Synthesis and Catalytic Properties of Niobium Carbides

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Abstract: The carburization of Nb₂O₅ (99.99%, Aldrich Chemical Co. Ltd.) was carried out using pure methane in a temperature-programmed manner. The variation in BET surface areas and oxygen uptakes of the niobium carbides was observed with different heating rates and molar hourly space velocity, suggesting that the sorption properties of these materials were strong functions of these preparative conditions used in this study. It was observed that these materials were active for ammonia decomposition reaction. While the oxygen uptake increased with increasing the BET surface area, the conversion of ammonia decomposition decreased. These results suggest that NH₃ decomposition over these materials is structure-sensitive. As in the case of other transition metal carbides (V, Ta, and Mo), this structure-sensitivity was considered to be ascribed to the variations of surface composition with surface area. The conversion of ammonia decomposition for the materials prepared in the current study was observed to be comparable to that determined for the commercial niobium carbides.

Keywords: niobium carbide, NH₃ decomposition, activity, surface area

Introduction

Previous reports show that transition metal carbides had the competitive activities for reactions including hydrogenation [1,2] and ethylene hydrogenation [3]. In particular, the catalytic activities of these transition metal carbides (V, Ta, Mo) for ammonia decomposition reaction were comparable or superior to those of platinum [4,5]. For instance, vanadium carbides had activities that were 1-3 orders of magnitude higher than Pt/C catalyst. Since catalysis takes place at surface, the surface properties (structure and stoichiometry) of these materials should be related to the catalytic function in order to completely understand the differences. In the case of transition metal carbides, the amount of carbon present in the host metal lattice could influence the catalytic and adsorptive properties. Recently, it was reported that the catalytic activities of vanadium carbides decreased with increasing the atomic ratio of C/V [5]. These results indicated that the most active catalyst was carbon-deficient at the surface. Similar result was reported for cyclohexane dehydrogenation over tungsten carbides, showing that the carbon-deficient tungsten carbides had the highest activity [6]. We also found that the pyridine hydrodenitrogenation activities over the Mo carbides varied with the surface area, suggesting a structure-sensitive reaction. These results led to the conclusion that the surface stoichiometry of transition metal carbides was a function of surface area. Based on these observations, it is important to attempt to relate the catalytic function of transition metal carbides to the surface area for the purpose of understanding the fundamental relationship between the catalytic activity and surface properties.

Here, in this study the surface and catalytic properties of niobium carbides were described. These carbides were synthesized by the temperature-programmed reaction of niobium oxide precursor (Nb₂O₅) with pure methane. We employed the characterization techniques including BET total surface area measurements and oxygen chemisorption to evaluate the sorptive properties of these materials. Finally, ammonia decomposition reaction was used for the evaluation of catalytic properties of these materials.

Experimental

The precursor niobium oxide (Nb₂O₅, 99.99%, Aldrich
Chemical Co. Ltd.) was used for the synthesis of niobium carbides using pure methane in a temperature-programmed manner. In order to obtain different structural and compositional properties of the final materials, it is necessary to use different preparative conditions such as heating rates and molar hourly space velocities. As the space velocity is defined as the CH₄ molar flow rate divided by the molar amount of Nb₂O₅, molar hourly space velocities of 25, 71, and 107 h⁻¹ were used in this study. Table 1 shows the effect of the synthesis conditions on BET surface area. As the catalyst code is given in Table 1, the NC-A indicates the commercial niobium carbide (Aldrich Chemical Co. Ltd.) and the highest and lowest surface area niobium carbides represent NC-2 and NC-1, respectively. The reaction temperature for carburization was quickly increased from room temperature to 873 K in one hour. The temperatures for all the samples except for NC-1 were then increased from 873 to 1173 K (heating rate I), and continuously from 1173 to 1373 K (heating rate II). The different linear temperature increases from 973 K to 1173 K, and from 1173 K to 1373 K were used for NC-1. These materials were held at the final temperature of 1373 K for an additional hour. After carburization, the temperature decreased then to room temperature and the product was passivated for 2 h in a mixture of 0.5% O₂/He (Taedug Gas Co.) flowing at 20 cc/min. It was necessary to passivate the final samples in order to prevent further bulk oxidation.

A Quantasorb model Chembet 3000 sorption analyzer was used for measurements of BET surface area and oxygen uptakes. Before measuring the BET surface area and oxygen uptake, the isothermal H₂ reduction was made at 673 K for 3 h at 20 cm³/min. After reduction, the sample was purged in flowing He (20 cm³/min) for 10 minutes then cooled to room temperature. A 30.1% N₂/He mixture (Taedug Gas Co.) and a purified N₂ (99.998%, Taedug Gas Co.) were used for standard single point BET measurements and calibration of the amount of adsorbed N₂, respectively. The same hydrogen pretreatment conditions were also used for measurements of oxygen chemisorption.Calibrated volumes of 9.98% O₂ in He (Taedug 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.

In this study, the main stream in performing the ammonia decomposition reaction, for example, reaction system (reactor size, catalyst weight,...) was the same as that of Choi and coworkers [5]. However, the reaction condition (reaction temperature) used in this study was different. We used ~0.2 g of catalyst which was spread over a 9 mm O. D. pyrex glass flow reactor. A chromel-alumel (K type) thermocouple was used to monitor the reaction temperature. At first, the catalyst was reduced using pure H₂ from room temperature to 673 K at a rate of 118.8 K/h, held at 673 K for at least 14 h then cooled to the reaction temperature. After reduction, the reactant ammonia gas (99.995%) was passed over the catalyst at atmospheric pressure with the inlet space velocity based on the bed volume of 7500 h⁻¹. The catalytic activities were measured at four different temperatures of 783, 798, 813, and 843 K. All of these measurements were in agreement with an estimated experimental error of ±10%. The catalytic properties of niobium carbides prepared in the current work were compared to that of commercial niobium carbide (99.95%, Aldrich Chemical Co. Ltd.) that was 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.

### Results and Discussion

Table 1 shows the BET surface areas of the niobium carbides. These results showed that the surface areas were dependent on the synthesis conditions employed such as heating rate and space velocity. It is not unusual to note that the resultant surface areas are strong functions of preparative conditions in the synthesis of transition metal carbides and nitrides [4-5,7-8]. The surface areas of niobium carbides prepared in this study are generally higher than that of the commercial niobium carbide (NC-A, Aldrich Chemical Co. Ltd.) (between 3

<table>
<thead>
<tr>
<th>Catalyst code</th>
<th>Heating rate I (K/h)</th>
<th>Heating rate II (K/h)</th>
<th>Space velocity (hr⁻¹)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-1</td>
<td>100</td>
<td>200</td>
<td>25</td>
<td>0.91</td>
</tr>
<tr>
<td>NC-2</td>
<td>100</td>
<td>200</td>
<td>107</td>
<td>5.15</td>
</tr>
<tr>
<td>NC-3</td>
<td>50</td>
<td>200</td>
<td>107</td>
<td>3.84</td>
</tr>
<tr>
<td>NC-4</td>
<td>100</td>
<td>100</td>
<td>107</td>
<td>3.38</td>
</tr>
<tr>
<td>NC-5</td>
<td>50</td>
<td>200</td>
<td>71</td>
<td>2.81</td>
</tr>
<tr>
<td>NC-A</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.34</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.67</td>
</tr>
</tbody>
</table>

* Heating rates (I and II) for all the samples except for NC-1 indicate the linear temperature increases from 873 K to 1173 K, and from 1173 K to 1373 K, respectively. The different linear temperature increases from 973 K to 1173 K, and from 1173 K to 1373 K were used for NC-1.

⁺ Ratio of molar flow rate of gas to moles of precursor.

⁻ Measured after pretreatment in H₂ flow at 673 K for 3 h.

⁺⁺ Samples were used for NH₃ decomposition.
and 15 times higher). The highest surface area niobium carbide (NC-2) shows 15 times higher in surface area than a commercial niobium carbide (NC-A). Compared to a precursor of Nb₂O₅, the increase rate in surface areas of niobium oxide carburized showed 760%. This result suggests that niobium carbides could be prepared using different synthesis conditions and a function of preparation conditions. The surface areas of niobium carbides increased with increasing heating rates. However, it was shown that the resulting surface areas were more dependent on space velocity than on heating rate. Generally, the surface areas of niobium carbides were smaller than those of molybdenum carbides prepared by Choi and coworkers [7]. These decreases in surface area were assumed to be due to the severe deposition of polymeric or graphitic carbon during carburization with pure CH₄. This speculation could be supported by the results that the surface areas of niobium carbides increased with increasing the H₂ treatment time. The results obtained using higher space velocities may also support this explanation by showing the higher surface area. Table 1 also shows the surface areas of fresh and used niobium carbides for ammonia decomposition reactions. Although pretreatment conditions for used samples were the same as those for fresh samples, the surface areas of the used niobium carbides were almost the same as those of the fresh ones, indicating that these materials were very stable.

The oxygen uptakes were measured at room temperature over the niobium carbides (Table 2). The average oxygen uptake was estimated to be 17 × 10⁻⁷ mol O₂/g except for one sample (NC-1). Generally the oxygen uptakes of the current study were about 10 times higher than that of commercial material. There was a nearly linear relationship between the O₂ uptake and the BET surface area of these materials (Figure 1), indicating that oxygen reflected the physical surface character of the niobium carbides. The similar relationship was also observed in other transition metal carbides such as V, Ta, Mo carbides [4-5,7,9]. The average site density of niobium carbides was estimated to be 2.7 × 10¹¹/cm².

The niobium carbides have proved to be active for NH₃ decomposition. Table 2 shows the catalytic behavior of niobium carbides for the decomposition of ammonia expressed as NH₃ conversion. Figure 2 shows the NH₃ conversion as a function of time on stream. Initially, all of the fresh catalysts of niobium carbide showed the highest conversion. However, the catalysts then lose activity little by little as a function of time. The NH₃ decomposition reaction rates decreased to the steady-state activities during the first 40 mins on stream and remained constant for several h on stream. Figure 3 exhibits that the catalytic conversion of the niobium carbides decreased with the increase of the surface area, implying that the catalytic properties of these materials were more relying on surface properties such as surface compositions. Accordingly, these results suggest that ammonia decomposition was structure-sensitive over these niobium carbides materials. The findings of structure-sensitivity in niobium carbides are based on the fact that the variations in the surface stoichiometries were responsible for this catalytic behavior. Recently, Choi and

**Table 2. Catalytic Activities of Niobium Carbides for NH₃ Decomposition at 843 K**

<table>
<thead>
<tr>
<th>Catalyst code</th>
<th>Surface area (m²/g)</th>
<th>Oxygen Uptake (× 10⁻⁷ mol O₂/g)</th>
<th>Site Density (× 10¹¹/cm²)</th>
<th>NH₃ Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-1</td>
<td>0.91</td>
<td>2.17</td>
<td>0.6</td>
<td>4.3</td>
</tr>
<tr>
<td>NC-2</td>
<td>5.15</td>
<td>18.5</td>
<td>2.9</td>
<td>1.1</td>
</tr>
<tr>
<td>NC-3</td>
<td>3.84</td>
<td>17.3</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>NC-4</td>
<td>3.38</td>
<td>15.1</td>
<td>2.7</td>
<td>1.6</td>
</tr>
<tr>
<td>NC-5</td>
<td>2.81</td>
<td>16.9</td>
<td>2.6</td>
<td>2.2</td>
</tr>
<tr>
<td>NC-A</td>
<td>0.34</td>
<td>1.70</td>
<td>0.3</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*Measured at room temperature after 3 h H₂ reduction.

**Figure 1.** The oxygen uptake as a function of BET surface area over niobium carbides.

**Figure 2.** The ammonia conversion as a function of time on stream for NC-3.
coworkers [5,7] also reported the concept of structure-sensitivity for ammonia decomposition over vanadium and molybdenum carbides. For example, the surface composition of the vanadium carbides was different ranging from 0.26 to 0.78, resulting in the production of different catalytic activity. Figure 4 showed that there was the effect of the reaction temperature on ammonia conversion for the niobium carbides. It can be seen that the increase of reaction temperature generally increased the catalytic conversion of niobium carbides. In particular, NC-1 catalyst containing the smallest surface area exhibits the highest conversion at each temperature. As can be shown in Table 2, NC-1 has the surface area of less than 1 m²/g. Similarly, the commercial catalyst, NC-A also has the small surface area but shows the high ammonia conversion comparable to this catalyst.

It is noteworthy that there was an influence of H₂ pretreatment condition on activity of niobium carbides. The catalytic conversion over niobium carbide catalysts increased with the increase of H₂ pretreatment time and temperature. The increase in the conversion over niobium carbide as a function of H₂ pretreatment condition might have been related to the removal of impurities (C and O) on the surface by H₂ treatment. The removal of polymeric carbon via H₂ treatment at high temperature could create the increase in the surface site of these materials. These newly exposed surface sites may be available for further catalytic reaction, resulting in the increase in the catalytic conversion. Generally, three different kinds of carbonaceous surface species are produced by methane decomposition reaction during the carburation of niobium oxides; carbide surface carbon, amorphous carbon, and graphitic carbon. Moreover, these different carbon species could be distinguished by their different hydrogenation temperatures [5]. It is generally known that carbide and amorphous surface carbon can be hydrogenated below 400 K and around 500 K, respectively [13-16]. In the mean time, the unreactive graphitic carbon reacts at higher temperatures than ~ 650 K to produce only methane. Due to the H₂ pretreatment temperature of 673 K used in the current study, it was considered that these above-mentioned carbon species may have been removed from the surface of niobium carbides. From the separate hydrogen temperature-programmed reduction experiments [10], we confirmed the carbon removal by the findings of methane production in niobium carbide catalysts.

The ammonia conversion of the niobium carbides was compared with that of the vanadium carbides. The niobium carbides generally exhibited two or three times lower reaction rates on a conversion percent basis than vanadium carbides. This activity difference between niobium and vanadium carbides is in a good agreement with previous experimental results reported for ethylbenzene dehydrogenation [11]. It was considered that the higher ammonia conversion for vanadium carbides might be attributed to the lower degree of charge transfer between metals and carbon. For instance, the electronegativity difference for niobium and vanadium carbides are estimated to be Δe = 0.95 and 0.92, respectively. Choi [12] has published the similar observations for other transition metal carbides (V and Mo) using the same reaction.

Conclusions

It was found that the niobium carbides were catalytically active for NH₃ decomposition. There was a nearly linear relationship found between the O₂ uptake and the BET surface area for the niobium carbides. The ammonia decomposition conversion of niobium carbides increased with decreasing surface area, suggesting that NH₃ decomposition over these materials is structure-sensitive. As in the case of other transition metal carbides, it was considered that the structure-sensitivity
over niobium carbides may be due to variations in the surface stoichiometry with surface area. It was also observed that there was an effect of the reaction temperature on ammonia conversion. Namely, the increase of reaction temperature generally increased the catalytic conversion of niobium carbides. In particular, NC-1 catalyst containing the smallest surface area exhibits the highest conversion at each temperature. The niobium carbides generally exhibited two or three times lower reaction rates on a conversion percent basis than vanadium carbides. This activity difference between niobium and vanadium carbides was considered to be related to the degree of electron transfer.

Acknowledgements

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References