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Preparation and characterization of niobium carbide crystallites

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Abstract The preparation and characterization of niobium carbide crystallites were investigated in this study, and in particular, the effect of preparation conditions were studied on the synthesis of niobium carbides crystallites. For this purpose, various characterization techniques including x-ray diffraction, BET surface area, and oxygen uptake measurements were employed to characterize the synthesized niobium carbide crystallites. The niobium carbide crystallites were prepared using niobium oxide and methane gas or methane-hydrogen mixture. Using x-ray diffraction a lattice parameter of 4.45 Å and a crystallite size ranging from 52 Å to 580 Å was found. BET surface areas ranged from 3.2 m^2/g to 16.6 m^2/g and oxygen uptake values varied from 0.5 μmol/g to 6.1 μmol/g. It was observed that niobium carbide crystallites were active for ammonia decomposition reaction. While the BET surface area increased with increasing the oxygen uptake, the conversion of ammonia decomposition reaction decreased. These results indicated that the ammonia decomposition over these materials was considered to be structure-sensitive.

Key words Niobium carbide crystallites, BET surface area, Oxygen uptake, Ammonia decomposition reaction

1. Introduction

Since it was reported that niobium carbide crystallites (NbC) have similar surface and electronic properties to noble metal materials such as Pt, Pd, Rh [1-3], there is a growing interest in using the niobium carbides. Such similarities as substitutes for the more expensive Pt based materials, on which the petroleum and chemicals processing industries so heavily depend, suggest that niobium carbides are attractive candidates for further development. Previous results have shown that niobium carbide crystallites can be used for oxidation [1] and dehydrogenation [2] reactions. An additional attractive feature of niobium carbide crystallites is that they can be produced with high surface areas. Traditional synthesis methods have only yielded low surface area transition metal carbides, however, it has been demonstrated that high surface area niobium carbides can be prepared by the temperature programmed reduction of niobium oxide in either methane or a methane-hydrogen mixture [3].

Here, in this study we have examined the effect of synthesis parameters on the structural properties and chemisorption uptake capacity of niobium carbide crystallites. These carbide materials were prepared by the temperature-programmed reaction of niobium oxide precursor (Nb_2O_5) with the methane gas or hydrogen-methane mixed gas. The three experimental variables examined were (1) heating rates, (2) molar hourly space velocity (MHSV), and (3) gas compositon. The resulting niobium carbide crystallites were examined using x-ray diffraction (XRD) to determine their bulk phases, crystallite sizes, and lattice parameters. Particular attention was also given to the effects of preparative conditions on the BET surface area and oxygen chemisorption uptake. Finally, ammonia decomposition reaction was used to evaluate the reactivity of niobium carbide crystallites.

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2. Experimental

The preparation reactor used in this work for synthesizing the niobium carbide crystallites was made of a quartz tube fitted with a quartz frit located 12 inches from the top fitted with a cooling water jacket to cool the exiting reaction gases. The reactor was 25 inches long and had a diameter of 0.625". Reaction temperatures reached 1313 K so both the quartz tube and the cooling jacket were necessary. The section of the reactor containing the frit and reaction materials was placed inside a Thermocraft Model 132 furnace controlled by an Omega, series CN2010 programmable temperature controller using a chromel-alumel thermocouple to monitor the temperature. Helium was purified by using a Matheson, 6406 filter to remove O_2 and water. Gas flow

Table 1
Experimental conditions for preparation of niobium carbide crystallites

Sample	Heating rate (K/h)	H_2/CH_4 ratio	MHSV CH_4 (h^{-1})
NbC-1	140	1.04	60
NbC-2	70	1.04	60
NbC-3	140	0	60
NbC-4	70	0	60
NbC-5	140	1.04	30
NbC-6	70	1.04	30
NbC-7	140	0	30
NbC-8	70	0	30

was controlled using needle valves and the flow rates were measured by a bubble flow meter. The niobium oxide (Nb_2O_5) was purchased from Alpha chemicals at a purity of 99.9985 %.

To assess the influence of the heating rate, the molar hourly space velocity, and the reaction gas composition on the preparation of niobium carbide crystallites, a series of eight niobium carbide crystallites were synthesized according to the schedule in Table 1. Molar hourly space velocity is defined as the ratio of the molar flow rate of CH_4 to the moles of Nb_2O_5. In order to synthesize the niobium carbide crystallites, first glass wool was packed on the quartz frit in the reactor tube. A measured amount of niobium oxide was then placed on top of the glass wool. The reactor was placed in the furnace with airtight seals on top and bottom providing the gas inlet and outlet respectively. Once this was accomplished, the gas flow was then started. The furnace was heated to 1073 K in 90 minutes. Then it was heated to 1313 K using one of the two variable heating rates and held at this temperature for 1 hour. The reactor was then allowed to cool rapidly by removing it from the furnace. When the reactor reached room temperature, the gas was switched to He for 30 minutes, then to 1 % O_2/He for a 2 hour passivation period. The niobium carbide crystallites were then collected and characterized.

The synthesized materials were so tested using a computer controlled Rigaku DMAX-B x-ray diffractometer. This method not only determines the composition of the material present, but also allows calculation of the crystallite size and the lattice parameter. Average crystallite size was calculated using the equation [4]: $d_c = K\lambda / (B\cos\Theta)$ where K is a constant, here taken to be 1, λ is the wave length of the radiation (1.5405 Å), B is the corrected peak width, and Θ is the Bragg angle of the diffraction peak. The peak width was taken to be the full width at half the intensity for the most intense peak. Lattice parameters were calculated assuming a face centered lattice structure.

The BET surface areas were measured using a Quantasorb® machine. The standard pretreatment of the niobium carbide crystallites consisted of heating the sample in pure H_2 gas at a flow rate of 20 cc/min for 3 h at a temperature of 673 K to remove the passivation layer and other impurities. After the 3 h period had elapsed, the crystallites were then outgassed at a flow rate of 20 cc/min in pure He gas at a temperature of 673 K for 5 minutes. When the 5 minute period had elapsed, the sample was allowed to cool to room temperature. Once the crystallites had reached room temperature, the gas sent through the sample cell was switched to a mixture of 29.3 % N_2/He at a flow rate of 20 cc/min. Next, the attenuation of the Quantasorb® machine was set to give a peak height of about 60~90 % of full scale. The next step in the procedure was that the sample was immersed in a dewar of liquid N_2 and the adsorption part of the BET method was then performed. A peak height and count was then determined by the Quantasorb® machine. Next, desorption was performed by lowering the dewar and hot-air heating the crystallite sample to room temperature. A peak height and the count was once again determined. A calibration was then performed by injecting a known amount of N_2/He gas, determined by the attenuation setting, into the Quantasorb® machine which then gave a peak height and count. The adsorption, desorption, and calibration steps were then performed two more times to minimize error. The crystallite sample was then removed from the machine and weighed.

The oxygen uptake experiment was also performed using the Quantasorb® machine. The crystallites were pretreated the exact same way as in the BET experiment but the He gas was left on for ten minutes rather than five. Once the pretreatment was complete, the He gas was left flowing for the remainder of the experiment. The O_2 uptake experiment was then performed at 351 K. The attenuation of the Quantasorb machine was then set at 2 and 0.5 cc injections of a mixture of 9.98 %O_2/He gas were then made. The injections were then repeated until a constant count on the machine was achieved for about 5 straight injections. The sample was then removed from the machine and weighed.

To evaluate the reactivity ~0.2 g of the crystallite sample was spread over a 9 mm O.D. pyrex glass flow reactor. The sample was reduced using pure H_2 from room temperature to 673 K at a rate of 120 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 sample at atmospheric pressure

with the inlet space velocity based on the bed volume of 7500/h. The reactor effluent was analyzed using an on-line gas chromatograph equipped with both flame ionization and thermal conductivity detectors. The products were separated using Porapak Q packed columns connected to a gas chromatography detector.

3. Results and Discussion

Based on XRD results, dark gray powders of NbC were produced in this work. Fig. 1 shows a typical XRD pattern for the NbC product. No niobium oxide appeared to be present after the reaction. Reactions producing NbC-7 and NbC-8 were both carried out at a MHSV of 30 h^{-1} with pure methane. Hydrogen appears to facilitate the formation of H_2. The lattice parameters were calculated based on an assumed face centered cubic lattice [4] (see Table 2). The lattice parameter averaged 4.45 Å for all eight synthesized crystallites. This compares very well with the lattice parameter of 4.41 Å reported by Il'chenko [1]. The ratio of the intensities of the (200) and (111) reflections for all samples

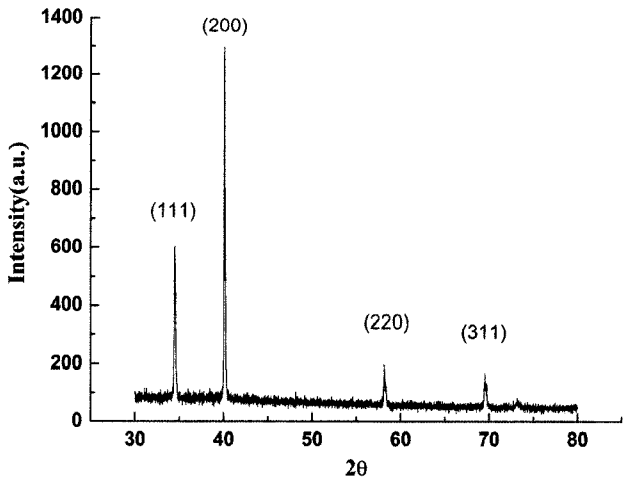

Fig. 1. Typical XRD patterns for niobium carbide crystallites.

Table 2
Bulk structural properties of niobium carbide crystallites

Sample	Crytallite size (Å)	Lattice parameter (Å)	I(111)/I(200)
NbC-1	580	4.41	0.64
NbC-2	175	4.48	0.63
NbC-3	325	4.46	0.64
NbC-4	150	4.45	0.74
NbC-5	52	4.45	0.41
NbC-6	195	4.43	0.51
NbC-7	200	4.47	0.76
NbC-8	251	4.47	0.62

Table 3. Crystallite and particle size of niobium carbide crystallites

Sample	D_{XRD}, nm	D_{BET}, nm
NbC-1	58	85
NbC-2	18	210
NbC-3	33	278
NbC-4	15	282
NbC-5	5	154
NbC-6	19	238
NbC-7	20	58
NbC-8	25	78

were between 0.41 and 0.76. There was a consistent relationship between crystallite size and the preparation parameters. With the higher space velocities slower heating rates produced smaller crystallites, but with the lower space velocities slower heating rates produced larger crystallites. It appears that the high MHSV disperses that gas through the solid more efficiently. This causes the carbide to form smaller crystals as it reacts. This would have an even greater effect if the heating rate is slow and the gas has more time to disperse in the solid. With the lower MHSV, slow heating rates probably cause fewer crystals to form simultaneously resulting in larger crystals. This would also explain why smaller crystals were formed with a slower initial heat ramp. In that case the gas would have more time to penetrate into the solid before the oven reached reaction temperatures.

Table 3 shows that for all the niobium carbide crystallites the crystallite size is smaller than the particle size, indicating that the particles are polycrystalline agglomerates. The most important trend in the preparation of niobium carbide crystallites appears to be getting the gas dispersed through the plug of solid material, especially with slower heat ramps. With the gas dispersed evenly through the reactor, the solid crystallite growth begins simultaneously throughout the solid leading to smaller crystallite sizes. If the gas is not dispersed well, less crystallites begin and grow larger. Also, fast heat ramps and low MHSVs also caused small crystallite sizes. This would have to be caused by the temperature rising fast enough to overcome the crystallite growth trends seen above. If the temperature rises fast enough, it will begin reactions throughout the solid faster than the reaction can spread from the existing carbide. To synthesize carbides with larger crystallite sizes the opposite trends must be followed. The goal then would be to react the material before the gas could penetrate and saturate the solid reactants.

In order for niobium carbide crystallites to be effec-

tive for reactions, it must have high specific surface area. When the niobium carbide crystallites were synthesized in pure CH_4, the highest specific surface areas were obtained with the high heating rate and low space velocity 30 h^{-1}. A possible reason for the effect of lower MHSV on surface area in pure CH_4 could be due to the fact that CH_4 was in contact with the niobium oxide for a greater period of time which would result in a greater conversion of the lower surface area niobium oxide to niobium carbide. Overall, the highest specific surface area niobium carbide crystallites were produced in pure CH_4 when the heating rate was 140 K/h and the molar hourly space velocity was 30 h^{-1}. As the results show (see Table 4), when the niobium carbide crystallites were synthesized in a H_2/CH_4 mixture, the highest surface areas were obtained when the heating rate and the molar hourly space velocity were 140 K/h and 60 h^{-1}, respectively. The most likely reason for the effect of greater MHSV on specific surface area is the rapid removal of water vapor from the vicinity of the reacting solid. Water vapor can cause hydrothermal sintering which lowers the surface area [5]. The effect of greater heating rate on surface area is that the reaction rate increased which also increased the conversion of niobium oxide to niobium carbide.

Oxygen uptake was taken as a measure of the number of potential active sites on the crystallites. When the MHSV was at its highest value, the oxygen uptake was the highest (see Table 4). Oxygen site densities were determined from the O_2 uptakes and the BET surface areas. The O_2 site density averages 2.0×10^7 O_2/m^2. Assuming a 1 : 1 Nb : O stoichiometry, surface coverages averaged ~2.4 %. As Fig. 2 shows the relationship between 0_2 uptake and BET surface area is somewhat linear. This result suggests that oxygen was a non-selective adsorbate to the niobium carbide crystallites. Overall, there seems to be no apparent trends in the amount of oxygen uptake under different synthesis conditions.

It was shown that the niobium carbide crystallites pre-

Table 4
Surface properties of niobium carbide crystallites+

Sample	Surface area (m^2/g)	O_2 uptake (μmol/g)	Site density* $(m^{-2})10^{-7}$	Surface coverage (%)
NbC-1	12.0	4.3	4.9	5.9
NbC-2	6.1	1.7	4.2	4.1
NbC-3	4.4	0.9	2.9	2.9
NbC-4	3.2	0.7	3.2	5.0
NbC-5	7.3	0.5	0.8	2.3
NbC-6	4.5	1.9	0.7	0.5
NbC-7	16.6	5.2	0.5	0.4
NbC-8	14.1	6.1	4.8	5.8
Nb_2O_5	0.67	-	-	-

+The average error of sorption analysis was estimated to be-1 5%.
*Based on O_2 uptake at 195 K.

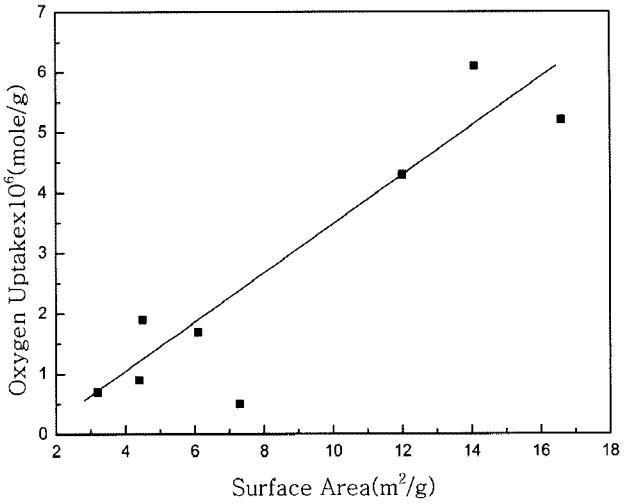

Fig. 2. The oxygen uptake as a function of BET surface area for niobium carbide crystallites.

Table 5
The relationship between surface area and reactivity of niobium carbide crystallites

Sample	Surface area (m^2/g)	Ammonia conversion (%)
NbC-1	12.0	2.9
NbC-2	6.1	6.5
NbC-3	4.4	7.9
NbC-4	3.2	9.0
NbC-5	7.3	6.3
NbC-6	4.5	6.5
NbC-7	16.6	1.4
NbC-8	14.1	2.8

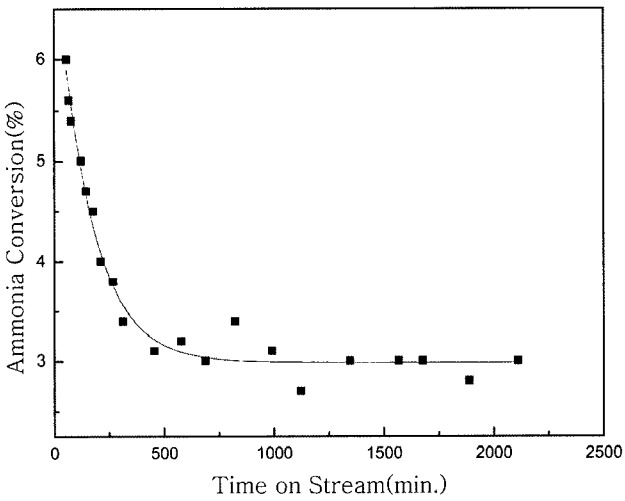

Fig. 3. Typical ammonia conversion (%) as a function of time on stream.

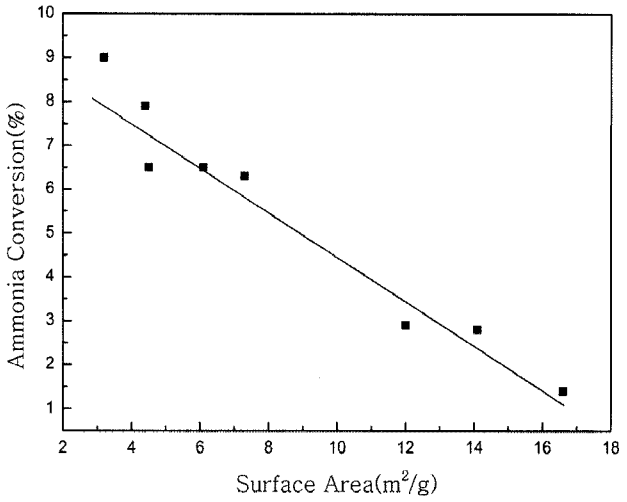

Fig. 4. The conversion versus surface area of niobium carbide crystallites.

pared in this paper were active for ammonia decomposition reaction. Table 5 shows the reactivity of niobium carbide crystallites for NH_3 decomposition expressed as ammonia conversion. Fig. 3 exhibits the ammonia conversion as a function of time on stream. At first, all of the niobium carbide crystallites showed the highest conversion. However, the crystallites then lose reactivity gradually as a function of time. The ammonia decomposition reaction rates decreased to the steady-state activities and remained constant for several hours on stream. Fig. 4 shows that the ammonia conversion of niobium carbide crystallites decreased with the increase of the surface area, implying that the reactivities of these materials are more dependent upon the surface properties such as surface compositions. Subsequently, these results suggested that the ammonia decomposition reaction was structure-sensitive for niobium carbide crystallites. Previously, Choi and coworkers also reported that ammonia decomposition was structure-sensitive over vanadium and molybdenum carbide crystallites [6, 7].

4. Conclusions

The niobium carbide crystallites were successfully synthesized in all eight preparation conditions. All eight niobium carbide crystallites had a lattice parameter of approximately 4.45 Å. For all the niobium carbide crystallites the crystallite size is smaller than the particle size, indicating that the particles are polycrystalline agglomerates. The most important trend affecting crystallite size in the preparation of niobium carbide crystallites is a combination of heat ramp and molar hourly space velocity. The relationship between 0_2 uptake and BET surface area is somewhat linear, suggesting that oxygen was a non-selective adsorbate to the niobium carbide crystallites. It was observed that the niobium carbide crystallites prepared in this work were active for ammonia decomposition reaction. The ammonia conversion of niobium carbide crystallites decreased with the increase of the surface area, implying that the reactivities of these materials are more relying on the surface properties.

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