Journal of Catalysis **210,** 1–6 (2002)
doi:10.1006/jcat.2002.3634

Catalytic Decomposition of Hydrazine on Tungsten Carbide: The Influence of Adsorbed Oxygen

J. B. O. Santos,* G. P. Valença,*,[1] and J. A. J. Rodrigues†

Department of Chemical Processes, School of Chemical Engineering, State University of Campinas, UNICAMP, C.P. 6066, 13081-970 Campinas, SP, Brazil; and †National Institute Space Researche, INPE, Rod. Presidente Dutra, Km 40, 12630-000 Cachoeira Paulista, SP, Brazil

Received June 18, 2001; revised March 15, 2002; accepted April 11, 2002

Passivated and nonpassivated tungsten carbide (WC) powders were prepared by a temperature-programmed reaction and used as catalysts in the hydrazine decomposition reaction. All catalysts were active at 313 K. The only products of reaction were nitrogen and ammonia, suggesting that the reaction route and the rate-determining step were not modified by adsorbed oxygen. Surface oxygen atoms reacted with hydrazine, resulting in a larger decrease in the rate of reaction for the passivated solids. Excess carbon on the surface of the carbide inhibited the decomposition of hydrazine and resulted in a decrease of ca. 48% in the specific surface area of the tungsten carbide. The excess carbon may be removed in flowing hydrogen at 1000 K. When compared to commercial Ir catalyst (Shell 405), WC is less active in the hydrazine decomposition reaction.

Key Words: **hydrazine decomposition; tungsten carbide; temperature-programmed reaction; WC catalyst; passivated WC powders; nonpassivated WC powders; surface oxygen.**

1. INTRODUCTION

Hydrazine, N_2H_4, has several applications and is one of the most frequently used liquid fuels in microthrusters (1). The use of N_2H_4 in satellite attitude control is due to the low activation energy of its decomposition and the high exothermicity of this reaction. These features combine two properties which are important for space applications: the injection of liquid reactants at room temperature (RT) and the formation of gaseous products at high temperature (>1000 K) in a short period of time (<1 s). For a solid to be a suitable catalyst for space applications, the decomposition of N_2H_4 should occur at RT. The commercial catalyst, SHELL 405 ($\sim$36% w/w Ir/Al_2O_3), has physical and chemical properties which are unique for space applications, such as thermal stability, bimodal distribution of pore diameters, and uniform size distribution of Ir particles ($d < 2$ nm) on the surface of the Al_2O_3. However, due to the high price of Ir and the high loading of metal necessary to prepare suitable catalysts for space applications, new materials have been studied as prospective catalysts for the decomposition of N_2H_4.

Several transition metals, such as Ir (2–4), Rh (2, 5), Ni (2), Co (2), Pt (2, 6), Ru (2), Pd (2), Ag (2), Cu (2), Fe (7), and W (8), are active catalysts for the decomposition of N_2H_4. The decomposition of N_2H_4 may occur by the following reactions:

$$N_2H_4 \rightarrow N_2 + 2H_2 \qquad [1]$$

$$3N_2H_4 \rightarrow N_2 + 4NH_3. \qquad [2]$$

Reactions 1 and 2 were observed on Rh (2), Pt (2), and Pd (2) between 333 and 433 K, with an activation energy of 46 kJ mol^{-1} for Rh and 67 kJ mol^{-1} for Pt and Pd, while only or mainly reaction 2 was observed on Ir, Ni, Co, Ru, Ag, and Cu, with activation energies varying between 46 and 71 kJ mol^{-1}. For a 4% Ni/γ-Al_2O_3 catalyst, at 292 K and a N_2H_4 partial pressure of 5.87 mbar, Valença (9) observed only reaction 1 while on Ni (111), the formation of diimide (10, 11) was also observed.

Rodrigues and co-workers (12–13) showed that either tungsten or molybdenum carbides or nitrides may be used as catalysts in the decomposition of N_2H_4. They observed that all catalysts were active in this reaction at RT. These authors also observed that at 333 K Mo_2C was the most active solid catalyst. On the other hand, during tests performed on a 2-N thruster rocket engine under conditions that simulate the actual conditions found in space, W_2C was the most efficient catalyst, and in some cases it was more active than the commercial catalyst (13).

Tungsten carbides or nitrides are interstitial alloys used in metallurgical applications (14). Passivated tungsten and molybdenum carbides were first used as catalysts for the isomerization of hydrocarbons, a reaction typically catalyzed by noble metals (15). The study of these materials as catalysts became feasible in the 1980s, when Oyama (16) and Volpe and Boudart (17, 18) developed a methodology to prepare high surface area tungsten or molybdenum carbides or nitrides. In spite of their similarities to noble metals, carbides and nitrides have unique features. For

[1] To whom correspondence should be addressed. E-mail: gustavo@feq.unicamp.br.

example, the catalytic properties of transition metal carbides may be affected by adsorbed oxygen. Iglesia *et al.* (19, 20) found that oxygen adsorbed on WC introduces WO_x sites that catalyze the isomerization of *n*-heptane with high selectivity. Ribeiro *et al.* (21, 22) found that oxygen adsorbed on WC or on β-W_2C inhibits the rate of hydrogenolysis and catalyzes the isomerization of neopentane and *n*-hexane, suggesting a bifunctional mechanism. Blekkan *et al.* (23) observed the bifunctional character of molybdenum carbide exposed to oxygen in the isomerization of *n*-heptane. In addition, excess carbon on the surface of carbides affects their catalytic properties.

Although the catalytic decomposition of N_2H_4 has been extensively studied, little is known about its sequence of steps. The mechanisms proposed in the literature involve the breaking of an N–N bond followed by recombination of adsorbed N atoms or a step-by-step dehydrogenation of the hydrazine molecule (24–26). For example, Maurel and Menezo (27) concluded that on metals between 333 and 573 K, N_2 is always formed from one hydrazine molecule without cleavage of the N–N bond. Alberas *et al.* (28), however, concluded that cleavage of both the N–N bond and the N–H bond could occur depending on the metal used. Thus, an understanding of the decomposition kinetics of N_2H_4 is necessary for the design of more efficient catalysts for space applications.

The objective of this work is to prepare and study passivated and nonpassivated WC in the decomposition of N_2H_4. As the tungsten and molybdenum are active catalysts for the decomposition of N_2H_4 (12, 13), an understanding of the kinetics of this reaction on these solids is of fundamental importance for the design of catalysts feasible for use in space applications. In addition, there is very little information in the literature on the decomposition of N_2H_4 on tungsten carbides. Moreover, the influence of adsorbed oxygen on the surface of tungsten carbides used for the decomposition of N_2H_4 has not been reported.

2. EXPERIMENTAL METHODS

2.1. *Catalyst Preparation*

Tungsten carbide, WC, was prepared by temperature-programmed reaction of WO_3 powder (Carlo Erba, 3 m^2 g^{-1}, 99.5%) in a flowing mixture of 20% v/v CH_4 (White Martins, 99.97%) and H_2 (White Martins, 99.999%) at an overall flow rate of 71 μmol s^{-1} at atmospheric pressure. Typically, ca. 0.5 g of WO_3 was spread over a quartz disk in a quartz cell. The sample was heated from RT to 1123 K at a rate of 5 K min^{-1} and then maintained at this temperature for 1 h. The sample was then cooled in He (White Martins, 99.999%) to RT. Samples thus prepared are called *fresh carbides, WC-f*. Some *WC-f* carbide samples were passivated in a flow of 1.0% O_2/He (White Martins) mixture for 1 h and these solids are called *passivated carbides, WC-p*. Some WC-f samples were treated with H_2 at 998 K for 1.5 h and these solids are called *freshly reduced carbides, WC-fr*. Finally, some WC-fr samples were passivated in a flow of 1.0% O_2/He mixture for 1 h. These samples are called *passivated-reduced carbides, WC-rp*. Each sample (ca. 0.5 g) was prepared at least twice.

The gases that evolved during the preparation of the WC samples were analyzed by an on-line gas chromatograph (CG 90), using a thermal conductivity detector and a Chromosorb 102 column maintained at 373 K.

2.2. *Catalyst Characterization*

The passivated samples were characterized by X-ray diffraction (XRD), N_2 adsorption, and chemical analysis. The bulk structure of the passivated samples was determined by the powder X-ray diffraction technique using a Philips model PW 1830 diffractometer, with Cu K_α radiation. The surface area was determined by the BET method (29). For nonpassivated samples, the analyses were performed in a glass adsorption system, while the passivated samples were analyzed in a Micromeritics-ASAP 2010C. To measure the nonpassivated carbides BET specific surface area, the cell was isolated and transferred to a glass volumetric adsorption system. The samples were then degassed at 1.33×10^{-5} Pa for 0.5 h at RT, while passivated samples were degassed at 673 K for 2 h prior to BET surface area measurements.

The amounts of carbon and oxygen in the samples were determined by chemical analysis. The amount of tungsten was determined as the difference between the amount of carbide and that of carbon and oxygen.

2.3. *Kinetic Measurements*

The rate of decomposition of N_2H_4 was measured in the system used to prepare the solids. The nonpassivated carbides were prepared and reduced *in situ* while the passivated carbides were prepared in advance and stored in a dissector. The amount of sample used in each experiment was ca. 10 mg. All reactions were carried out at atmospheric pressure. The catalysts were spread as a thin layer in the reactor that was attached to the reaction rig. The system was then purged with flowing He for at least 1 h and the catalyst was reduced in flowing H_2 (1.64 cm^3 s^{-1}) at 623 K for 1 h. The flow of H_2 was then switched to He and the temperature was decreased to RT. The system remained at RT for 1 h until no H_2 was observed by gas chromatography. Helium (0.93 cm^3 s^{-1}) was then flowed first through a saturator containing N_2H_4 and then through a condenser, maintained at 303 K and 293 K, respectively. At 293 K, the partial pressure of N_2H_4 is 1.24 kPa (30). After 0.5 h, the N_2H_4/He mixture was flowed through the reactor and the decomposition of N_2H_4 was studied for at least 1 h. The gases that evolved during the decomposition of N_2H_4 went through a H_2SO_4 trap that removes NH_3 and unreacted N_2H_4. The remaining gases, H_2 or N_2, were analyzed by gas chromatography (CG 90), using a thermal conductivity detector and a Carboxen 1000 column maintained at 323 K.

The reaction temperature for the decomposition of N_2H_4 on WC was varied between 303 and 333 K and the partial pressure of hydrazine was fixed at 1.24 kPa for the calculation of the apparent activation energy. To determine the reaction order with respect to N_2H_4, the partial pressure of hydrazine was varied between 0.63 and 1.24 kPa by varying the saturator temperature.

3. RESULTS AND DISCUSSION

Both WC-p and WC-rp have the same hexagonal crystal structure as that of WC reported in the literature. No other phases, such as W, W_2C, WO_3, or WO_2, were observed for these solids (Fig. 1). In addition, the XRD patterns suggest that flowing H_2 at 1000 K for 1.5 h did not change the bulk structure of the carbide and that the carbon removed was only excess carbon on the surface of the sample. This result is in good agreement with a previous result (12).

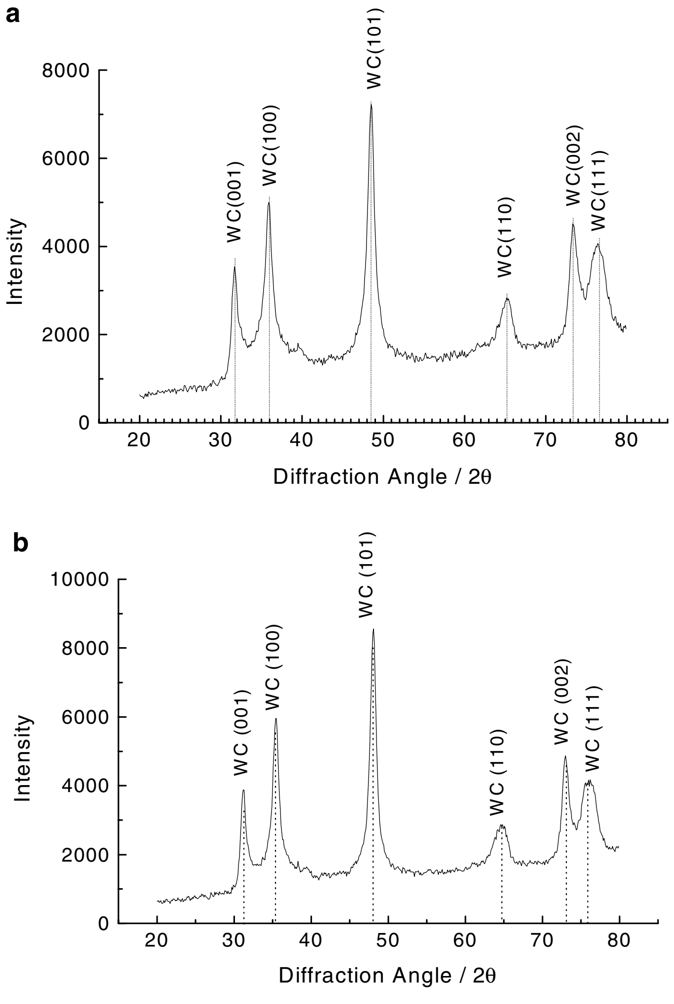

FIG. 1. X-ray diffraction patterns. (a) WC-p; (b) WC-rp.

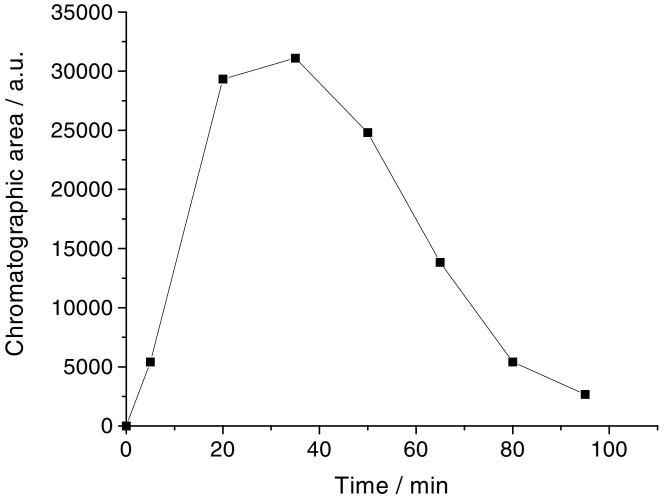

FIG. 2. Removal of the excess carbon from the WC-f surface.

The specific surface areas of the WC-f and WC-p were about 13 $m^2\ g^{-1}$, indicating that passivation had little influence on the surface structure of the sample containing excess carbon. The formula of the WC-p sample calculated from chemical analysis was $WC_{1.14}O_{0.07}$, suggesting that little O is added to the sample surface after passivation. Thus, excess carbon decreases the amount of adsorbed oxygen and it can be used as a passivation layer (31).

To remove the excess carbon from the surface of the carbide, the standard procedure is to expose the solid to a flow of H_2 at high temperatures (21, 32). However, carbon from the bulk may also be removed if the carbide is exposed to flowing H_2 at high temperatures for long periods of time (32). Thus, in this work the excess carbon on the surface of the WC-f was removed as CH_4 by treating the carbide with H_2 at 1000 K for 1.5 h. The CH_4 that evolved was measured by gas chromatography (Fig. 2) using a thermal conductivity detector.

Figure 2 shows the areas of the chromatographic peaks corresponding to methane partial pressure versus reduction time. The methane partial pressure increases quickly during the first 20 min, reaching a maximum after about 40 min. Then the amount of methane decreases slowly until it reaches a constant pressure at about 80 min. Leclercq *et al.* (32) found that a longer treatment of carbides with H_2 can change their bulk structure. In this work, the carbide samples were exposed to a flow of H_2 for 90 min and no change in the bulk structure was observed by XRD.

The specific surface area of the WC-rp sample was about 25 $m^2\ g^{-1}$, a 90% increase from that of the WC-f sample. This fact suggests that the carbon removed was located on the surface of the carbide, in agreement with the results of XRD.

No products were observed when N_2H_4 was flowed through WC-f or WC-p at 313 K, suggesting that excess carbon on the carbide surface prevented the decomposition of N_2H_4. After excess carbon was removed from the carbide surface (WC-fr and WC-rp samples), N_2 and NH_3 (reaction 2) were observed as products for the decomposition of N_2H_4 at 313 K. This is in good agreement with the results reported by Rodrigues (12), who also observed that excess carbon totally prevents the decomposition of N_2H_4.

In this work the reaction rate is defined as moles of N_2H_4 decomposed per gram of catalyst per second. The initial value of the reaction rate is the same within the experimental error for passivated and nonpassivated tungsten carbide samples. In addition, the reaction rate for the decomposition of N_2H_4 on all carbide samples decreases with time (Fig. 3). On passivated carbides, however, the decrease in the reaction rate is larger during the first 20 min of reaction, while on nonpassivated samples (Fig. 3) the decrease in the reaction rate is continuous over time. For example, after 60 min the reaction rate on WC-rp is 30% lower than the initial value while on the WC-fr the reaction rate is 10% lower than the initial value.

Since the rate has units of moles per gram per second it is important to know whether the observed decrease is due to a change in the surface structure of the carbide or to a decrease in the number of sites available for reaction. Although the XRD patterns of the carbide samples used in this work were not taken after reaction, in a similar experiment one of the authors observed that the XRD of passivated tungsten carbides did not change after reaction between 303 and 313 K compared to those of the solid prior to reaction. However, when the reaction was done under the same conditions as those used in satellite microthrusters (1100 K) (13), the XRD of the solid after reaction had patterns of tungsten nitrides in addition to the carbide patterns (12). In addition, the chemical analysis after reaction at 313 K was similar to that of the solid prior to reaction, suggesting that the formation of nitrides did not occur or was restricted to the surface.

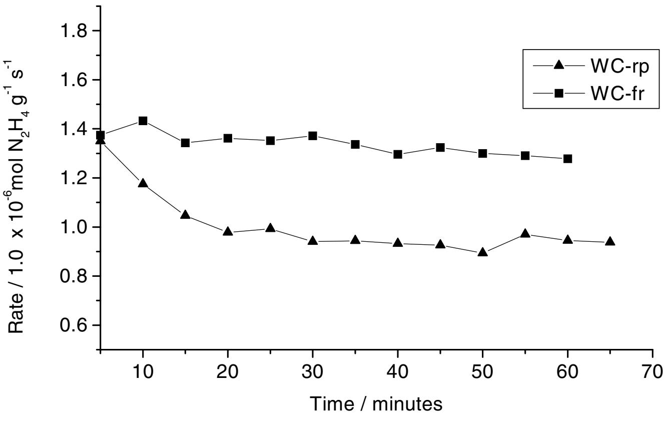

FIG. 3. Rate of decomposition of hydrazine on WC-fr and WC-rp at 313 K.

However, the larger initial decrease in reation rate observed for the passivated carbide could be due to a decrease in the area of the solid exposed to N_2H_4. Thus, although the passivated carbide was reduced in flowing H_2 at 623 K for 1 h prior to reaction, only a small fraction of the adsorbed O can be removed by H_2 at this temperature. For example, Ribeiro *et al.* (33) found that only 10% of the surface oxygen can be removed by H_2 below 700 K. Thus, since there were O atoms on the surface of the passivated carbides, H_2O could be formed upon reaction with N_2H_4. In that case, H_2O would fill the micropores of the carbide. In a similar experiment one of the authors observed that after reaction at 313 K the surface area decreased ca. 50%. However, when the sample was heated in vacuo above 600 K the surface area had the same value as that of the carbide prior to reaction (12), suggesting that H_2O was formed during the reaction between N_2H_4 and adsorbed O. The blocking of micropores of α-WC with H_2O was also observed after titration of adsorbed O with H_2 by the decrease in intensity of the ^{129}Xe NMR peak (34) and in the reaction between H_2 and O_2 (33). Thus, although the formation of surface nitrides cannot be ruled out, none of the techniques used in this work suggest this and a more sensitive surface technique would be necessary to observe it. However, the decrease observed in the reaction rate can be explained by filling the micropores of the carbide with H_2O formed during the reaction between N_2H_4 and surface O.

The reaction order with respect to N_2H_4 was zero for the WC-rp catalyst, in good agreement with that reported by Rodrigues (12). A zero-order reaction suggests that the carbide surface is covered with a strongly adsorbed species. From the measured value for the initial rate of reaction at 303 K (8.7×10^{-7} mol $g^{-1}s^{-1}$), the surface area (25 m^2 g^{-1}), and the value of surface density obtained by Ribeiro *et al.* (33) (0.4×10^{15} cm^{-2}), the estimated turnover rate for the decomposition of N_2H_4 at 303 K is 5×10^{-3} s^{-1}. From the values for partial pressure of N_2H_4, activation energy of adsorption (vide infra), and preexponential factor for adsorption (37) it is possible to estimate the fraction of empty sites on the surface of the carbide as 7.7×10^{-7}, suggesting an almost covered surface during reaction.

The reaction temperature was varied between 303 and 313 K for calculation of the apparent activation energy (Fig. 4). The initial rates varied between 8.7×10^{-7} and 2.5×10^{-6} mol $g^{-1}s^{-1}$ and the activation energy for WC-rp was about 50 kJ mol^{-1}. Ribeiro *et al.* (33) observed that NH_3 adsorbs strongly on the surface of WC and that it desorbed from the surface as $N_2$with a temperature maximum of 1200 K. Thus, a rough estimation of the enthalpy of adsorption of N atoms, Q_N, is 300 kJ mol^{-1} K^{-1}.

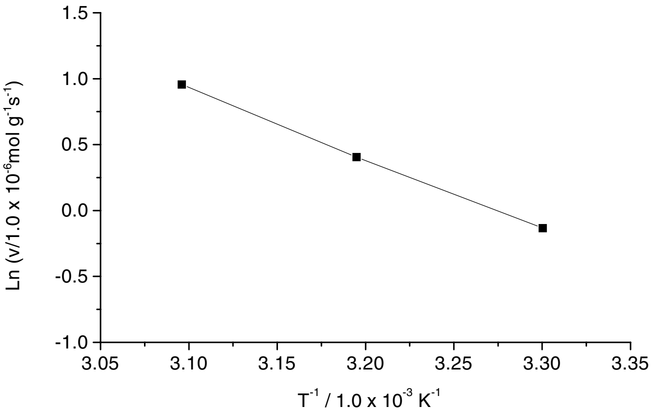

FIG. 4. Arrhenius plot for catalyst WC-rp.

Using this value we estimated the activation energy for some elementary steps of the catalytic decomposition of N_2H_4 (35) based on the bond order conservation method of Shustorovich (36). The first step in the decomposition of N_2H_4 is a dissociative adsorption on a bare surface. N_2H_4 may be adsorbed according to

$$N_2H_4 + 2^* \rightarrow N_2H_3^* + H^* \qquad [3]$$

or

$$N_2H_4 + 2^* \rightarrow NH_2^* + NH_2^* \qquad [4]$$

where $*$ represents an empty surface site.

Of these two steps the more favorable is the breaking of one N–H bond on the surface to form adsorbed N_2H_3 and H ($E_a = 67$ kJ mol^{-1}). Once adsorbed N_2H_3 is formed it may react with adsorbed H to form NH_3 and NH or it may break one N–N bond or one N–H bond. The activation energy for reaction with adsorbed H is 0 kJ mol^{-1} while the activation energies for the breaking of the N–N bond is 128 kJ mol^{-1} and that for the N–H bond is 67 kJ mol^{-1}. Thus, even on a bare surface the most favorable step for decomposition of adsorbed N_2H_3 is the reaction with H to form NH_3 and adsorbed NH. Details about the calculation of the activation energy for different steps in the catalytic decomposition of N_2H_4 can be found elsewhere (35).

Adsorbed NH may react with adsorbed H, NH, or NH_2 to form adsorbed NH_2, adsorbed N and NH_2, or adsorbed N and NH_3, respectively. All these steps have $E_a = 0$ kJ mol^{-1}. Adsorbed NH_2 may react with adsorbed H or NH_2 to form NH_3 and NH_3 and adsorbed NH. The activation energy for these steps is also equal to zero. The possible steps are as follows:

$$N_2H_4 + 2^* \rightarrow N_2H_3^* + H^* \qquad [5]$$

$$N_2H_3^* + H^* \rightarrow NH_3 + NH^* + {}^* \qquad [6]$$

$$NH^* + NH^* \rightarrow NH_2^* + H^* \qquad [7]$$

$$NH_2^* + NH^* \rightarrow NH_3 + N^* + {}^* \qquad [8]$$

$$NH_2^* + NH_2^* \rightarrow NH_3 + NH^* + {}^* \qquad [9]$$

$$NH_2^* + H^* \rightarrow NH_3 + 2^* \qquad [10]$$

$$NH^* + H^* \rightarrow NH_2^* + {}^* \qquad [11]$$

$$N^* + N^* \rightarrow N_2 + 2^* \qquad [12]$$

$$N^* + H^* \rightarrow NH^* + {}^* \qquad [13]$$

$$N^* + NH^* \rightarrow N_2 + H^* + {}^*. \qquad [14]$$

The activation energies for steps 6 through 11 are each equal to zero. In addition, for Q_N less than 450 kJ mol^{-1} the activation energy for the combination of two adsorbed N atoms is also zero. Thus, as adsorbed NH_x fragments form on the carbide surface they react to form either NH_3 or adsorbed N. Once NH_3 is formed, it is desorbed from the carbide surface while adsorbed N accumulates on the surface. In addition, no H_2 was observed as a product and the estimated activation energy for the bimolecular desorption of H_2 is ca. 100 kJ mol^{-1}. Thus, as reaction proceeds, the probability of finding two neighboring NH_x species or adsorbed H decreases and the only possible steps on the surface are those involving adsorbed N. These possible steps include the reaction between adsorbed N and adsorbed H (step 13) or adsorbed NH (step 14). The activation energy for step 13 is 56 kJ mol^{-1} and for step 14 it is 44 kJ mol^{-1}, values close to the 50 kJ mol^{-1} value we measured in this work. In addition, the activation energy for the reverse reaction for step 14 is 223 kJ mol^{-1}, a value that suggests that this step is irreversible. Thus, it seems that the rate-determining step involves adsorbed N but is not the bimolecular desorption of adsorbed N.

4. CONCLUSION

WC was prepared by a temperature-programmed reaction of WO_3 with a 20%v/v CH_4/H_2 mixture. We were able to prepare ca. 0.5 g of tungsten carbide reproducibly, as confirmed by XRD, BET surface area measurements, and chemical analysis. This reproducibility is an advance in the preparation of tungsten carbides as it is difficult to control the solid state reaction ($WO_3 \rightarrow WC$). Indeed, there is very little work in the literature on the preparation of the tungsten carbide samples of more than 0.4 g.

Excess carbon on the carbide surface reduced the specific surface area by 40%. Samples of WC with excess carbon on the surface showed no catalytic activity during the decomposition of N_2H_4 at 313 K, suggesting that excess carbon totally inhibits the reaction.

Removal of excess carbon in flowing H_2 at 1000 K for 1.5 h did not change the hexagonal structure of the carbide and resulted in solids with a specific surface area of 25 m^2 g^{-1}. The only products of decomposition of N_2H_4 on WC-fr and WC-rp were N_2 and NH_3, suggesting that this reaction takes place on the same sites on the surface of both passivated and fresh carbides. Although the initial rate of reaction was the same for both carbides, passivated catalysts deactivated more rapidly due to formation of H_2O by the reaction of adsorbed O and N_2H_4. Analysis of kinetic data and estimated activation energy of elementary steps suggest a surface covered with N during reaction and a rate-determining step involving these species.

Finally, the decomposition of N_2H_4 on the tungsten carbides prepared in this work has values of activation energy and order of reaction similar to those found for commercial catalysts, indicating that carbides are promising catalysts for space applications.

ACKNOWLEDGMENTS

J.B.O.S. acknowledges the financial support received from FAPESP (Grant N. 96/2108-6). We are also grateful to INPE (LCP), where this work was conducted.

REFERENCES

1. Schmidt, E. W., *in* "Hydrazine and Its Derivatives: Preparation, Properties, Applications" (E. W. Schmidt, Ed.), Chap. 6, p. 714. Wiley-Interscience, New York, 1984.
2. Maurel, R., Menezo, J. C., and Barrault, J., *J. Chim. Phys.* **70**, 1221 (1973).
3. Sawin, H. H., and Merrill, R. P., *J. Chem. Phys.* **73**(2), 996 (1980).
4. Wood, B. J., and Wise, H., *J. Catal.* **39**, 471 (1975).
5. Prasad, J., and Gland, J. L., *Langmuir* **7**, 722 (1991).
6. Alberas, D. J., Kiss, J., Liu, Z. M., and White, J. M., *Surf. Sci.* **278**, 51 (1992).
7. Grunze, M., *Surf. Sci.* **81**, 603 (1979).
8. Cosser, R. C., and Tompkins, F. C., *Trans. Faraday Soc.* **67**, 526 (1971).
9. Valença, G. P., *in* "Anais do 7° Seminário Brasileiro de Catálise," Vol. 1, p. 375. IBP, Intituto Brasibin de Pehóleo, Rio de Janeiro, 1993.
10. Huang, S. X., Rufael, T. S., and Gland, J. L., *Surf. Sci.* **290**, L673 (1993).
11. Gland, J. L., Fisher, G. B., and Mitchell, G. E., *Chem. Phys. Lett.* **119**(1), 89 (1985).
12. Rodrigues, J. A. J., Thèse de Doctorat, Université Paris VI Pierre et Marie Curie, Paris, 1996.
13. Rodrigues, J. A. J., Cruz, G. M., Bugli, G., Boudart, M., and Djéga-Mariadassou, G., *Catal. Lett.* **45**, 1 (1997).
14. Toth, L. E., *in* "Transition Metal Carbides and Nitrides" (John L. Margrave, Series Ed.), p. 29. Academic Press, New York, 1971.
15. Boudart, M., and Ptak, L. D., *J. Catal.* **16**, 90 (1970).
16. Oyama, S. T., Ph.D. dissertation, Stanford University, 1981.
17. Volpe, L., and Boudart, M., *J. Solid. State Chem.* **59**, 332 (1985).
18. Volpe, L., and Boudart, M., *J. Solid. State Chem.* **59**, 348 (1985).
19. Iglesia, E., Baumgartner, J. E., Ribeiro, F. H., and Boudart, M., *J. Catal.* **131**, 523 (1991).
20. Iglesia, E., Ribeiro, F. H., Boudart, M., and Baumgartner, J. E., *Catal. Today* **15**, 455 (1992).
21. Ribeiro, F. H., Dalla Betta, R. A., Boudart, M., Baumgartner, J. E., and Iglesia, E., *J. Catal.* **130**, 86 (1991).
22. Ribeiro, F. H., Boudart, M., Dalla Betta, R. A., and Iglesia, E., *J. Catal.* **130**, 498 (1991).
23. Blekkan, E. A., Cuong, P. H., Ledoux, M. J., and Guille, J., *Ind. Eng. Chem. Res.* **33**, 1657 (1994).
24. Khomenko, A. A., and Apel'Baum, L. O., *Kinet. Katal.*, **17**(3), 691 (1976).
25. Contour, J. P., and Pannetie, G., *J. Catal.* **24**, 434 (1972).
26. Szware, M., *Proc. R. Soc. London* **198**, 267 (1949).
27. Maurel, R., and Menezo, J. C., *J. Catal.* **51**, 293 (1978).
28. Alberas, D. J., Kiss, J., Liu, Z. M., and White, J. M., *Surf. Sci.* **278**, 51 (1992).
29. Brunauer, S., Emmet, P. H., and Teller, E. J., *J. Am. Chem. Soc.* **60**, 309 (1938).
30. Lange, N. A., *in* "Handbook of Chemistry" (John A. Dean, Ed.), 13th ed., pp. 10–32. McGraw Hill, New York, 1985.
31. Keller, V., Wehrer, P., Garin, F., Ducros, R., and Maire, G., *J. Catal.* **153**, 9 (1995).
32. Leclercq, G., Kamal, M., Giraudon, J. M., Devassine, P., Feigenbaum, L., Leclercq, L., Frennet, A., Bastin, J. M., Lofberg, A., Decker, S., and Dufour, M., *J. Catal.* **158**, 142 (1996).
33. Ribeiro, F. H., Dalla-Betta, R. A., Guskey, G. J., and Boudart, M., *Chem. Mater.* **3**, 805 (1991).
34. Valença, G. P., Ph.D. dissertation, Stanford University, 1990.
35. Medeiros, J. E., and Valença, G. P., *Brazilian J. Chem. Eng.* **15**, 126 (1998).
36. Shustorovich, E., *Adv. Catal.* **37**, 101 (1990).
37. Boudart, M., and Djéga-Mariadassou, G., *in* "Kinetics of Heterogeneous Catalytic Reactions" (John M. Prausnitz and Leo Brewer, Series Eds.), p. 74. Princeton University Press, Princeton, NJ, 1984.