

# Synthesis of Niobium Carbide from Niobium Oxide Aerogels

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Niobium carbide (NbC) synthesis was studied by the temperature-programmed reaction (TPR) between niobium oxide precursors of different textural properties and a 20% (v/v) CH<sub>4</sub>-H<sub>2</sub> mixture. Surface areas ranging between 13 and 74 m<sup>2</sup>/g were obtained depending on the temperature and on the nature of the precursor (Nb<sub>2</sub>O<sub>5</sub> or an aerogel precursor). The high synthesis temperatures (1173–1373 K) caused surface contamination by carbon from methane decomposition and led to low CO uptakes (15–28 μmol/g). Environmental scanning electron microscopy (ESEM) analysis showed that the transformation oxide → carbide is a pseudomorphous process. The results suggest that the reaction occurs in two steps: reduction by H<sub>2</sub> leading to NbO<sub>2</sub> formation and carburization/reduction of the NbO<sub>2</sub> to NbC.

## Introduction

Transition-metal carbides and nitrides find uses as structural materials resistant to high temperatures and corrosive atmospheres, abrasives, superconductors, and high-performance permanent magnets.<sup>1,2</sup> Application of transition-metal carbides and nitrides to catalysis has been made possible by improvements in synthesis which have resulted in materials with specific surface areas (*S<sub>g</sub>*) in the range 50–200 m<sup>2</sup>/g.<sup>3–5</sup> The materials have been tested in a variety of reactions such as ammonia synthesis,<sup>6</sup> hydrogenation,<sup>7</sup> methanation,<sup>8</sup> isomerization,<sup>9</sup> and hydrotreating<sup>10–12</sup> and have attracted attention because of improvements in activity and selectivity over the parent transition element.<sup>13–15</sup>

Most of the work on the application of transition-metal carbides and nitrides to catalysis has focused on Mo<sub>2</sub>C, Mo<sub>2</sub>N, and WC, with little being reported on other compounds such as NbC. The focus on Mo<sub>2</sub>C, Mo<sub>2</sub>N,

and WC has occurred in part because they can be prepared in high surface area form at moderate synthesis temperatures in the range 900–1100 K. On the other hand, niobium carbide has a predicted synthesis temperature of 1370 K,<sup>16</sup> which results in materials of low surface area and, therefore, limited use in catalysis.

In this paper we report the synthesis of NbC with medium (13 and 42 m<sup>2</sup>/g) and high (74 m<sup>2</sup>/g) specific surface areas (*S<sub>g</sub>*), the latter being obtained by maximizing the area of the starting material through use of a Nb<sub>2</sub>O<sub>5</sub> aerogel precursor, while the former was obtained using a commercial Nb<sub>2</sub>O<sub>5</sub> as starting material. Synthesis of these materials was carried out by temperature-programmed reaction (TPR)<sup>16</sup> in which an oxide precursor is exposed to a reductive carburizing stream while the temperature is raised in a uniform manner. Our results demonstrate a new application of oxide aerogels as potential precursors to catalytic materials.<sup>17,18</sup>

## Experimental Section

The gases employed in this study were He, N<sub>2</sub>, CO, 0.5% (v/v) O<sub>2</sub>-He, and 20% (v/v) CH<sub>4</sub>-H<sub>2</sub> (all of them from Linde, UHP Grade). All gases except the O<sub>2</sub>-He mixture were passed through oxygen-removing purifiers before use.

The chemicals used were Nb<sub>2</sub>O<sub>5</sub> (B-Phase, Johnson Matthey Electronics, 99.9%) and NbC (Johnson Matthey Electronics, 99.0%) and were employed without further purification. The preparation of an Nb<sub>2</sub>O<sub>5</sub> aerogel precursor was described elsewhere.<sup>19</sup> Briefly, 25 mmol of niobium(V) ethoxide [Nb(OEt)<sub>5</sub>, Alfa] was dissolved in 25 mL of *sec*-butyl alcohol (99+% anhydrous, Aldrich). This solution was quickly added to a well-mixed solution containing 25 mL of *sec*-butyl alcohol, 250 mmol of doubly deionized water, and 20 mmol of nitric acid (70% Fisher). Under these conditions the resulting solution turned into a clear gel in about 10 s. The gel was then dried in a standard autoclave (Autoclave Engineers,

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(1) Kirk Othmer Encyclopedia of Chemical Technology, 1993.

(2) Toth, L. E. *Transition Metal Carbides and Nitrides*; Academic Press: New York, 1971.

(3) Volpe, L.; Boudart, M. *J. Solid State Chem.* **1985**, *59*, 332.

(4) Volpe, L.; Boudart, M. *J. Solid State Chem.* **1985**, *59*, 348.

(5) Oyama, S. T. Ph.D. Dissertation; Stanford University: Stanford, CA, 1981.

(6) Volpe, L.; Boudart, M. *J. Phys. Chem.* **1986**, *90*, 4874.

(7) Vidick, B.; Lemaître, J.; Leclercq, L. *J. Catal.* **1986**, *99*, 643.

(8) Saito, M.; Anderson, R. B. *J. Catal.* **1981**, *67*, 296.

(9) Ribeiro, F. H.; Dalla Betta, R.; Boudart, M.; Iglesia, E. *J. Catal.* **1991**, *130*, 523.

(10) Markel, E. J.; van Zee, J. W. *J. Catal.* **1990**, *126*, 643.

(11) Abe, H.; Bell, A. T. *Cat. Lett.* **1993**, *18*, 1.

(12) Sajkowsky, D. J.; Oyama, S. T. Preprints, Division of Petroleum Chemistry, Symposium on "The Chemistry of W/Mo Catalysts", 199th ACS National Meeting, Boston, MA, Apr 22–27, 233, 1988.

(13) Lee, J. S.; Oyama, S. T.; Boudart, M. *J. Catal.* **1987**, *106*, 125.

(14) Oyama, S. T.; Haller, G. L. *Catalysis, Spec. Period. Rep.* **1981**, *5*, 333.

(15) Leclercq, L. *Surface Properties and Catalysis by Non-Metals*; Bonenelle, J. P., Ed.; Reidel: New York, 1983.

(16) Oyama, S. T.; Schlatter, J. C.; Metcalfe III, J. E.; Lambert Jr., J. M. *Ind. Eng. Chem. Res.* **1988**, *27*, 1639.

(17) Pajonk, G. M. *Appl. Catal.* **1991**, *72*, 217.

(18) Ko, E. I. *Chemtech* **1993**, *23–4*, 31.

(19) Maurer, S. M.; Ko, E. I. *J. Catal.* **1992**, *135*, 125.

Model 08U-06-60FS) with supercritical CO<sub>2</sub> (Airco) at ca. 343 K and  $2.07 \times 10^7$  Pa (3000 psi). With a CO<sub>2</sub> flow rate of  $2.36 \times 10^{-5}$  m<sup>3</sup>/s (0.05 SCFM), a typical drying lasted for 2–3 h for the complete removal of the solvent. The product after supercritical drying is strictly not a niobium oxide because it contains residual organics such as surface alkoxides that need to be removed by calcination.<sup>19</sup> For this reason it will be referred as an Nb<sub>2</sub>O<sub>5</sub> aerogel precursor.

The synthesis procedure of the carbides consisted of passing a 20% (v/v) CH<sub>4</sub>–H<sub>2</sub> mixture flow (1000 cm<sup>3</sup>/min  $\approx$  670  $\mu$ mol/s) over the commercial Nb<sub>2</sub>O<sub>5</sub> or Nb<sub>2</sub>O<sub>5</sub> aerogel precursor (400 mg  $\approx$  1500  $\mu$ mol) at a molar space velocity of 1640 h<sup>-1</sup> and then starting the heating program. This high value of space velocity was chosen to minimize the H<sub>2</sub>O partial pressure and avoid loss of surface area. During the TPR experiments, a portion of the effluent from the U-shaped quartz reactor was leaked to a mass spectrometer (Ametek/Dycor Model MA100) through a variable leak valve (Granville Phillips Model 203) and the masses 2 (H<sub>2</sub>), 15 (CH<sub>4</sub>), 18 (H<sub>2</sub>O), 28 (CO), and 44 (CO<sub>2</sub>) were monitored continuously. Lag time due to flow between the reactor and mass spectrometer was of the order of seconds, negligible in the time scale of the experiments. A local chromel–alumel thermocouple monitored the temperature of the sample and this signal, as well as the mass spectrometer signal were recorded by a computer (Thoroughbred, 80386SX-16) equipped with an A/D RS-232 board.

After completion of the synthesis, the gas flow through the reactor was switched from the CH<sub>4</sub>–H<sub>2</sub> mixture to a flow of pure He (200 cm<sup>3</sup>/min  $\approx$  130  $\mu$ mol/s) and the reactor was quenched by quickly removing the furnace. Once room temperature was reached, the surface was characterized by irreversible CO chemisorption and physisorption of N<sub>2</sub> at liquid nitrogen temperature.

CO chemisorption is a technique used in catalysis to titrate surface metal atoms and was carried out by pulsing pure CO through a sampling valve using pure He as a carrier. The total CO uptake was calculated by comparing the areas under the CO signal peaks to the known quantity of 38  $\mu$ mol for a single peak.

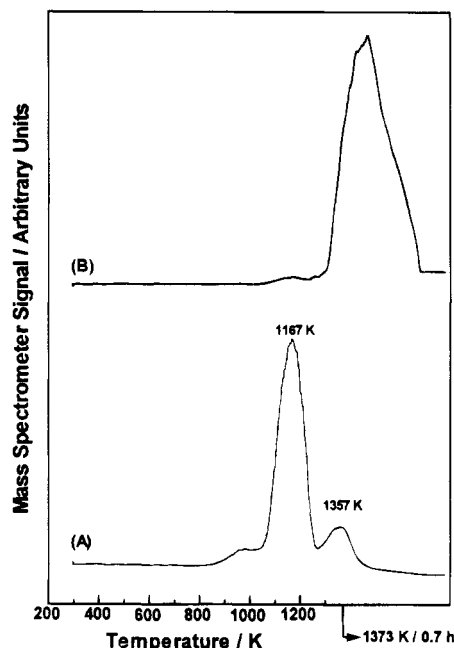
Surface areas were measured immediately after CO chemisorption and degassing in helium by a similar flow technique using a 30% (v/v) N<sub>2</sub>–He mixture. The gas mixture was passed over the sample maintained at liquid nitrogen temperature, and the amount of physisorbed N<sub>2</sub> was obtained by comparing the area of the desorption peak with the area of calibrated N<sub>2</sub> pulses containing 38  $\mu$ mol N<sub>2</sub>/pulse.  $S_g$  values were then calculated from the single-point BET equation.<sup>20</sup>

After the surface characterization, the sample was passivated by flowing a 0.5% (v/v) O<sub>2</sub>–He mixture (3 h/g at 150  $\mu$ mol/s) through the reactor to form a monolayer of protective oxide in order to avoid bulk oxidation. X-ray powder patterns were obtained with a powder diffractometer (Siemens, Model D500 with a Cu K $\alpha$  monochromatized radiation source) operated at 40 kV and 30 mA. The samples were also analyzed by environmental scanning electron microscopy (Electroscan E-SEM E-3 operated at 20 KeV, 1.90 mA, and a total pressure of  $6.7 \times 10^{-4}$  Pa under water vapor atmosphere) in order to investigate the external morphology of the starting and product materials.

Crystallite sizes of the synthesized carbides were obtained using the Scherrer equation,  $D_C = K\lambda/\beta \cos(\theta)$ , where  $\lambda$  is the wavelength of the X-ray radiation, 0.154 nm,  $\beta$  is the width of the peak at half-maximum corresponding to the (200) plane and corrected for instrumental broadening (0.1°),  $\theta$  is the Bragg angle, and  $K$  is a constant taken to be 0.9. Corresponding particle sizes were calculated from the equation  $D_p = 6/(S_g \rho)$ , where  $\rho$  is the density of the solid, and  $S_g$  the specific surface area of the sample.

## Results

Using commercial Nb<sub>2</sub>O<sub>5</sub> ( $S_g = 3$  m<sup>2</sup>/g) as starting material, a first experiment was done using a heating



**Figure 1.** Water (A) and carbon monoxide (B) formation profiles during the carburization of a commercial Nb<sub>2</sub>O<sub>5</sub> (final temperature = 1373 K/0.7 h, heating rate = 0.167 K s<sup>-1</sup>).

rate ( $\beta$ ) of 0.167 K s<sup>-1</sup> and raising the temperature uniformly from 298 to 1373 K. Past work indicated that this was an appropriate heating rate.<sup>3,4,6,13</sup> Water and carbon monoxide formation profiles were followed by mass spectrometry (Figure 1). Even at the final temperature ( $T_f$ ) of 1373 K carbon monoxide formation was continuing, and for this reason the temperature was kept at 1373 K for 0.7 h until the CO signal returned to baseline. The water formation profile consisted of two main peaks with maxima at 1167 and 1357 K. The small shoulder at 970 K could be due to strongly adsorbed water in the form of hydroxyls. The carbon monoxide profile consisted of a broad peak in the isothermal region at 1373 K and a very small peak in the temperature region 1000–1200 K.

The X-ray diffraction pattern of the synthesized carbide did not have any of the reflections of the starting Nb<sub>2</sub>O<sub>5</sub> oxide and was virtually identical to that of a commercial NbC (Figure 2). Comparison with a standard pattern from a powder diffraction file<sup>21</sup> confirms that this compound is NbC with a B1 rocksalt structure (space group  $Fm\bar{3}m$ ). The only difference between the patterns was that the relative intensity of the (111) reflection to the (200) reflection was slightly higher for the synthesized carbide than for the commercial carbide.

Because carbon monoxide formation had been observed to begin at 1173 K, the synthesis was repeated using 1173 K as  $T_f$ . The lower temperature synthesis did not affect the first water formation peak but caused the disappearance of the second and led to the formation of a broad CO formation peak (Figure 3). In this experiment the final temperature was maintained for 3.0 h until the CO signal returned to baseline. The X-ray diffraction pattern of the sample synthesized at 1173 K/3.0 h was similar to that prepared at 1373 K/0.7

(20) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

(21) Powder Diffraction Data File 38-1364, Inorganic Phases, JCPDS International Center for Diffraction Data, Swathmore, PA, 1981.

Table 1. Surface Properties of the Synthesized Carbides

niobium oxide precursor	synthesis condition	obtained compound	surface area $S_g$ (m <sup>2</sup> /g)	CO uptake ( $\mu$ mol/g)	crystallite size $D_c$ (nm)	particle size $D_p$ (nm)
commercial	1373 K/0.7 h	NbC	13.0	15.0	30	59
commercial	1173 K/3.0 h	NbC	42.0	28.0	18	23
aerogel	1173 K/0.9 h	NbC	74.0	25.0	12	10
aerogel	1000 K/1.0 h	NbO <sub>2</sub>	82.0			

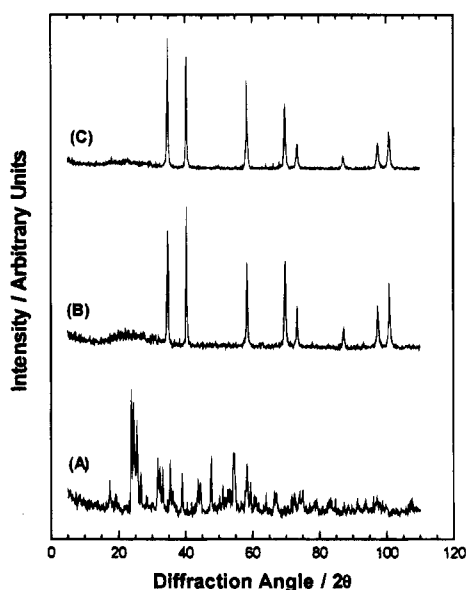


Figure 2. X-ray diffraction patterns of (A) Nb<sub>2</sub>O<sub>5</sub>, (B) commercial NbC, and (C) NbC synthesized at 1373 K/0.7 h.

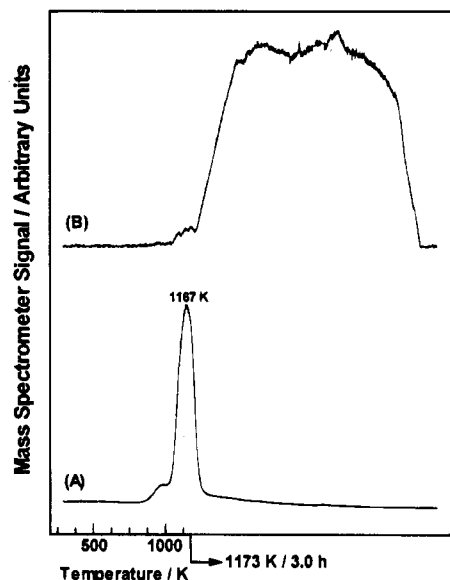


Figure 3. Water (A) and carbon monoxide (B) formation profiles during the carburization of a commercial Nb<sub>2</sub>O<sub>5</sub> (final temperature = 1173 K/3.0 h, heating rate = 0.167 K s<sup>-1</sup>).

h showing that this sample was also NbC with a rocksalt structure. The lower synthesis temperature, however, resulted in a smaller particle size and higher surface area (Table 1).

Another synthesis was carried out at the same conditions ( $SV_{\text{molar}} = 1640 \text{ h}^{-1}$  and  $\beta = 0.167 \text{ K s}^{-1}$ ), but using the Nb<sub>2</sub>O<sub>5</sub> aerogel precursor ( $S_g = 344 \text{ m}^2/\text{g}$ ) as the starting material instead of the commercial Nb<sub>2</sub>O<sub>5</sub>. In this case, when the final temperature of 1173 K was reached, monitoring the CO production revealed that only 0.9 h was necessary for the CO signal to return to baseline. The water, carbon monoxide, and carbon

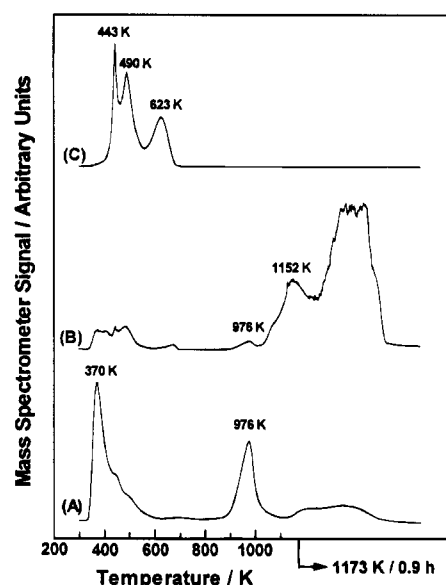


Figure 4. Water (A), carbon monoxide (B), and carbon dioxide formation profiles during the carburization of a Nb<sub>2</sub>O<sub>5</sub> aerogel precursor (final temperature = 1173 K/0.9 h, heating rate = 0.167 K s<sup>-1</sup>).

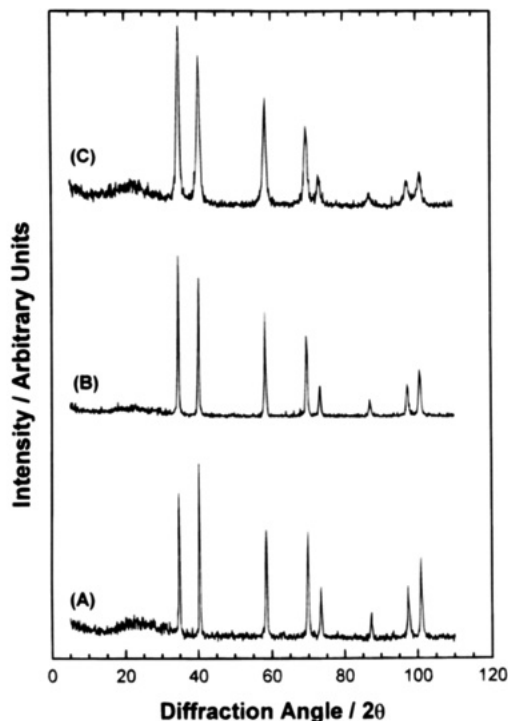
dioxide formation profiles are shown in Figure 4. These profiles are completely different from those presented in Figures 1 and 3, not only because of water and carbon dioxide formation at low temperatures but also because of lowering of the temperature for the main water formation peak from 1167 to 976 K and the broadening of the high-temperature water formation peak. X-ray diffraction analysis after the synthesis revealed that the synthesized material was also NbC (Figure 5), with substantially broadened peaks.

The reasoning for stopping the heating program immediately after the first water formation peak used in the carburization of the commercial Nb<sub>2</sub>O<sub>5</sub> was also applied to the carburization of the Nb<sub>2</sub>O<sub>5</sub> aerogel precursor. In this case, however, the final synthesis temperature employed was 1000 K, while keeping constant all other preparation conditions, i.e.,  $SV_{\text{molar}} = 1640 \text{ h}^{-1}$  and  $\beta = 0.167 \text{ K s}^{-1}$  (Figure 6). In this experiment, monitoring of mass 28 (CO) revealed that holding the final temperature for 1.0 h did not result in any CO formation.

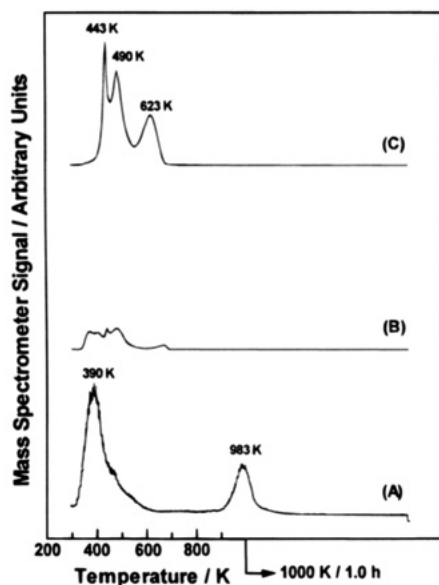
Moreover, the use of a lower synthesis temperature (Figure 6) did not affect the water and carbon dioxide profiles in the temperature region 300–1000 K (Figure 4). On the other hand, no water and carbon monoxide profiles are present in the isothermal region at 1000 K/1.0 h.

Comparing the XRD pattern of the material synthesized at 1000 K/1.0 h to commercial samples of NbO<sub>2</sub> and NbC, revealed that the synthesized material is NbO<sub>2</sub> with a rutile structure<sup>22–24</sup> (Figure 7).

(22) Powder Diffraction Data File 17-717, Inorganic Phases, JCPDS International Center for Diffraction Data, Swathmore, PA, 1981.



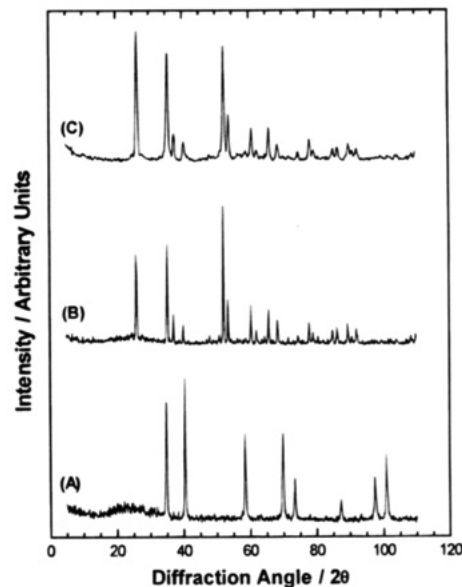
**Figure 5.** X-ray diffraction patterns of (A) commercial NbC, (B) NbC synthesized at 1373 K/0.7 h, and (C) carburized Nb<sub>2</sub>O<sub>5</sub> aerogel precursor (final temperature = 1173 K/0.9 h, heating rate = 0.167 K s<sup>-1</sup>).



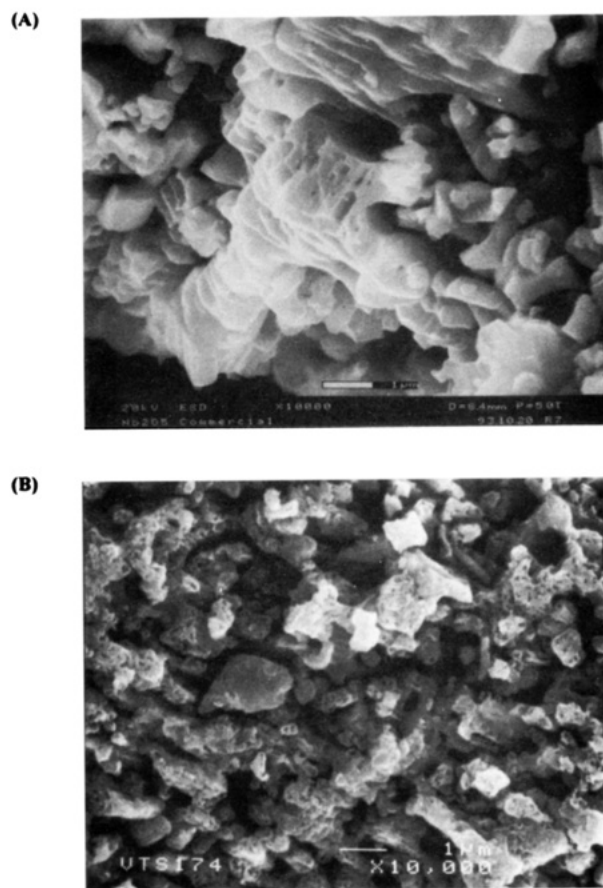
**Figure 6.** Water (A), carbon monoxide (B), and carbon dioxide formation profiles during the carburization of a Nb<sub>2</sub>O<sub>5</sub> aerogel precursor (final temperature = 1000 K/1.0 h, heating rate = 0.167 K s<sup>-1</sup>).

Table 1 lists the synthesis conditions used and the surface properties of the obtained carbides. The table shows that all the synthesized materials have small CO uptakes. This was probably due to the deposition of surface carbon from methane decomposition due to the high temperatures employed.<sup>13</sup>

The environmental scanning electron microscopy pictures of the synthesized carbides, NbO<sub>2</sub>, commercial



**Figure 7.** X-ray diffraction patterns of (A) commercial NbC, (B) commercial NbO<sub>2</sub>, and (C) compound synthesized at 1000 K/1.0 h.



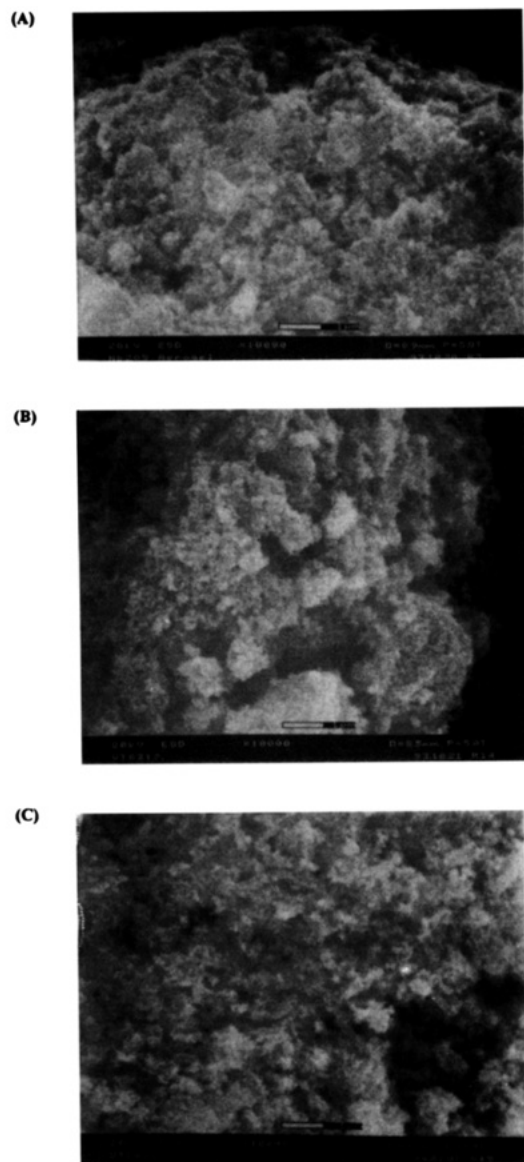
**Figure 8.** Environmental scanning electron micrographs of samples: (A) commercial Nb<sub>2</sub>O<sub>5</sub>; (B) NbC, 1373 K/0.7 h.

Nb<sub>2</sub>O<sub>5</sub>, and Nb<sub>2</sub>O<sub>5</sub> aerogel precursor are presented in Figures 8 and 9. Comparison of Figures 8A (commercial Nb<sub>2</sub>O<sub>5</sub>) and 9A (Nb<sub>2</sub>O<sub>5</sub> aerogel precursor) reveals substantial morphological differences between the two compounds. While the former is composed of large well-defined crystallites, the latter has a spongelike structure consistent with its high surface area.

The crystallites of the NbC product (Figure 8B) have similar shape and size as those of the commercial Nb<sub>2</sub>O<sub>5</sub>

(23) Sakata, T.; Sakata, K.; Nishida, I. *Phys. Stat. Solidi* **1967**, *20*, K155.

(24) Rao, C. N. R.; Natarajaa, M.; Subba Rao, G. V.; Loehman, R. E. *J. Phys. Chem. Solids* **1971**, *21*, 1147.



**Figure 9.** Environmental scanning electron micrographs of samples: (A)  $\text{Nb}_2\text{O}_5$  aerogel precursor; (B) NbC, 1173 K/0.9 h; (C)  $\text{NbO}_2$ , 1000 K/1.0 h.

starting material, except that they are riddled with pores. The external morphology of the  $\text{NbO}_2$  (Figure 9C) and NbC (Figure 9B) materials formed from the aerogel are identical to those of the starting material (Figure 9A).

### Discussion

Several studies on the synthesis of  $\text{Mo}_2\text{C}$ <sup>13,16,25</sup> and  $\text{Mo}_2\text{N}$ <sup>3,10,16,26,27</sup> using the TPR method show that low heating rates and high space velocities are necessary to obtain high  $S_g$ . The use of low heating rates allows the reaction to take place at lower temperatures while high space velocities remove byproduct water vapor rapidly from the vicinity of the reacting solid avoiding inhibition of the reaction<sup>28</sup> or hydrothermal sintering.<sup>10,26,27</sup> As Table 2 shows, the surface areas correlate with reactive gas flow rate.

**Table 2. Effect of Space Velocity on  $\text{Mo}_2\text{C}$  Surface Area**

$\text{SV}_{\text{molar}}$ ( $\text{h}^{-1}$ )	$S_g$ ( $\text{m}^2/\text{g}$ )	ref
9	29	16
28	36	16
51	60	13
100	100	25

However, in contrast to the synthesis of  $\text{Mo}_2\text{C}$ , additional studies of NbC preparation by TPR showed that neither the variation of the molar space velocity by a factor of 4 (from 410 to 1640  $\text{h}^{-1}$ ) nor the variation of the heating rate for a fixed value of SV (from 10 to 2.5 K/min) caused appreciable changes in  $S_g$  of the synthesized carbides.<sup>29</sup>

The insensitivity of  $S_g$  to variations in space velocity or heating rate observed in the synthesis of NbC can be associated with the very severe conditions employed, i.e., temperatures up to 1373 K and holding times of 0.7 h for completion of carburization. Under these extreme synthesis conditions the occurrence of thermal sintering is not surprising. In fact, analyzing the values of  $D_P$  and  $D_C$  for the carbide 1373 K/0.7 h presented in Table 1 it can be seen that  $D_P$  is 2 times bigger than  $D_C$ , indicating that the use of the high final temperature caused some particle agglomeration.

In reducing the synthesis temperature from 1373 to 1173 K, it was necessary to increase the time at the final temperature (soaking time) from 0.7 to 3.0 h to have complete carburization of the commercial  $\text{Nb}_2\text{O}_5$ . The carbide (1173 K/3.0 h) had a  $S_g$  of 42  $\text{m}^2/\text{g}$  corresponding to an increase of approximately 1400% relatively to the  $S_g$  of the starting  $\text{Nb}_2\text{O}_5$ . Although 42  $\text{m}^2/\text{g}$  is small compared to the surface areas of the materials commonly used as catalysts, it is a moderate value for an unsupported material.

Although a surface area of 42  $\text{m}^2/\text{g}$  was obtained with 1173 K as the final temperature, this temperature was still high enough to promote sintering. Table 1 shows that  $D_P > D_C$  for the carbide 1173 K/3.0 h confirming that consolidation of crystallites had occurred.

Volpe and Boudart<sup>4</sup> have concluded that the increase in surface area during the  $\text{MoO}_3$  nitridation might be attributed to the development of porosity during the reaction. Examination of ESEM pictures (Figure 8) shows that while the commercial  $\text{Nb}_2\text{O}_5$  starting material is formed of big and dense crystallites (Figure 8A), the carbide 1373 K/0.7 h (Figure 8B) particles are permeated by holes or cracks.

The appearance of these new features was not accompanied by changes in the solid's external form, and the increase in surface area is probably due to the development of porosity. However, while for  $\text{Mo}_2\text{N}$  micropores<sup>3,10,26,27</sup> are formed, in the case of NbC the size regime appears to be in the range of macropores. The difference may be due to the lower temperature of synthesis required for  $\text{Mo}_2\text{C}$ .

The small CO chemisorption presented by the carbides (1373 K/0.7 h and 1173 K/3.0 h) in Table 1 can be due to a weak interaction of the CO molecule with the surface<sup>30</sup> or to some kind of surface contamination. Lee et al.<sup>13</sup> have shown for  $\text{Mo}_2\text{C}$  that samples containing large amounts of polymeric carbon had negligible CO

(25) Boudart, M.; Oyama, S. T.; Volpe, L. U.S. Patent 4,515,763, 1985 (assigned to Stanford University).

(26) Wise, R. S.; Markel, E. J. *J. Catal.* **1994**, *145*, 335.

(27) Choi, J. G.; Curl, R. N.; Thompson, L. T. *J. Catal.* **1994**, *146*, 218.

(28) Kapoor, R.; Oyama, S. T. *J. Solid State Chem.* **1992**, *99*, 303.

(29) Teixeira da Silva, V. L. S.; Schmal, M.; Oyama, S. T., unpublished data.

(30) Kojima, I.; Orita, M.; Miyazaki, E.; Otani, S. *Surf. Sci.* **1985**, *160*, 153.

chemisorption. Similar results were obtained by Boudart et al.<sup>31</sup> for carbides with graphitic carbon in the case of hydrogen chemisorption. For niobium carbide it is likely that thermal decomposition of methane occurs at the high temperatures of the synthesis also resulting in the deposition of carbon. Preliminary experiments indicate that the carbon forms a dense layer on the surface and does not contribute to  $S_g$ . For example it cannot be reduced by  $H_2$  treatment even at 973 K, but it is partially removed by  $O_2$  treatment at 623 K without changes in  $S_g$ . Uptakes of CO on such samples (after reduction at 723 K) increase from 28 to 99  $\mu\text{mol/g}$  with surface area remaining at 42  $\text{m}^2/\text{g}$ . One way to overcome the problem of excess carbon formation may be to carry out the synthesis with lower concentrations of methane,<sup>16</sup> but in this case a lower  $S_g$  would be expected.<sup>13</sup>

Changing the starting material in the NbC synthesis from the commercial  $\text{Nb}_2\text{O}_5$  to the  $\text{Nb}_2\text{O}_5$  aerogel precursor caused not only drastic changes in the TPR profiles but also the formation of a carbide with completely different textural properties. The major differences in the TPR profiles were the presence of water and carbon dioxide peaks (Figures 4 and 6) in the temperature range 300–700 K not observed when the commercial  $\text{Nb}_2\text{O}_5$  was used as a starting material (Figures 1 and 2).

These peaks are most likely due to the decomposition of surface alkoxide groups present in the aerogel. This was confirmed in a separate experiment where the temperature program was interrupted at 800 K and X-ray analysis showed only the presence of crystalline  $\text{Nb}_2\text{O}_5$  ( $S_g = 150 \text{ m}^2/\text{g}$ ). Water and carbon dioxide formation was accompanied by the transformation of the amorphous material into a crystalline oxide of high surface area, consistent with previously reported results.<sup>19</sup>

As shown in Figure 4, when the aerogel precursor was used instead of commercial  $\text{Nb}_2\text{O}_5$ , not only was the total time at the final temperature decreased from 3.0 to 0.9 h but also the NbC formed had a higher specific surface area ( $S_g = 74 \text{ m}^2/\text{g}$ ). Apparently, the nature of the starting material plays an important role on the textural properties of the obtained product.

This difference between starting materials could be associated with shorter diffusion distances for oxygen and carbon in the solid matrix leading to shorter reaction times and decreased sintering. The carbide 1173 K/0.9 h presents a good agreement between  $D_P$  and  $D_C$ , indicating that the particles are not polycrystalline. This result, in conjunction with the value of  $S_g$ , indicates that sintering by agglomeration did not occur during the synthesis.

Decreasing the synthesis temperature from 1173 to 1000 K led not to the formation of NbC as presented in

Figure 7 but rather to  $\text{NbO}_2$  with  $S_g = 82 \text{ m}^2/\text{g}$ . During this experiment no carbon monoxide formation was observed in the isothermal region at 1000 K/1.0 h, indicating that no carburization was occurring. Since only the water formation peak was seen in the high temperature region (976 K), it is probable that a reductive process  $\text{Nb}_2\text{O}_5 \rightarrow \text{NbO}_2$  precedes the carburization reaction during NbC synthesis. Although further experiments are necessary to clarify the mechanism of the solid state transformation  $\text{Nb}_2\text{O}_5 \rightarrow \text{NbC}$ , the results when the aerogel precursor was used as starting material indicate that the transformation oxide  $\rightarrow$  carbide occurs in two steps: (i)  $\text{Nb}_2\text{O}_5$  reduction to form  $\text{NbO}_2$ ; (ii)  $\text{NbO}_2$  carburization/reduction to form NbC.

The ESEM pictures of the compounds obtained by reaction of the  $\text{Nb}_2\text{O}_5$  aerogel precursor at 1173 K/0.9 h or 1000 K/1.0 h reveal that the external morphology of the starting material is preserved during the reaction. This means that the transformation  $\text{Nb}_2\text{O}_5 \rightarrow \text{NbC}$  belongs to the class of pseudomorphic solid-state reactions.<sup>4</sup>

Although there is a big decrease in the specific surface area as the aerogel reacts at 1173 K/0.9 h ( $344 \rightarrow 74 \text{ m}^2/\text{g}$ ), the  $S_g$  of 74  $\text{m}^2/\text{g}$  obtained is the highest value reported in the literature for NbC. However, taking into account that the carburization reaction occurs via formation of a  $\text{NbO}_2$  intermediate with  $S_g = 82 \text{ m}^2/\text{g}$ , the decrease in the specific surface area during carbide formation is small.

## Conclusions

Niobium carbide with  $S_g = 74 \text{ m}^2/\text{g}$  can be prepared by temperature-programmed reaction between the corresponding niobium oxide aerogel precursor and methane/hydrogen mixtures. So far, this is the highest value of  $S_g$  for NbC reported in the literature.

Using  $\text{Nb}_2\text{O}_5$  compounds as starting materials, the solid-state transformation oxide  $\rightarrow$  carbide occurs in two steps, the first being a hydrogen reduction leading to  $\text{NbO}_2$  formation and the second carburization/reduction of the  $\text{NbO}_2$  to NbC. Environmental scanning electron microscopy indicates that the transformation  $\text{Nb}_2\text{O}_5 \rightarrow \text{NbC}$  is a pseudomorphic process with preservation of the external form of the starting material. The present results suggest the possibility of using aerogel oxides in the production of other carbides with high predicted synthesis temperatures such as VC (1940 K), TiC (1600 K), ZrC (1980 K), and HfC (2040 K).<sup>16</sup>

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(31) Boudart, M.; Lee, J. S.; Imura, K.; Yoshida, S. *J. Catal.* **1987**, *103*, 30.