

CO₂ adsorption on porous NiO as a cathode material for molten carbonate fuel cells

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Abstract

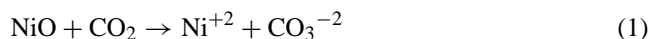
Molten carbonate fuel cells (MCFC) are the systems suitable for large-scale energy production. The cathode material used in these cells is NiO. In this study the NiO cathode was synthesized by tape-casting method and the adsorption of CO₂, one of the cathode feeding gases, was investigated on it. The adsorption studies were carried out by the use of packed column and the adsorption analysis were performed using pulse response technique. There were two 1/4 in. diameter and 5 and 10 cm length columns prepared for the experiments and they were packed with 3 mm average particle sized NiO. The experiments were carried out with gas chromatography using He as a carrier gas. The response curves were taken after pulsing the columns with CO₂. The equilibrium constants and heat of adsorption of CO₂ on NiO were determined by the use of the first absolute moment equations corresponding to retention times. It was observed that the adsorption was physical in nature. From the adsorption constants determined at different temperatures and the heat of adsorption, ΔH^0 , was found as $-1299 \text{ cal mol}^{-1}$. © 2004 Elsevier B.V. All rights reserved.

Keywords: Pulse response; Adsorption; Molten carbonate fuel cells; Cathode; NiO; CO₂

1. Introduction

Hydrogen fuel cells regarded as the energy converter of our century started to be used in many field such as transport vehicles, electrical power stations, portable electronic devices, etc. Among these fuels cells molten carbonate fuel cells (MCFC) have a great potential to be used for large scale energy production due to their high power yield (45–60%), low investment per kW power of energy and elevated temperature range (600–700 °C) suitable for recycling of the heat of the waste gases [1]. In these cells the cathode is NiO, the anode is Ni and the electrolyte is carbonate compounds of the alkaline metals (Li₂CO₃, K₂CO₃, etc.). The fuels employed are natural and coal gas as well as hydrogen. The conversion of natural gas and hydrogen is possible in the cell since these cells operate at elevated temperatures. They need no additional conversion unit.

In order for a MCFC to be economically viable the life of the cell should be above 40,000 h [2]. The major factor, which decreases the life of the cell is the dissolution of the NiO cathode as



The resulting Ni⁺² deposit upon the anode and cause short circuits within the cell. There are two methods proposed in literature to ameliorate this situation: the change of the electrolyte composition and improve the properties of NiO cathode. Motohira et al. investigated the effect of MgO and Fe₂O₃ upon the solubility of NiO cathode and showed that the solubility decreased by the addition of these agents [3]. Han et al. on the other hand coated the NiO cathode with LiCoO₂ using solution immersion method [2]. They tested this cathode at three different working pressures and found that the dissolution was decreased by 50% at lower pressures. Kuk et al. carried out the same process with sol-gel method and observed that the solubility of NiO decreased by 50% [4].

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Nomenclature

C	concentration of the adsorbable gas in the interparticle space (mol cm^{-3})
\bar{C}	concentration in Laplace domain
C_{ads}	concentration of the adsorbed gas per unit weight of adsorbent (mol g^{-1})
C_i	concentration of the adsorbable gas in the pore space (mol cm^{-3})
C_0	concentration of the adsorbable gas in the input concentration (mol cm^{-3})
D_e	effective intraparticle diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
D_z	effective axial dispersion coefficient ($\text{cm}^2 \text{s}^{-1}$)
ΔH^0	heat of adsorption (cal mol^{-1})
L	pack length (cm)
ΔL	packed length difference (cm)
k_f	mass transfer coefficient (cm s^{-1})
K_0	frequency factor
K_A	adsorption equilibrium constant ($\text{cm}^3 \text{g}^{-1}$)
m_n	n th degree moment ($n = 0, 1, 2, \dots$)
R	radius of the spherical particle of adsorbent (cm)
R_g	gas constant (g cal mol K^{-1})
t	time (s)
t_0	pulse injection time (s)
T	temperature (K)
U_0	linear velocity in the empty column (cm s^{-1})
<i>Greek letters</i>	
ε_b	interparticle void fraction in the adsorbent bed
ε_p	interparticle void fraction (internal porosity) of the adsorbent
$\Delta\mu_1$	first absolute moment difference (s)
μ_n	n th degree absolute moment
ρ_p	apparent density of particles (g cm^{-3})

NiO is widely used as MCFC cathode material. Also it is used alone or together with some metal and metal oxide compounds for the synthesis of some organic compounds [5–7] and widely used in methane reforming with CO_2 , H_2O and O_2 reaction and removal of NO_x [8]. Dewaele and Froment [9] have used single pulse and alternating pulse techniques in the adsorption of CH_4 on NiO and it is found that CH_4 adsorption rate is between 0.0178 and $0.0283 \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$. Similarly in some studies it was observed that the adsorption of same gases and H_2 and CO fit to Elovich kinetics and adsorption rate is proportional with the square root of the pressure [10]. Unfortunately studies reported in the literature are not sufficient for the determination of adsorption parameters of CO_2 gas.

The studies related to the physical and chemical phenomena taking place between cathode and cathode feeding gases

are very limited. These type studies are important to provide necessary data for the understanding of the working principles, theoretical modeling and practical calculations of the fuel cells.

2. Dynamic analysis of adsorption

The transfer and kinetic parameters of a system can be reliably determined by the use of pulse–response dynamic method. This method is particularly useful in the determination of parameters such as diffusion coefficient, adsorption coefficient, kinetic rate constants and mass transfer coefficient [11–13]. The principle of pulse–response also named as moment technique is making the system dynamic by an internal or external impulse and determining its parameters. In this method first the theoretical models defining the system are written in the light of related assumptions and the resulting linear model statements are solved in Laplace plane. The theoretical moments of the model equations, solved in Laplace plane, are taken by the use of Eq. (11) and the model parameters are determined by the comparison of these moments with the experimental moments.

The mass balance equations for the NiO particle packed column at constant temperature are given by Eqs. (2) and (3) for the bulk and the particle phase

$$\varepsilon_b \frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - U_0 \frac{\partial C}{\partial z} - (1 - \varepsilon_b) \frac{3D_e}{R} \left(\frac{\partial C_i}{\partial r} \right)_{r=R} \quad (2)$$

$$\varepsilon_p \frac{\partial C_i}{\partial t} = D_e \left(\frac{2}{r} \frac{\partial C_i}{\partial r} + \frac{\partial^2 C_i}{\partial r^2} \right) - \rho_p \frac{\partial C_{\text{ads}}}{\partial t} \quad (3)$$

The adsorption rate in Eq. (3) were assumed to be linear because tracer concentration is too low in experiment conditions and adsorption equilibrium is given in Eq. (4)

$$\frac{\partial C_{\text{ads}}}{\partial t} = K_A \frac{\partial C_i}{\partial t} \quad (4)$$

The boundary and initial conditions for the solution of the equation defining system are given in Eqs. (5)–(10).

$$C = 0 \quad \text{for } t = 0 \quad \text{and } z > 0 \quad (5)$$

$$C_i = 0 \quad \text{for } t = 0 \quad \text{and } r \geq 0 \quad (6)$$

The following boundary conditions (7) and (8) were employed since the following current is given as a pulse in an interval of t_0 .

$$C = C_0 \quad \text{for } 0 \leq t \leq t_0 \quad \text{and } z = 0 \quad (7)$$

$$C = 0 \quad \text{for } t > t_0 \quad \text{and } z = 0 \quad (8)$$

$$\frac{\partial C_i}{\partial r} = 0 \quad \text{for } t > 0 \quad \text{and } r = 0 \quad (9)$$

Between solid and gas phases diffusion limiting condition given by Eq. (10) was employed.

$$D_e \left(\frac{\partial C_i}{\partial r} \right)_{r=R} = k_f (C - C_i) \quad (10)$$

The dynamic model given by Eqs. (2) and (3) was solved with moment technique. According to this technique the model equations, initial and boundary conditions were solved after being taken to Laplace plane.

2.1. General moment equations

The theoretical moments of the Eqs. (2) and (3), solved in Laplace plane, were taken according to Eq. (11) (zeroth and first moments) and from these theoretical moment equations the first absolute moment equations corresponding to tracer's average retention time were computed by the use of n th absolute moment equation given by Eq. (13).

The n th degree moment as a function in Laplace plane is given by

$$m_n = (-1)^n \lim_{s \rightarrow 0} \frac{d^n (\bar{C}/s)}{ds^n} \quad (11)$$

the n th degree moment as a function in time domain is:

$$m_n = \int_0^{\infty} t^n C(t) dt \quad (12)$$

The absolute moment in n th degree is given by

$$\mu_n = \frac{m_n}{m_0} = \frac{\int_0^{\infty} t^n C(t) dt}{\int_0^{\infty} C(t) dt} \quad (13)$$

Table 1
Physical properties of NiO

Color	Olive green
Apparent density (g cm^{-3})	3.76
Solid density (g cm^{-3})	6.76
Porosity	0.44

The moments of experimental response curves were computed by the use of n th degree moment equation for $C(t)$ (Eq. (12)) and the Simpson method among the numerical integration methods. The numerically calculated values were equated to theoretically calculated moment equation to determine the adsorption equilibrium constant. Schneider and Smith [13] solved the adsorption of some hydrocarbons on silica gel packed column proposing a similar model. Eqs. (2) and (3) were solved in Laplace plane by the use of similar initial and limiting conditions and the first theoretical moment equation of model equations was given by Eq. (14).

$$\mu_1 = \frac{\varepsilon_b L}{U_0} \left[1 + \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \varepsilon_p \right) \left(1 + \frac{\rho_p}{\varepsilon_p} K_A \right) \right] + \frac{t_0}{2} \quad (14)$$

3. Experimental

The experiments of this study were carried out in two stages where the synthesis of NiO the cathode material of MCFCs and the adsorption of CO_2 on this material were investigated. The first stage was the preparation of NiO and the determination of its some physical properties and the second stage was performance of the experiments by the use of packed columns.

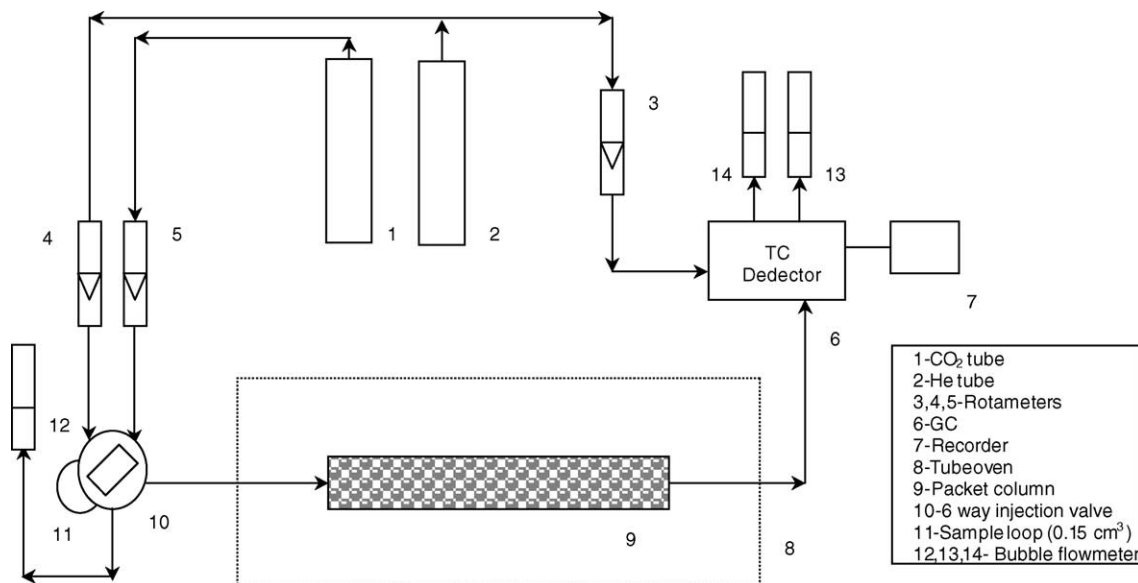


Fig. 1. Schematic representation of the experimental set up.

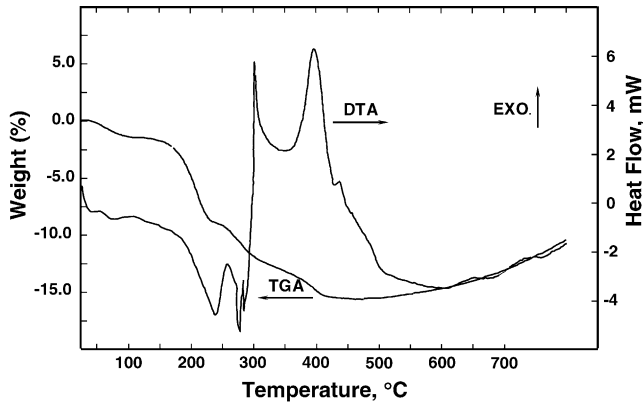


Fig. 2. Thermogravimetric analysis of Ni plate.

3.1. The preparation of NiO

The NiO samples used in the experiments were prepared with tape-casting method outlined in literature [14]. Accord-

Table 2
Adsorption equilibrium constants for the adsorption of CO₂ on NiO at three different temperatures

Temperature (°C)	Adsorption equilibrium constant, K_{CO_2} (cm ³ (g-NiO) ⁻¹)
50	0.092
300	0.067
400	0.061
600	0.037
700	0.030

ing to this method first a paste of pure nickel was prepared with organic binders and it was then sintered. There were 5 g of polyvinylalcohol (PVA), 9 g glycerin and 15 cm³ water added on 50 g Ni and mixed in mechanical stirrer for 2 h. The mixture thus obtained was spread as a thin layer in a glass cuvette kept there for 48 h. The sample was then removed from the cuvette and sintered for an hour at 300 and 400 °C and 30 min at 700 °C in air atmosphere. Some of the physical properties of NiO cathode material obtained as a porous

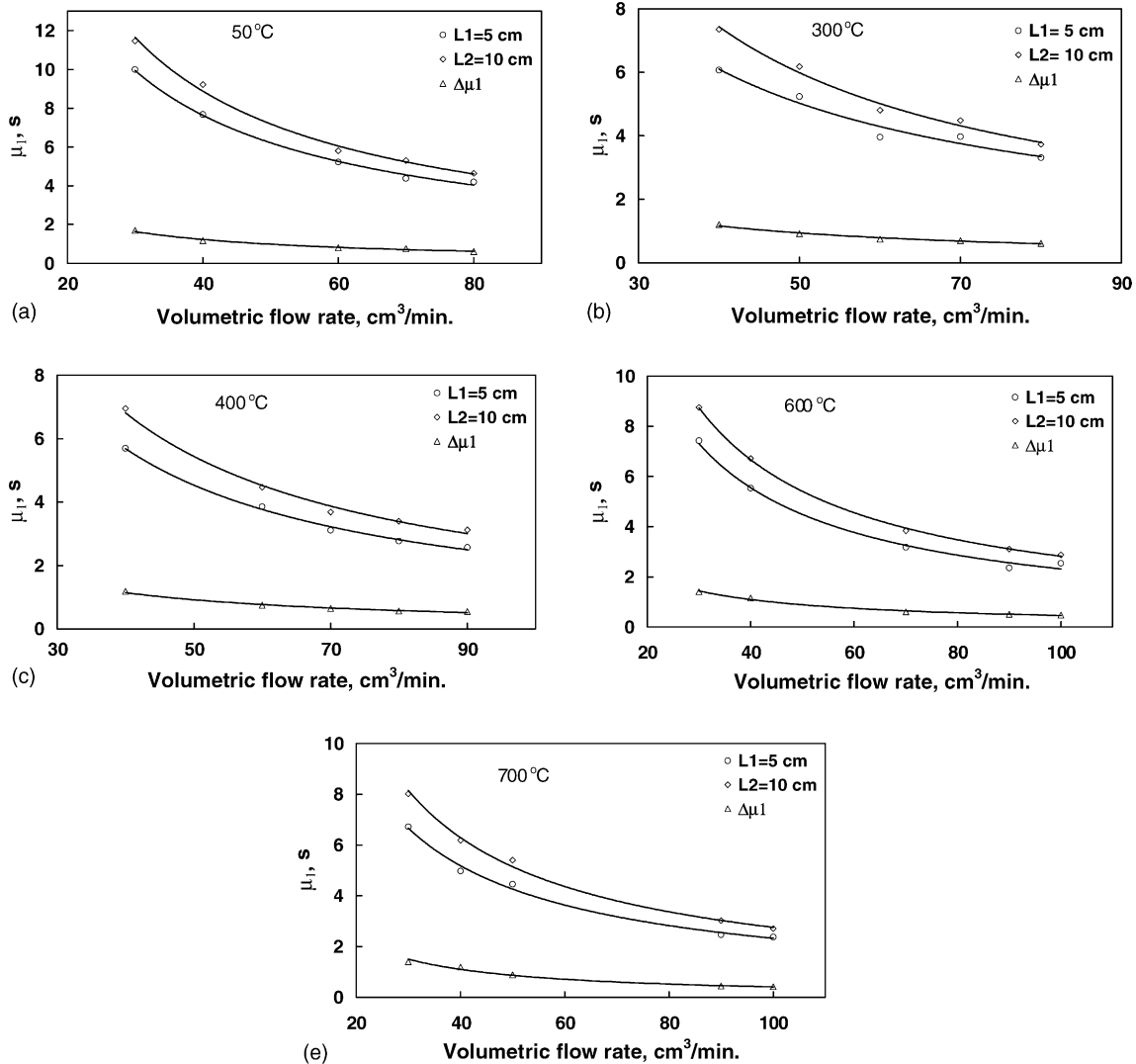


Fig. 3. The plot of the first absolute moments and the difference of first absolute moments against the flow rates for 5, 10 cm column length.

plate are given in Table 1. The sample was used in adsorption experiments after being grounded into 3 mm particle size.

3.2. Adsorption experiments

The schematic representation of the experimental set up used for the determination of the CO₂ adsorption NiO is given in Fig. 1. The packed columns prepared by packing NiO in two steels reactors with different lengths ($L_1 = 5$ cm, $L_2 = 10$ cm) were placed in a tube oven. There was a six way injection valve mounted at the entrance of the reactor and the carrier gas (He) was passed through it by the help of this valve. Again the tracer gas CO₂ was continuously passed from the 0.15 cm³ sample loop through another channel. At the instant of the pulse 0.15 cm³ CO₂ tracer gas was injected into the carrier. The outlet of the reactor was connected to TC detector

of a Gow-Mac 350 gas chromatograph with 1/8 in. connector. The response data were taken after pulsing the tracer gas in to the carrier gas the flow rate of which was adjusted by the use of rotameter and bubble flow meters. The experiments were carried out at different flow rates (30–100 cm³ min⁻¹) and repeated at five different temperatures (50, 300, 400, 600 and 700 °C).

4. Results and discussion

TGA and DTA curves of Ni tape are given in Fig. 2. The thermogravimetric analyses were carried out in air at a heating rate of 5 °C min⁻¹. There are four regions observed in the TGA curve. There is a rapid loss of weight of by 2.5% at 25–170 °C. This is attributed to the removal of the water

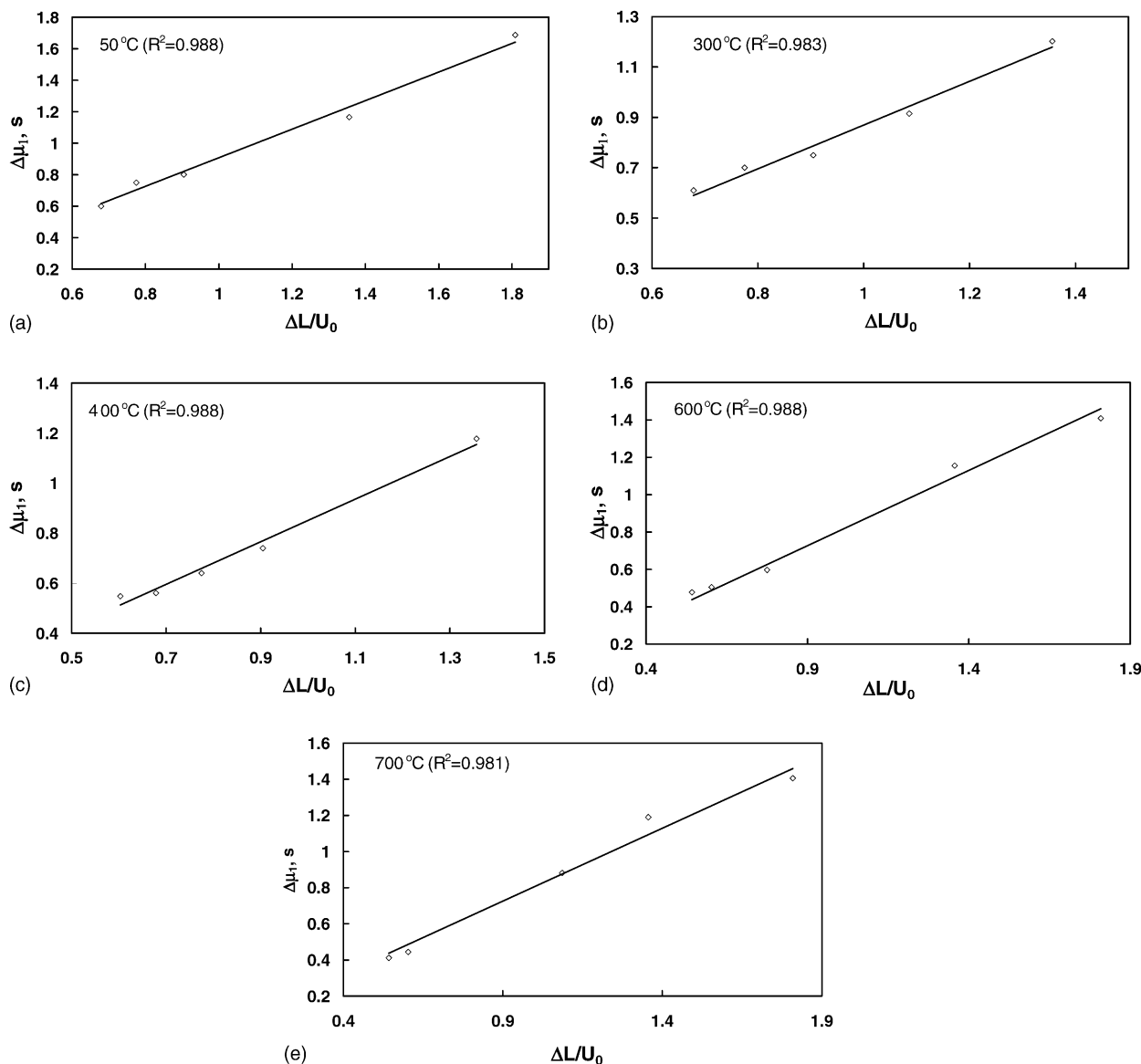


Fig. 4. The plot of absolute moments against $\Delta L/U_0$ values at different temperatures.

in the sample. This is further verified by the change of TGA curve in endothermic direction. There is also an endothermic weight loss at 170–235 °C. The amount of loss is 6.5%. This is due to the evaporation and removal of the glycerin in the tape. The loss of weight observed in a temperature range of 235–420 °C takes place as result of an exothermic reaction. This is due to removal of PVA from the structure. The loss is approximately 6.5%. The organic compounds in the structure are observed to be exhausted when the temperature reaches to 420 °C. From that point on the oxidation of nickel takes place resulting an increase in weight.

The first absolute moments (μ_1) and difference of first absolute moments obtained from the response curves of the adsorption experiments carried out by the use of two different column lengths at three different temperatures are plotted against the volumetric flow rates in Fig. 3.

In order to eliminate the pre- and post-reactor retention times the difference of the moments obtained for two different column lengths were taken ($\Delta\mu_1$) and plotted against $\Delta L/U_0$ in Fig. 4. The slopes of these lines passing through the origin were read and the adsorption equilibrium constants of CO₂ were computed by the use of slope function given in Eq. (15).

$$\Delta\mu_1 = \frac{\varepsilon_b \Delta L}{U_0} \left[1 + \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \varepsilon_p \right) \left(1 + \frac{\rho_p}{\varepsilon_p} K_A \right) \right] \quad (15)$$

The adsorption equilibrium constants determined for three different temperatures are listed in Table 2.

The heat of adsorption was calculated by the use of Vont Hoff equation given in Eq. (16).

$$K_A = K_0 e^{-\Delta H^0/R_g T} \quad (16)$$

According to Eq. (16) $1/T$ values were plotted against $-\ln(K_{CO_2})$ and the slope and the intercept gave heat of adsorption ΔH^0 as $-1299 \text{ cal mol}^{-1}$ and K_0 as $0.013 \text{ cm}^3 \text{ g}^{-1}$.

The data revealed that the amount of CO₂ adsorbed upon NiO ($0.092 \text{ cm}^3 \text{ g}^{-1}$ -NiO at 50 °C) is quite small and the heat of adsorption ($-1299 \text{ cal mol}^{-1}$) is low. The low heat of adsorption shows that the adsorption of CO₂ on NiO is physical in nature. It was concluded that the potential difference formed between anode and cathode is important as regards to the adsorption of CO₂ upon NiO. It was not possible to carry out a comparative study regarding to the type and degree of adsorption since there are no studies in literature relating to the adsorption of CO₂ upon NiO.

Moment technique is known as fast and reliable ones in order to obtain diffusion and adsorption parameters in packed and solid porous catalytic systems [11–13]. Since this method is suitable for linear systems as can be seen from Eqs. (2) and (3), the adsorption rate given in Eq. (4) is assumed as linear. Experimental errors appear in Figs. 4 and 5. ($R^2 = 0.988 - 0.968$) may be explained by the chromatographic systems noise, which causes errors in the first absolute moment values and the assumption that the adsorption rate is linear. On the

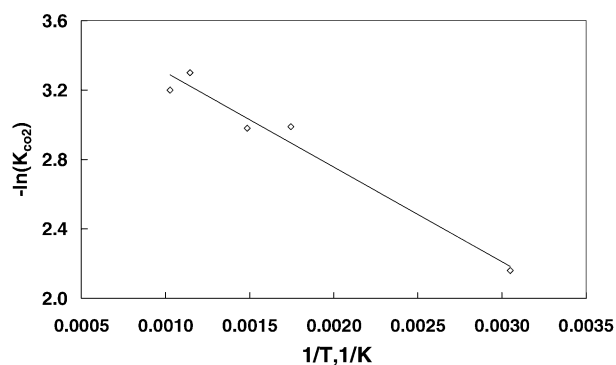


Fig. 5. The change of adsorption equilibrium constants with temperature ($R^2 = 0.968$).

other hand, selected tracer volume in the experimental studies ($0.15 \text{ cm}^3 \text{ CO}_2$) may not be sufficiently small to provide that adsorption takes places in linear zone. Because at this tracer volumes (under these experimental conditions) CO₂ spill over on to the catalyst active surface may take occur place.

Acknowledgements

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