



Avaliation of gas phase kinetics of the carburization and deactivation reactions aimed to produce NbC

F.A.O. Fontes^a, J.F. de Sousa^{b,*}, C.P. Souza^b, M. Benachour^c, M.B.D. Bezerra^b

^a Universidade Federal do Rio Grande do Norte, Centro de Tecnologia, Departamento de Engenharia Mecânica, Campus Universitario, 59072-970 Natal, RN, Brazil

^b Universidade Federal do Rio Grande do Norte, Centro de Tecnologia, Departamento de Engenharia Química, Campus Universitario, 59072-970 Natal, RN, Brazil

^c Universidade Federal de Pernambuco, Centro de Tecnologia, Departamento de Engenharia Química, Cidade Universitária, 50740-521 Recife, PE, Brazil

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ABSTRACT

The gas phase kinetic study referent the carburization of NbO₂ to NbC is presented in this paper. The reaction took place in a rotating cylinder reactor, with rotation velocity (*r*) of 5 rpm, at temperatures of 1148, 1173 and 1223 K, gas phase flow of 4.033×10^{-6} m³/s and Nb₂O₅ initial mass of 0.004 kg. The reaction mechanism is represented by the reduction of Nb₂O₅ into NbO₂ (first reaction), followed by the carburization of NbO₂ into NbC (second reaction). In this work the kinetic model of gas phase was carried out for the second reaction which is represented by two steps: the first regards the consumption of CH₄ and second, the deactivation of NbO₂. From chromatographic analysis of the gas products at the reactor outlet, the molar consumption of CH₄ with reaction time was determined. The results showed the kinetic behavior in the first step represented by a pseudo-first-order model and in the second step by first-order deactivation models. In the present study, it was determined the kinetic constant (*k*), the activation energy (*E*) of the first and second steps, the velocity constant for deactivation *k*' and the decline constant *k_d* that expresses the deactivation factor of NbO₂. Statistical parameters showed satisfactory agreement between the experimental data and those predicted by the model.

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1. Introduction

The kinetic study for the formation of NbC through a gas–solid reaction obtained significant contributions from other investigations that presented stoichiometric equation models and determined the kinetic constant and activation energy for the first step reduction reaction of Nb₂O₅ to NbO₂, Teixeira da Silva et al. [1].

Although final products of a balanced reaction are determined only by temperature, pressure, and the chemical species present, the mechanism and reaction rates depend on a large number of variables such as solid particle size, diffusion rates, gas concentration, porosity and impurity.

The reaction rate equations are grouped under different mechanisms and can be represented by the expression: $F(x) = k \times t$ where $k = k_0 \times e^{(-E/(R_g \times T))}$, where *k*₀ is the Arrhenius pre-exponential factor, *k* (s^{−1}) is the reaction rate constant, *E* (kJ/mol) is the activation energy, *R_g* is the universal gas constant, and *T*(K) is the temperature. The activation energy values reported for carburization reactions are in general between 200 and 800 kJ/mol, which indicates high temperature sensitivity. Reduction/carburization processes

involving highly endothermic gas–solid reactions favor contact efficiency under isothermal conditions as well as the removal of CO as a co-product, Weimer and Alan [2].

High-temperature rotating oven applications for the reduction and carburization of metallic oxides have been reported only in small scale operations, focused merely on theoretical aspects such as heat transfer or material transport. A considerable number of patents have been published, but most of the applications are still in development.

This article presents the gas phase kinetic study results of the gas–solid reaction of Nb₂O₅ to NbC in a rotating cylinder reactor with respect to first (consumption of methane) and second steps (deactivation) of carburization reaction of NbO₂ to NbC (isothermal region) estimating the kinetic constant (*k*), activation energy (*E*) the velocity constant for deactivation *k_d* and the decline constant that expresses the deactivation factor of NbO₂.

Niobium carbide was prepared by carbothermic reduction, Fontes et al.[3], starting from commercial niobium pentoxide powders. The results showed that the rotational effect of the rotating cylinder reactor reduced substantially the total reaction time of carbothermic reduction of NbO₂ to NbC, and influenced significantly the conversion. The solid conversion remained above 74%.

The NbC was produced from commercial niobium pentoxide, using a similar procedure adopted by Kim et al. [4]. Preliminary

* Corresponding author. Tel.: +55 84 9981 2989.

E-mail address: jao@eq.ufrn.br (J.F. de Sousa).

results showed that the conversion depends on the rotation, temperature, mixture flow, CH₄/H₂ ratio and the heating rate.

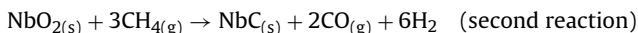
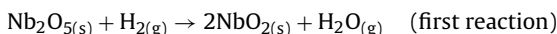
2. Materials and methods

The investigation of the gas phase consisted in adapting a chromatographer/FID system at the reactor outlet to measure the molar consumption of CH₄ throughout the reactions. The concentration of CH₄ in the reactor outlet was checked each 5 min, by direct injection using a 6-way valve. A flow meter with continuous gas flow measurement at the outlet was set in order to measure and record, in concurrence with chromatographic analysis, the variation of outlet gas flow during the reaction. The reactions were carried out at several temperatures (1148, 1173 and 1223 K).

This study presents also a kinetic model of solid deactivation for the second step to obtain the variation in concentration of methane as a function of time, adopting parameters optimized by Fontes et al. [3] for initial mass (nominal) of sample $m_i = 0.004$ kg; heating rate $\beta = 0.167$ K/s; reactor rotation $r = 5$ rpm; $C_{CH_4,i} = 3.64$ mol/m³; CH₄/H₂ flow $Q_m = 4.033 \times 10^{-6}$ m³/s; CH₄ flow $Q_{CH_4,i} = 0.37 \times 10^{-6}$ m³/s; reactor chamber volume $V_R = 22 \times 10^{-6}$ m³, atmospheric pressure $p_{atm} = 1 \times 10^5$ Pa and temperature $T_{atm} = 303$ K.

2.1. Reaction rate of the first step of the second reaction

The stoichiometric equations for the carburization of Nb₂O₅ to NbC is presented by heterogeneous and consecutive reactions, Kim et al. [4]:



In this paper, the kinetic model is applied to the second reaction.

The reaction rate for the first step of the second reaction was considered to be pseudo-first-order, Eq. (1), since the initial concentration of the solid is greater than that of the gas:

$$-r_{CH_4} = -\frac{dC_{CH_4}}{dt} = k \times C_{CH_4} \quad (1)$$

Eq. (1) can be integrated as following:

$$-\ln(1 - X_{CH_4}) = -\ln\left(\frac{C_{CH_4}}{C_{CH_4,i}}\right) = \ln\left(\frac{C_{CH_4,i}}{C_{CH_4}}\right) = k \times t \quad (2)$$

where $C_{CH_4,i}$ and C_{CH_4} are the concentration of methane, initial and at time t , respectively, and X_{CH_4} is the conversion of methane.

The moles of methane consumed ($n_{CH_4,1^a}$) as a function of time, in the first step of the second reaction, at temperatures of 1148, 1173 and 1223 K, can be obtained through the models developed, using Eq. (3), as following:

$$n_{CH_4,1^a} = \int_{t_{is}}^{t_s} F_{CH_4,i} \times X_{CH_4,1^a} \times dt \quad (t_{is} < t < t_s) \quad (3)$$

$$X_{CH_4,1^a} = 1 - \frac{C_{CH_4}}{C_{CH_4,i}} = 1 - e^{-k(t-t_{is})} \quad (4)$$

being:

$t_{is}(s)$: initial isothermal zone time;

$t_s(s)$: final first step time of the second reaction;

$F_{CH_4,i}$: initial molar flow of methane (mol/s), calculated by Eq. (5):

$$F_{CH_4,i} = \frac{Q_{CH_4,i} \cdot p_{atm}}{R_g \cdot T_{atm}} = 1.456 \times 10^{-5} \quad (5)$$

where R_g is the ideal gas constant, $R_g = 8.314$ (J/mol.K).

The moles of methane can be obtained by Eq. (6):

$$n_{CH_4,1^a} = Q_{m,i} \times \int_{t_{is}}^{t_s} (C_{CH_4,i} - C_{CH_4}) \, dt \quad (6)$$

$$\text{where } Q_{m,i} = \frac{F_{CH_4,i}}{C_{CH_4,i}}$$

2.2. Kinetic constants of the first step of the second reaction

The procedure to obtain the kinetic constants of the first step of the second reaction was performed plotting experimental data (concentration of CH₄) as a function of time and constructing straight lines of $\ln(C_{CH_4,i}/C_{CH_4})$ versus time (Eq. (2)) for the temperatures 1148, 1173 and 1223 K, thus obtaining the respective kinetic constants from their respective slopes.

2.3. Activation energy (E)

The activation energy for the interval of the first step of the second reaction was determined using the Arrhenius Equation, Eq. (7), from the slope of the curve $\ln(k)$ versus $1/T$.

$$k = k_0 \times \exp(-E/(R_g \times T)) \quad (7)$$

2.4. Study of the second step of the second reaction

The reaction rate for the second step of the second reaction was represented by models of catalytic deactivation, Levenspiel [5], Fontes et al. [6]. The reactor is discontinued for the solid phase which can be described by Eqs. (8) and (9) as follows:

$$-r'_{CH_4} = -k' \times C_{CH_4} \times a \text{ with } (\varepsilon_{CH_4} = 0) \quad (8)$$

$$-\frac{da}{dt} = k_d \times a \rightarrow a = e^{-k_d \times t} \quad (9)$$

where (a) is the activity factor of the solid dependent on methane concentration, k' (m³/kg.s) is the velocity constant for deactivation, k_d (s⁻¹) is the decline constant that expresses the deactivation factor of the solid, and ε_{CH_4} is the expansion factor or contraction of the gas phase. Assuming the behavior of the reactor near the plug flow model, the equation can be represented by:

$$\frac{m_i}{F_{CH_4,i}} = \int \frac{dX_{CH_4}}{-r'_{CH_4}} = \frac{1}{k' \times a} \times \int \frac{dX_{CH_4}}{C_{CH_4}} \quad (10)$$

where

$$C_{CH_4} = C_{CH_4,i} \cdot (1 - X_{CH_4,2^a}) \quad (11)$$

$X_{CH_4,2^a}$ is the conversion of methane in the second step.

Substituting Eqs. (9) and (11) into Eq. (10):

$$\frac{m_i \times C_{CH_4,i}}{F_{CH_4,i}} = \tau' = \frac{1}{k' \times a} \times \ln \frac{C_{CH_4,i}}{C_{CH_4}} = \frac{1}{k' \times e^{-k_d \times t}} \times \ln \frac{C_{CH_4,i}}{C_{CH_4}} \quad (12)$$

where

$$\tau' = m_i \times \frac{C_{CH_4,i}}{F_{CH_4,i}} \quad (13)$$

(kg s/m³) is the weight-time.

Rearranging Eq. (12):

$$\ln \left[\ln \left(\frac{C_{CH_4,i}}{C_{CH_4}} \right) \right] = \ln(k' \times \tau') - k_d \times t \quad (14)$$

The procedure below shows how k_d and k' were determined.

Table 1
Time depending on the levels of temperatures.

T (K)	t_{is} (h)	t_o (h)	t_s (h)	t_f (h)	m_i (10^3 kg)
1148	1.42	2.60	5.74	8.00	4.0125
1173	1.50	2.34	5.32	7.40	4.0015
1223	1.66	2.34	3.83	5.83	4.0022

2.5. Kinetic constants of the second step of the second reaction

By constructing graphs of $\ln [C_{CH_4,i}/C_{CH_4}]$ versus (t) , it was possible to determine the constant k_d (s^{-1}) through experimental data fitting using the Origin/Excel programs. The velocity constant of deactivation $k'(\text{m}^3/\text{kg.s})$ was calculated from the linear coefficient $\ln(k' \times \tau')$ of Eq. (14) which represents the intersection, determining thus τ' .

The number of moles of methane consumed ($n_{CH_4,2^a}$) as a function of time, in the isothermal interval of the second step of the second reaction at temperatures of 1148, 1173 and 1223 K, were obtained using Eq. (15):

$$n_{CH_4,2^a} = \int_{t_s}^{t_f} F_{CH_4,i} \times X_{CH_4,2^a} \times dt \quad (t_s < t < t_f) \quad (15)$$

where

$$X_{CH_4,2^a} = 1 - \frac{C_{CH_4}}{C_{CH_4,i}} = 1 - e^{-k' \times \tau' \times e^{-k_d(t-t_s)}} \quad (16)$$

The molar consumption of methane in the isothermal zone could be determined by the sum of the consumption of the first and second steps using Eq. (17):

$$n_{CH_4} = n_{CH_4,1^a} + n_{CH_4,2^a} \quad (t_{is} < t < t_f) \quad (17)$$

3. Results and discussion

Table 1 shows the times of the different reaction steps for the 3 temperature levels studied.

3.1. Gas-phase kinetics

The curves obtained for the concentration of CH_4 at the reactor outlet as a function of time evidenced a reduction in the concentration up to a certain moment, subsequently increasing progressively until the end of the reaction, as shown in Fig. 1. This behavior

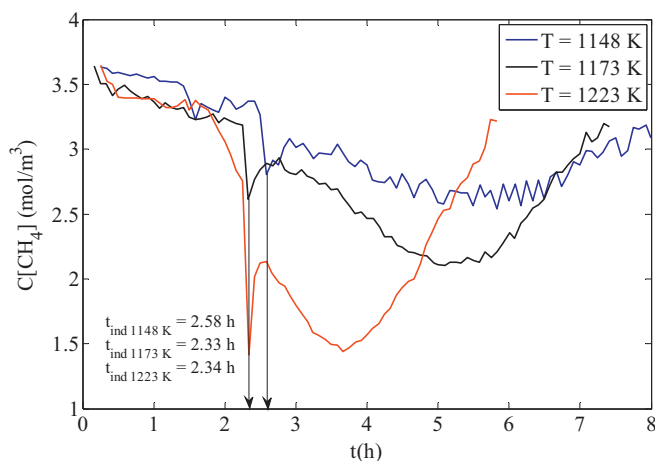


Fig. 1. Methane concentration versus reaction time $C_{CH_4,i} = 3.64 \text{ mol/m}^3$; $Q_{CH_4,i} = 0.37 \times 10^{-6} \text{ m}^3/\text{s}$; $T = 1173 \text{ K}$.

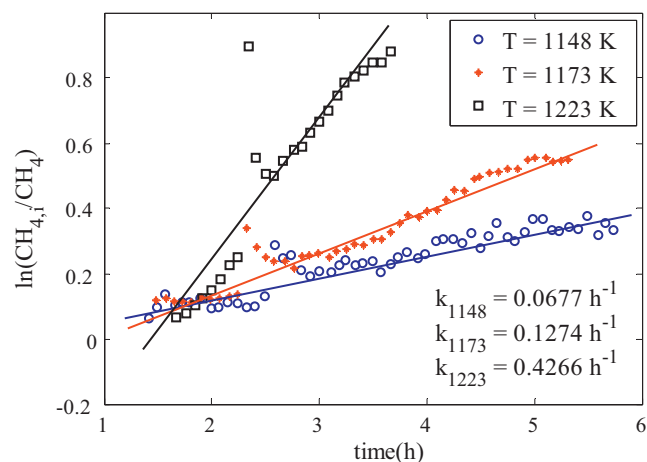


Fig. 2. Constant kinetic k of the first step of the second reaction versus time at different temperatures $C_{CH_4,i} = 3.64 \text{ mol/m}^3$; $Q_{CH_4,i} = 0.37 \times 10^{-6} \text{ m}^3/\text{s}$.

suggested a division of the reaction into two steps during the construction of the kinetic model: the first step (descending part of the curve), until the time between 2.33 and 2.58 h that represents the consumption of the methane, and the second step (ascending part of the curve) representing the loss in activity of the solid reagent (NbO_2) due probably to the methane dehydrogenation reaction and the deposit of carbon on the surface of the particle. The deactivation is more intense at high temperatures.

3.2. Kinetic constants of the first step of the second reaction

Fig. 2 shows the kinetic constants obtained from the slope of the curves corresponding to the first step of the second reaction (Eq. 2) at temperatures of 1148, 1173 and 1223 K.

It can be noticed that there is a tendency towards the linear behavior of the points represented by $\ln(C_{CH_4,i}/C_{CH_4})$ versus reaction time (t), which validates the hypothesis for pseudo-first-order reaction. The kinetic constant values k (s^{-1}) assessed, as expected, increase with temperature, resulting in an increase in reaction rate.

3.3. Activation energy

The activation energy for the first step of the second reaction was determined by the Arrhenius Equation (Eq. 7) from the slope of the curve $\ln(k)$ versus $1/T$, (Fig. 3). A value of 286 kJ/mol (with overall uncertainty $w_E = \pm 43 \text{ kJ/mol}$) was obtained.

The activation energy found for the second reaction was between 200 and 800 kJ/mol range as reported by Weimer and Alan [2] for the carburization reaction activation. This value is around three times that obtained by Teixeira da Silva et al. [1] for activation energy of the first reaction (98–105 kJ/mol).

3.4. Reaction rate and kinetic constants of the second step of the second reaction

Fig. 4 shows respectively the graphs for obtaining k_d and k' at temperatures of 1148, 1173 and 1223 K and Table 2 shows their the estimated values. It can be observed that the temperature

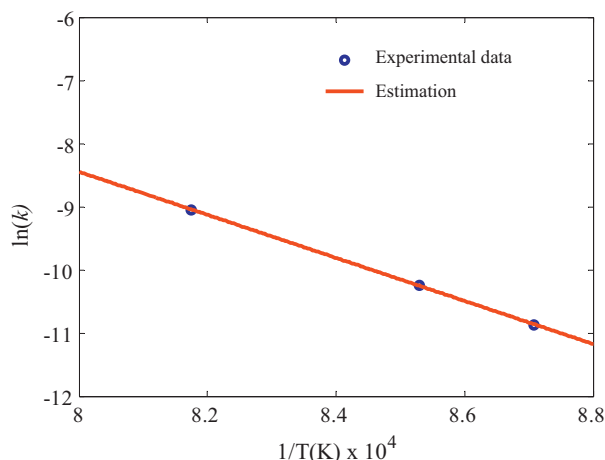
Table 2
Estimated values of k' , k_d and τ' .

T (K)	k' ($\text{m}^3/\text{kg.h}$)	k_d (h^{-1})	τ' (kg.h/m^3)
1148	1.324	0.399	0.274
1173	2.426	0.644	0.276
1223	3.430	0.979	0.273

Table 3Molar consumption of CH₄ in the carburization of NbO₂ to NbC.

T (K)	$n_{\text{CH}_4,0}$ (mol)	$n_{\text{CH}_4,1^a}$ (mol)		$n_{\text{CH}_4,2^a}$ (mol)		n_{CH_4} (mol)		$n_{\text{CH}_4}^s$ (mol)
	exp	exp	mod	exp	mod	exp	mod	
1148	0.002	0.043	0.041	0.026	0.025	0.069	0.066	0.087
1173	0.005	0.054	0.057	0.031	0.032	0.085	0.089	
1223	0.005	0.049	0.046	0.038	0.035	0.087	0.081	

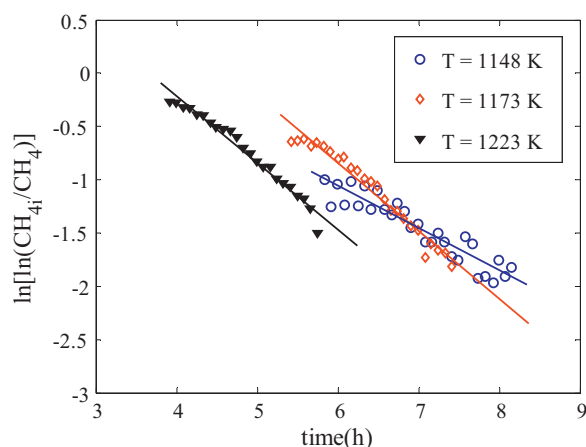
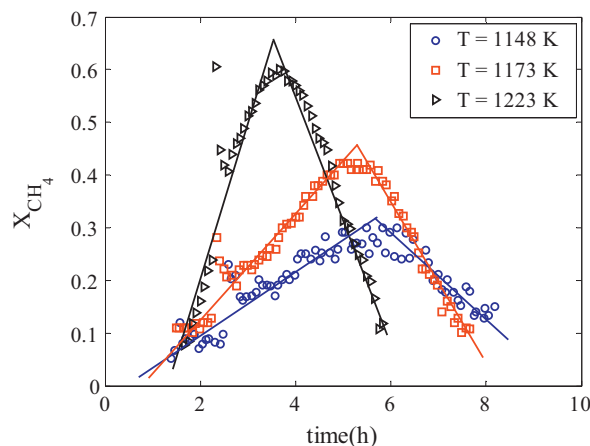
$n_{\text{CH}_4,0}$ consumption in the RTP zone ($t_{\text{ind}} < t < t_{\text{is}}$); t_{ind} : beginning of the induction period of the second reaction; $n_{\text{CH}_4}^s$ stoichiometric consumption; $n_{\text{CH}_4,1^a}$ consumption in the first step of the second reaction; $n_{\text{CH}_4,2^a}$ consumption in the second step of the second reaction.

**Fig. 3.** Activation energy of the first step of the second reaction: NbO₂→NbC.

significantly favors the deactivation velocity (k'), as well as the decline constant (k_d). The increase in k' with temperature justifies the intensity of activity loss due to the solid carbon deposition on the particle surface. The weight-time was approximately constant as expected.

Fig. 5 shows the behavior of the conversion of CH₄ (X_{CH_4}) versus time at temperatures of 1148, 1173 and 1223 K, where it is possible to observe it reaching its maximum point that delimits the transition from the first step to the second step of the second reaction. At 1148, 1173 and 1223 K, the maximum conversions of CH₄, around 30, 45 and 60%, was achieved after 5.6, 5.32 and 3.84 h of reaction. The increase in temperature causes an increase in the conversion of methane conversion and shortens the reaction time.

Table 3 shows the molar consumption of methane calculated by graphic integration from the chromatogram peaks obtained (exp) and estimated (mod), Eqs. (3) and (15) were used for such purpose,

**Fig. 4.** Estimate of constants k' and k_d .**Fig. 5.** Conversion of CH₄ in the carburization of NbO₂ to NbC in the second reaction.

they make reference to the first and second steps of the second reaction at temperatures of 1148, 1173 and 1223 K. There was a good agreement between the experimental data and those predicted by the model. A higher consumption of methane was observed in the second phase of the second reaction. The overall standard deviation between experimental and estimated data was 0.004 mol.

4. Conclusions

Using chromatographic analysis (Flame Ionization Detector) to detect CH₄, it was possible to monitor the carburization reaction and, along with the solid phase investigation, identify the mechanism of the second reaction (NbO₂ into NbC), thus making it possible to determine the kinetic parameters of the reaction, with the activation energy of the reaction estimated at 286 kJ/mol. Statistical parameters led to conclude that the models can represent the experimental data. It is recommended the investigation of the production of CO₂ and H₂O during the first stage of the reaction, when NbO₂ is present. The results showed that the amount of methane adsorbed at 1148 K is less than the stoichiometric value, which explains the incomplete conversion of NbO₂ to NbC. However, it is believed that the methane adsorbed until the moment (2.33–2.58 h) in which the solid is not affected by deposit of carbon on the surface favors the stoichiometric balance of the second carburization reaction, considering that the pyrolytic carbon deposited is included in this balance.

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