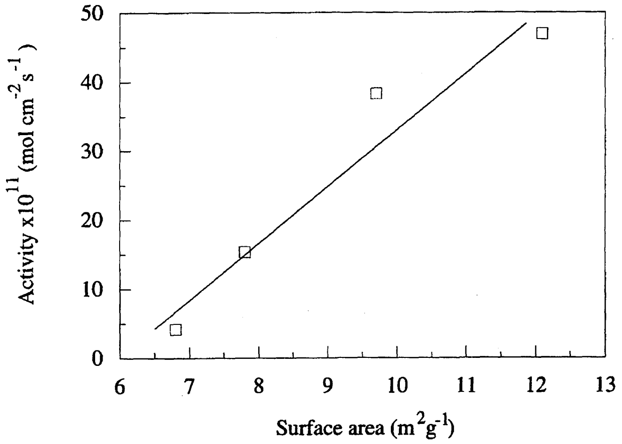

Fig. 2. Activities as a function of surface area over vanadium nitrides.

Table 2. Catalytic Reaction Rates of Vanadium Nitrides for NH_3 Decomposition

Catalyst	Surface area	Reaction rate[a]	Activity[a]	$D_p/(D_c)^2$ [d]
code	$m^2\,g^{-1}$	$\times 10^6$ mol $g^{-1}s^{-1}$	$\times 10^{11}$ mol $cm^{-2}s^{-1}$	$\times 10^2$
VN-a	6.8	2.2	3.3	1.32
VN-b	7.8	9.7	12.5	2.27
VN-c	12.1	48.1	43.7	3.46
VN-c	12.1	38.8 [b]	35.3 [b]	3.46
VN-d	9.7	29.7	30.6	2.09
$Ni/SiO_2–Al_2O_3$	—	38.8	2.1	—
VN[c]	25.2	5.1	2.0	—

a) Reaction rates and activities measured at ca. 101 kPa and 653 K. b) Measured at ca. 101 kPa and 593 K. c) From Ref. 10. d) D_p and D_c indicate the particle and crystallite sizes, respectively.

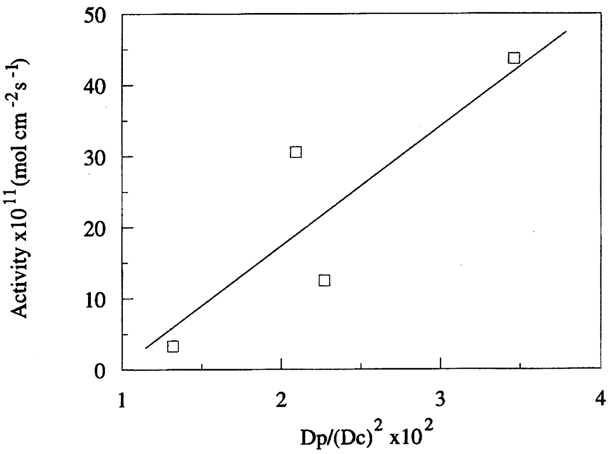

Fig. 3. Activities versus particle size/(crystallite size)^2 over vanadium nitrides.

associated with the grain boundary, which is proportional to particle size/(crystallite size)^2. For the vanadium nitrides, there was a direct correlation between the activity and the surface grain boundary length (Fig. 3). It can be seen that the most active catalyst, VN-c which contained the δ-phase, had the greatest grain boundary length. We have consequently concluded that for decomposition of NH_3, the active sites of vanadium nitride catalysts resided along grain boundaries.

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