Simulation of Syngas Production via Carbon Dioxide Reforming of Methane in a Fluidized Bed Reactor

By

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Dissertaion submitted in partial fulfillment of

The requirement for the Bachelor (Hons)

(Chemical Engineering)

NOVEMBER 2002

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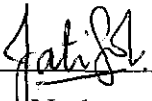*3. CE -- Thesis*

CERTIFICATE OF APPROVAL

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A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

In partial fulfillment of the requirements for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH

November 2002

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Abstract

The paper produced is to present the simulation results of an experiment. The experiment is about the reaction engineering of carbon dioxide reforming of methane in a fluidized bed reactor. The model to be constructed will be used to analysed mechanism and activity of the reaction.

Carbon dioxide reforming is the latest method of obtaining syngas a valuable feedstock for many petrochemical industries. The product varies from naphtha to diesel and fuel additives in automotive industry.

The project involves a study on surface engineering that is catalytic mechanism and activity of the process. Generally the study is based on a journal, which has been selected as the case study. Upon understanding of the basic mechanism, a simple simulation will be carried out for the selected process.

Extensive literature review will give sufficient information towards the development of the model. Some calculations were made in order to obtain some parameters and variables, which will be used in the computer simulation.

From the model created, it is found that the concentration profile along the catalyst bed drops at a very high rate before slowing down. Factors affecting the behavior of the reactant concentration will be discussed further.

Acknowledgement

In the Name of Allah Most Gracious Most Merciful

Praise be to Allah Lord of the Worlds

Most Gracious Most Merciful

Owner of the Day of Judgement

Thine aid we seek

Show us the straight path

The path of whom thou hast favored

Not of those who earn Thine anger nor of those who go astray

Many at hand have encourage me from all aspect of project development. My acievement lie not only within my desire to perform but also a burning fire rekindled by parties of whom we feel greatly gratified to. Rendering me with guidance, support and love which are vital elements of this project and for spiritual harmony. These parties are as follows:

Miss Nurhayati Mellon, lighting a fire that surely inspires and light the path of which is taken, Winding roas then seem straightened and restless wandering minds soon enlightened. Utmost gratitude I shower upon her for brightening up what was once dim...

Thank you for all the guidance and insights shown throughout the entire course duration. I shall kept all the knowledge obtained in my mind as ideas and in my heart as inspiration.

My parents, morning comes showering light, unto the earth blissful bright, and which lays a never ending care showered by dew and warm sea brew. A care shown for seedlings sown are those shown by parents grown, never ending never less, always loving entirely blessed...

My humble gratitude and love to my parents for their support in completing this project. My success is their pride and my achievement is their smile.

And to other parties that may have contributed to us in any form we humbly offer a word of gratitude. Thank you.

Abbreviation and Nomenclature

C_b Concentration at carbon dioxide at bubble phase, ppm

C_e Concentration of carbon dioxide at emulsion phase, ppm

d_p particle diameter, μm

D_{eff} effective diffusivity, cm^2/s

D_{ze} dispersion coefficient in emulsion phase, m^2/s

f_b bed fraction covered by bubbles phase

f_e bed fraction covered by emulsion phase

g earth acceleration, $m\ s^{-2}$

g_b mass of solid in bubble phase, kg/m^3

g_e mass of solid in emulsion phase, kg/m^3

h bed height, m

k_{CO2} interchange coefficient, atm^{-2}

k adsorption constant, atm^{-1}

k_1 mass transfer coefficient, m

m mass of catalyst, g

p_{CH4} partial pressure of methane, kPa

p_{CO2} partial pressure of carbon dioxide, kPa

p_{CO} partial pressure of carbon monoxide, kPa

ρ_s catalyst solid density, $g\ cm^{-3}$

ρ_g gas density, $g\ cm^{-3}$

r_{CO2} rate of reaction of carbon dioxide, $mol\ s^{-1}\ kg_{cat}^{-1}$

u_b bubble velocity, m/s

u_{mf} minimum fluidization velocity, m/s
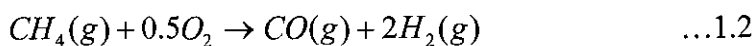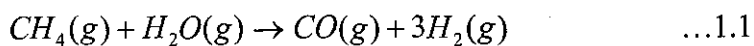
1   INTRODUCTION

1.1   Background

Methane is a single tetravalent carbon atom surrounded by four hydrogen atoms arranged in a tetrahedral geometry. Methane is extremely important as it can be considered as the "parent" of organic chemistry. All organic compounds are methane with the hydrogen atoms replaced by other atoms or functional groups.

Methane is a flammable, odorless, non-toxic gas formed naturally by bacteria, which release single carbon atoms from digested organic material. It occurs as marsh gas when it is not trapped by rock and it is the main component of natural gas. When methane is burnt in air, the hydrogen atoms are stripped from the carbon by oxygen to form water molecules, while the carbon quickly reacts to form carbon dioxide molecules.

Gas to Liquid (GTL) technology is a paradigm shift of petrochemical processes. It partially solves the problem of extinction of hydrocarbon resources by generating liquid hydrocarbon from gas hydrocarbon.

GTL comprises of two distinct and separate processes. Hydrocarbon gas that is methane will first react to form synthesis gas also known as syngas. This syngas is a mixture of hydrogen and carbon monoxide. This is the main feedstock for Fischer-Tropsch process where syngas is converted to a long chain liquid hydrocarbon. The GTL products are referred as synfuels ranging from naphtha to diesel.

Two common method of producing syngas is steam reforming and partial oxidation of methane. Steam reforming is denoted by equation (1.1) while partial oxidation is denoted by equation (1.2).

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \qquad \ldots 1.1$$

$$CH_4(g) + 0.5O_2 \rightarrow CO(g) + 2H_2(g) \qquad \ldots 1.2$$

Latest discovery of syngas production is carbon dioxide reforming of methane as given below:

$$CH_4(g) + CO_2(g) \rightarrow CO(g) + H_2(g) \qquad \ldots 1.3$$
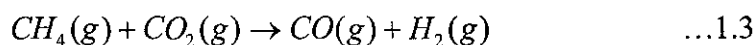
1.2   Problem statement

Currently syngas is mainly produced mainly by steam reforming and partial oxidation of methane. Recent discovery of carbon dioxide reforming of methane has attracted renewed global interest. An advantage of producing synthesis gas by carbon dioxide reforming instead of processes such as steam reforming and partial oxidation is the low H_2: CO ratio obtained, which is of particular interest to the synthesis of valuable oxygenated chemicals.

The carbon dioxide reforming offer some other important advantage compared to other synthesis gas production. The low ratio of H_2: CO is favorable for Fischer-Tropsh synthesis. It also reduces carbon dioxide and methane emission, which are both greenhouse gases. Yet, the reaction still has no commercial application. This is due to the economics of the reaction, which have very high requirements.

Major disadvantage of carbon dioxide reforming is the high thermodynamic potential in coke formation. A lot of effort has been directed towards the development of the reaction. This involves study on the usage of catalysts, reactors and other reaction conditions in order to acquire optimum reaction condition, where highest yield can be achieved at lowest condition requirement.

1.3   Objective and Scope of Study

The main objective of this project is to model the reaction of carbon dioxide reforming of methane. The reaction model shall be tested and the result will be analyzed on the behavior of the reactants. In order to model the equation, a study on the reaction mechanism is required. After obtaining the reaction rate equation, the design equation will be derived based on type of reactor used. The reaction model will be constructed by using Matlab.

All experimental data for the case study in this project is based on a selected journal from a variety of journals obtained through the library and the Internet. Decision is made based on the information included in the journal.

Development of carbon dioxide reforming reaction model require an extensive studies. Focus is given on the reaction mechanism, which will involve adsorption and desorption on the catalyst surface. The type of catalyst used and the ways the catalyst behaves towards the reaction will also be studied. The study will also covers on the kinetics of the reaction where the rate of reaction will be determined.

Understanding the reaction mechanism will give the factors that influence the yield of that reaction. This includes type of reactors used and the reaction condition that will influence the reaction. Information obtained from this study will be used later to develop the design equation to model the synthesis gas production.

Familiarization of computer software, Matlab is crucial in order to make the project successful. Modelling of the reaction will be performed using Matlab. From this model, optimum condition of the reaction could be estimated based on validity of assumptions made in deriving the model.

2   LITEATURE REVIEW AND THEORY

2.1   The reaction

Carbon dioxide reforming of methane will produce carbon monoxide and hydrogen using one percent of nickel on alumina oxide catalyst. This process is more preferred compared to steam reforming and partial oxidationdue to the low H_2: CO ratio of 1:1 which is desirable for Fischer-Tropsh synthesis.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta_k H^\circ = +247.9 \text{ kJ/mol} \quad \ldots 2.1$$

As been stated above, the reaction is endothermic, which require a good temperature control reactor system to ensure sufficient heat is provided for the reaction. The reaction is performed at 800°C inside a laboratory-scale fluidized bed reactor. Information on the fluidized bed reactor will be explained in the later part of the chapter.

2.2   Reaction Kinetics

The rate of reaction can be expressed as a change of concentration of methane and carbon dioxide with time. The reaction rate is given as

$$r = \frac{-d[CH_4]}{dt} = \frac{-d[CO_2]}{dt} = k[CH_4]^1[CO_2]^1 \qquad \ldots 2.2$$

The reaction is a second order reaction with respect to both carbon dioxide and methane. The determination of the rate law is based on concentration of reactants. Further integration of equation 2 gives

$$\ln \frac{[CO_2]_0}{[CO_2]} = kt([CH_4]_0 - [CO_2]_0) + \ln \frac{[CH_4]_0}{[CH_4]} \qquad \ldots 2.3$$

The equation can be plotted on a graph as y = mx + c. The alternative way of describing this second order process of this type is by using extent of reaction, x. If the same reaction occur, having both reactant at the same amount,

$$\frac{dx}{dt} = k(a - x)(b - x)$$
...2.4

Integration gives

$$\frac{1}{b - a} \ln \frac{a(b - x)}{b(a - x)} = kt$$
...2.5

However these methods applies if there is no catalyst present in the reaction. [3] Catalyzed reaction will involved adsorption and desorption of reactants (carbon dioxide and methane) and products (syngas) which on solid catalyst surface (nickel). This is called heterogeneous catalysis where a solid (catalyst) has gaseous reactant attached to it and subsequently react. Heterogenous catalysed reaction involves the possibility of either or both reactant and product of reaction being adsorb or desorb on the catalyst surface. The nickel catalyst impregnated in alumina oxide carrier functioned to enhance rate of reaction by lowering activation energy for the reaction and increase selectivity of desired product.

Heterogeneous catalytic reaction involves several different steps. The reaction occur when reactant (carbon dioxide and methane) flow through bed of catalyst and absorbed to the catalyst active site (nickel) before being converted to product. [2] In order for conversion of carbon dioxide and methane to syngas these viable steps must occur:

- Transport of carbon dioxide and methane from the bulk fluid to the stagnant film surrounding catalyst particle
- Diffusion of both carbon dioxide and methane into alumina oxide catalyst pores
- Adsorption of reactants (carbon dioxide and methane) onto nickel active site surfaces

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- Reaction of carbon dioxide and methane to syngas on the nickel surfaces
- Desorption of products (syngas) through porous alumina oxide to its pore mouth
- Transport of syngas from the stagnant film around the catalyst to bulk fluid

In the carbon dioxide reforming of methane, both carbon dioxide and methane will adsorb on the surface of catalyst active site while syngas desorp from it continuously. There are 2 types of adsorption; physical and chemical adsorption. [4]

Physical adsorption is weak forces between adsorbate and adsorbent. It usually occurs because of condensation of reactants on catalyst surface. Meanwhile, chemisorption releases high energy during adsorption and this energy will give the reactants energy to overcome the reaction activation energy barrier. That is why reaction is always linked to chemisorption and not physical adsorption.

Since the reaction involves catalytic activity, the rate of reaction is developed based on adsorption isotherm. Langmuir proposed simple formulation for adsorption and desorption of gases on solid catalyst surface. The formula was derived based on several important assumptions:

- All the surface of the active site of the catalyst is uniform. This will make the adsorption and desorption have the same activity or rate.
- The amount of reactant adsorbed has no effect on further rate of adsorption.
- Adsorptions occur with the same mechanism and adsorbed reactants posses similar structure
- The adsorption which is mainly chemisorption is limited to monomolecular layer on the active site surface.

The adsorption and desorption process will continuously occur and eventually an equilibrium between both processes will be established. Therfore, the rate of adsorption, r_a will equal to rate of desorption r_d. [2] Rate of adsorption is equal to

$$r_a = kp(1-\theta) \qquad \qquad ...2.6$$

Where k is a constant involving proportionality between r_a and p, pressure of the reactants. Since the adsorption is limited to monomolecular layer, the surface is presented by fraction θ covered by adsorbed reactants and 1-θ which is bare. Meanwhile the rate of desorption is presented by:
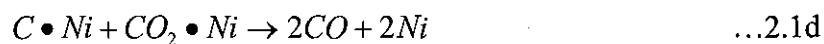
$$r_d = k'\theta \qquad \qquad ...2.7$$

Due to equilibrium, equation 2.6 is equal to reaction 2.7. The resulting equation is given by:

$$\theta = \frac{kp}{k'+kp} = \frac{K_p}{1+K_p} \quad \text{where } K_p = k/k' \qquad ...2.8$$

The determination of rate of reaction is now getting more complicated. This is because the seven step of reaction involving adsorption, diffusion and desorption must be taken into consideration.

Every reaction actually comprises of several elementary step. These elementary steps will present the adsorption, reaction and desorption process during the reaction. These are elementary steps of carbon dioxide reforming of methane, equation 1

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \qquad ...2.1$$
$$CH_4 \rightarrow C + 2H_2 \qquad \qquad ...2.1a$$
$$CO_2 + Ni \rightarrow CO_2 \bullet Ni \qquad \qquad ...2.1b$$
$$C + Ni \rightarrow C \bullet Ni \qquad \qquad ...2.1c$$
$$C \bullet Ni + CO_2 \bullet Ni \rightarrow 2CO + 2Ni \qquad \qquad ...2.1d$$

Since the reaction occur in series, the slowest or rate determining step will determine the overall reaction rate. Rate determining step is the slowest elementary steps and controls overall rate of reaction. In this reaction, the rate determining step is equation 1d, where reaction is the rate determining step or the rate controlling reaction. [12]

Since the surface reaction controlling case is generally the most important for industrial conditions, the discussion of bimolecular reactions will be restricted to this case. There are two different mechanism for bimolecular surface-catalyze reactions. [2]

1. The Langmuir-Hinshelwood mechanism for the reaction of two adsorbed surface species to products.
2. The Rideal-Eley mechanism for the reaction of a gas phase species with an adsorbed species to products.

Reaction rate of carbon dioxide reforming was calculated using a Langmuir-Hinshelwood rate expression. The rate expression for carbon dioxide reforming is

$$r_{CO2} = k_1 C_{CH4-Ni} C_{CO2-Ni} - k_2 C_{CO-Ni} C_{H2-Ni}$$

$$= \frac{k'_1 k_{CH4} k_{CO2} p_{CH4} p_{CO2} - k_{CO} k_{H2} p_{CO} p_{H2}}{(1 + k_{CH4} P_{CH4} + k_{CO2} P_{CO2})(1 + k_{CO} P_{CO} + k_{H2} P_{H2})} \qquad \ldots 2.9$$

where

$$k'_1 = k_1 n_1 n_2 \quad \text{and} \quad k'_2 = k_2 n_1 n_2$$

Further derivation will give

$$r_{CO2} = \frac{k_{CO2} - P_{CH4} P_{CO2}}{(1 + k_1 P_{CH4} + K_2 P_{CO})(1 + k_3 P_{CO2})} \qquad \ldots 2.10$$

where all the k and P variables represent for the coefficient of each substance that take part in the reaction.

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2.3   Reactor Design

Fluidized bed reactors involve catalyst beds, which are not packed rigid but suspended in fluid. Flow through bed is upward to reduce pressure drop at high velocity. At high velocity, the frictional drag force on particles becomes greater than their weight thus the bed start to expand. As the velocity increases, the bed seems to loose its form and is fluidized. [6]

The advantage of having fluidized bed reactor is that the reactor offers good mixing of particles. Intimate mixing and rapid heat transfer ensures easy control of reactor temperature. Fluidized bed also works with finer catalyst particles since pressure drop is no longer a problem.

The model is based on the two-phase theory of fluidization. According to the theory, the bed is divided into two phases; emulsion and bubble phases. Gas flows through the emulsion phase with the minimum fluidization velocity. The excess gas flows in the form of bubbles. The bubbles phase consists of particle-free bubbles. The hydrodynamics for both phases can be modeled as below

Equation for bubble phase,

$$u_b A f_b C_{Ab}\big|_z - u_b A f_b C_{Ab}\big|_{z+\Delta z} + k_1 \left(C_{Ab} - C_{Ae}\right) A \delta z + g_b f_b r_A' A \delta z = 0 \qquad \ldots 2.11$$

$$u_b A f_b \frac{dC_{Ab}}{dz} + k_1 C \left(C_{Ab} - C_{Ae}\right) + g_b f_b r_A' = 0$$

Equation for emulsion phase,

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$$u_e A f_e C_{Ae}\big|_z - u_e f_e A C_{Ae}\big|_{z+\Delta z} + A f_e D_{ze} \frac{dC_{Ae}}{dz}\bigg|_z - A f_e D_{ze} \frac{dC_{Ae}}{dz}\bigg|_{z+\Delta z} - k_1\left(C_{Ab} - C_{Ae}\right) A \Delta z + g_e\left(1 - f_b\right) r_A' = 0$$

$$u_e f_e \frac{dC_{Ae}}{dz} - f_e D_{ze} \frac{d^2 C_{Ae}}{dz^2} - k_1\left(C_{Ab} - C_{Ae}\right) + g_e\left(1 - f_b\right) r_A' = 0 \qquad \dots 2.12$$

3. PROJECT WORK AND METHODOLOGY

Initial stage of the project require an understanding of the fundamental and knowledge about the reaction. This is done through references from books, journal, article and website. This method is a preliminary to the literature research. Literature reviews will give depth to the project where most of the discussion will be backup by these information.

The project basically is a further study of a journal entitled "Reaction Engineering Investigations of CO_2 Reforming in a Fluidized Bed Reactor". Please refer appendix 1 for the journal. The paper will be taken as case study and the experimental data from it will be used in the later stages of this project which is modeling. The whole research initiates from the paper and other related topics will be included as further knowledges.

The study will involve some calculation where rate of reaction and the design equation for the whole process will be determined. The results from calculation will be discussed and used as assumptions to solve for problems encountered in the later stage of the project.

The final part of the project is simulation of the carbon dioxide reforming. A model of the reaction will be constructed using computer software, which is Matlab. The model will give opportunity for users to find the best combination of reaction condition in order to achieve highest yield.

Summary of project activity can be referred in the project Gant-Chart. Please refer Appendix 2 for the project Gant-Chart.

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4   DISCUSSION

4.1   Rate of reaction

Currently the reaction rate includes the surface reaction and the mass transfer terms. The reaction rate depends on the controlling reaction step. In order to determine the controlling reaction step, Thiele modulus ϕ, should be known. This is done using equation

$$\phi_{pore} = L\left(\frac{k\rho_s}{D_{eff}}\right)^{1/2} = 0.1628 < 0.4 \qquad \ldots 4.1$$

Catalyst pores length, $L = 40\ E^{-12}m$ [J]

Diffusion coefficient, $K_{CO2} = 0.0150$

Effective Diffusivity, $D_{eff} = 0.163\ cm^2/s$ [P]

For Thiele modulus smaller than 0.4, the drop in concentration of reactants through the pore is small, whereas for Thiele modulus larger than 0.4, the reactants concentration drop is large. [2]

From the calculation above, it is found that the Thiele modulus is smaller than 0.4 indicating that the reaction is the slower step or the rate determining step. Thus the mass transfer diffusion can be neglected.

There is another reason for the neglecting mass transfer diffusion terms in order to model the catalytic mechanism for the reaction. Since the particle size of the catalyst is small, ($\rho_s = 110\mu m$) there will be no diffusion of reactant through the pores of catalyst particle. Hence the mass transfer diffusion terms can be totally left behind. [5]

4.2 Design Equation

At high velocity, the fluidization may become more vigorous. The situation may lead to big bubbles thus creating slugs of gas, which occupies the entire cross section of the bed. Thin bubble formation could cause extinction of the emulsion phase. To prove this, the minimum fluidization velocity must be calculated and then compared with the bubble phase velocity.

The volume of reactor, V and the catalyst particle density ρ_s, must first be determined to perform minimum fluidized velocity calculation.

$$V = \pi \left(\frac{d^2}{2} \right) h = 3.142 \left(\frac{5}{2} \right)^2 5 = 98.175 cm^3 \qquad \ldots 4.2$$

Diameter of reactor, d = 5 cm [9]

Height of catalyst bed, h = 5 cm [9]

Catalyst particle density, ρ_s

$$\rho_s = \frac{m}{V} = \frac{177.2g}{98.175cm^3} 1.805 gcm^{-3} = 1805 kgm^{-3} \qquad \ldots 4.3$$

Total mass of catalyst, m = 140 g [9]

Minimum fluidized velocity, U_{mf}

$$u_{mf} = \frac{1}{180} \frac{\varepsilon_{mf}^3}{1 - \varepsilon_{mf}} \frac{-d_p^2 \left(\rho_s - \rho_g \right) g}{\mu} = 0.006 ms^{-1} \qquad \ldots 4.4$$

Bed porosity, ε_{mf} = 0.4, assuming for a bed of isometric particles [6]

Average catalyst particle diameter, ρ_s = 110μm [9]

Gas density ρ_g = 0.3135gcm^{-3} [1]

Viscosity μ = 1.445 x 10^{-7} cp [1]

Bubble velocity, u_b

$$fluidization\,number = \frac{u_b}{u_{mf}} \qquad \qquad ...4.5$$

$$u_b = fluidization\,number * u_{mf} = 11.8 * 0.006 m/s = 7.1 m/s$$

Huge bubble velocity compared to minimum fluidized bed, $u_b \gg u_{mf}$, ($u_b = 7.1$ m/s; $u_{mf} = 0.06$ m/s) shows the rigorous mixing in the emulsion phase. [6] The huge differences between both bubbles and minimum velocity proves that there is no emulsion phase presents. Thus emulsion phase equation of the fluidized bed (equation 2.12) will be reduced to

$$K_I(C_{Ab} - C_{Ae}) = (1 - f_b)g_e r_a \qquad \qquad ...4.6$$

4.3 Modeling

The reaction is modeled by the design equation of the reaction. The rate of reaction (equation 2.10) will be fitted into the design equation (equation 2.11 and 4.6). All the experimental values are substituted into the formula. Concentration profile of carbon dioxide along the catalyst bed will be investigated using the simulation model. The initial concentration of carbon dioxide is 100 ppm and the concentration will be tested through a catalyst bed of 5 cm height. The Matlab coding can be found in appendix 3.
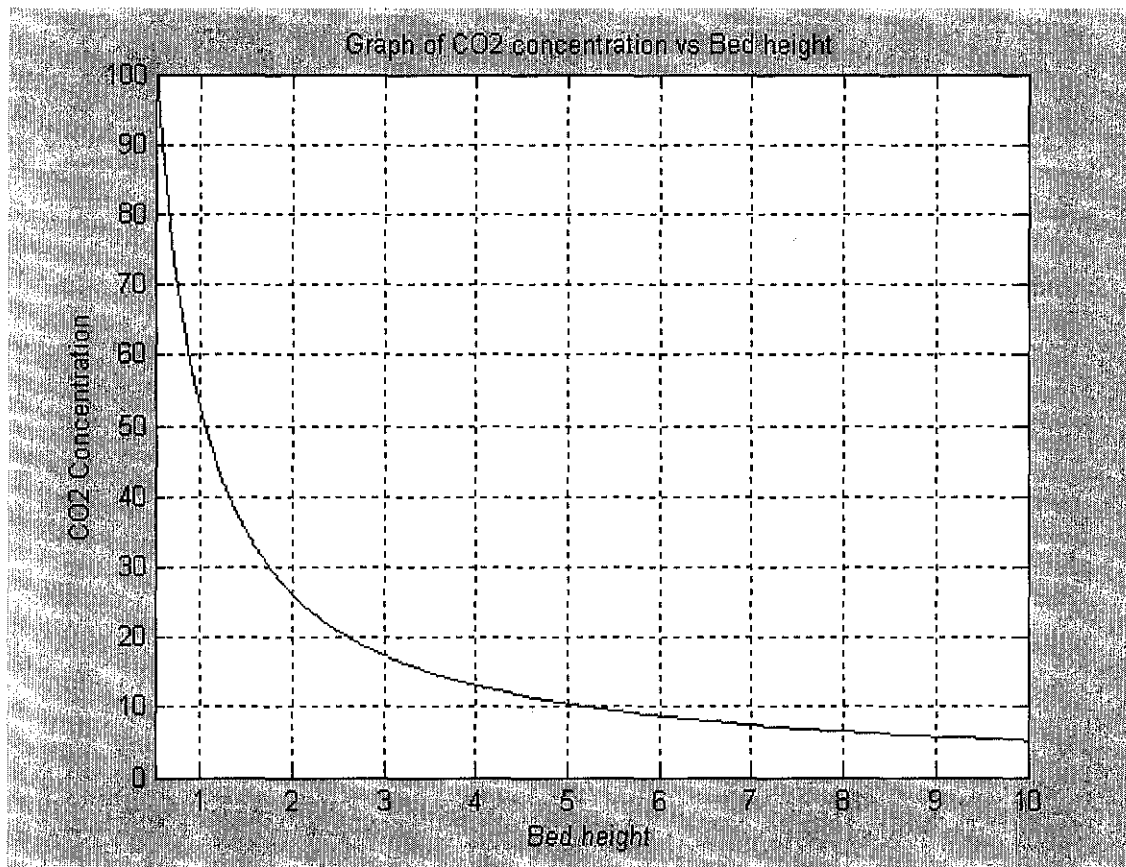
Figure 1. Graph of Carbon Dioxide versus Bed Height

4.4 Concentration Profile

Initially the catalytic activity of a carbon reforming of methane was predicted to be similar to partial oxidation or steam reforming of methane. However, it is observed that the carbon dioxide concentration decreases with the increasing height of catalyst bed. The reduction of the catalytic stability is much more in carbon dioxide reforming compared to the other two methods of methane reforming.

Carbon dioxide concentration decreases because of its reaction with methane to form carbon monoxide and hydrogen. The concentration also dropped at a very quick rate at the beginning and began to react slowly towards the end of the catalyst bed.

There are several reasons of why the concentration decreases quickly in the beginning and began to react slowly at halfway through the catalyst bed. One of them is the

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decrease in the reactant concentration. Initially the reactant concentration is high, contributing to large reaction rate along the earlier part of the catalyst bed. Further along the catalyst bed, reactant concentrations begin to drop causing the reaction rate to become lower.

Main reason for rapid reaction rate in the beginning and slow rate towards the end of the catalyst bed is because of catalyst deactivation. The dissociation of methane into carbon and hydrogen has resulted the carbon formation and deposits on the catalyst surface. The formation of carbons onto catalyst active site has decreased the catalytic activity by hindering of catalyst active site from the reactants particle.

Another reason for the decrease in reaction rate can be related to catalyst deactivation. Study shows that the catalyst starts to deactivate after 50 hours of operation [9]. The main reason for catalyst deactivation is the deposition of carbon onto catalyst surface as a result of methane dissociation into carbon and hydrogen. The deposition of carbon onto catalyst surface reduces the fraction of active site and prevents reactant from being attach to the active catalyst site, hence hinder further reaction.

At the beginning freshly reduced catalyst has no carbon deposit to block the reaction from occurring. However as the reaction occurs, carbon created from the methane deformation accumulates on the catalyst active site first because of its high adsorption properties. There will be at certain point where the carbon deposit will start to decrease the activity of the catalyst since large amount of reactants leaves the reactor without reacting.

Another reason for rapid concentration decay of the reactants may probably because of the reverse water-gas shift reaction (RWGS). [10]

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{298K} = 41 \text{ KJ/mol} \qquad ...4.7$$
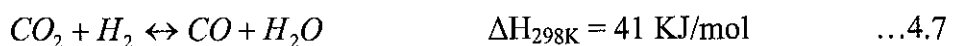
This reaction is one of an elemental reaction that might occur during the carbon dioxide reforming. The reaction has caused the concentration of carbon dioxide to drop whereas it should dissociate into carbon monoxide and oxygen.

Formation of oxygen atom during reforming process can also decrease the catalyst activity. Oxidation of catalyst active site has caused the catalytic activity to drop since the some of the catalyst active sites have change into different material thus having different adsorption and desorption properties.

Catalytic activity can also drop because of inhibition effect. The slow desorption of product from the catalyst active site might occur thus hindering reactants from being adsorbed on the active site. This also occurs because of insufficient active site available since most of the active sites have been occupied with other reactant while some others have been blocked by carbon deposits.

There is also loss of catalyst material which contributes to the low catalytic activity after a certain period of the reaction. This loss is due to sintering effects where the dynamics of the catalyst beds become too rigorous causing a small volume of catalyst active sites to be destroyed.

The catalyst also suffers from sintering by presence of water particle in the RWGS reaction. Water particles initially will adsorb onto catalyst active site. Rapid heating of the reactor temperature will cause the water to evaporate at high rate thus damaging the catalyst structure. Some of the catalyst also experience carryover (entrainment) into downstream line of the process plant.

4.5   Validity of Assumption

Without all the assumptions made, there could be no possible way of achieving the result. All the assumptions made were applied to the Mathlab model to imitate the real experimental situation.

In order to achieve the rate of reaction, it is assumed that the reaction occurs only at the external surface of a catalyst particle. This assumption was made since the size of catalyst particles is about 110μm. The small size of catalyst particles will have smaller pores size hence restricting the entrance of reactant particles.

Since the reaction only occurs at the external surface of the catalyst particles, the diffusion terms in the reaction mechanism can be neglected. These assumptions were found to be true when the model was tested with larger catalyst particles. (The test will be discussed in later stages of this chapter).

In the test, the concentration profile was observed to drop at higher rate because of the presence of micropores. Bigger catalyst particles posses bigger micropores that can acquire more catalytic activity due to maximization of catalyst active site on the catalyst surfaces.

In the process of obtaining the design equation, the only assumption made was the simplification of the emulsion phase equation. This assumption was made due to the large ratio of bubble velocity to the minimum fluidized bed.

From the ratio of both bubble velocity and minimum fluidized velocity, it can be said that the reactor experience mostly bubble phase rather than emulsion phase. In other words, the reaction occurs mainly in the bubble phase and only in a very small portion of the reactor, reaction occurs in the emulsion phase hence the emulsion part can be simplified.

Provided if the emulsion and the bubble phase have the same amount of volume in the fluidized reactor, the concentration profile might behave a little different. The concentration profile may probably differ from the one that has been proven in the experiment. The profile is expected to decrease at linear rate and at a slow pace. This is because less reaction to occur in the emulsion phase due to small reactant flow rate. The reactor also will need to add more height to the catalyst bed in order to achieve optimum yield.
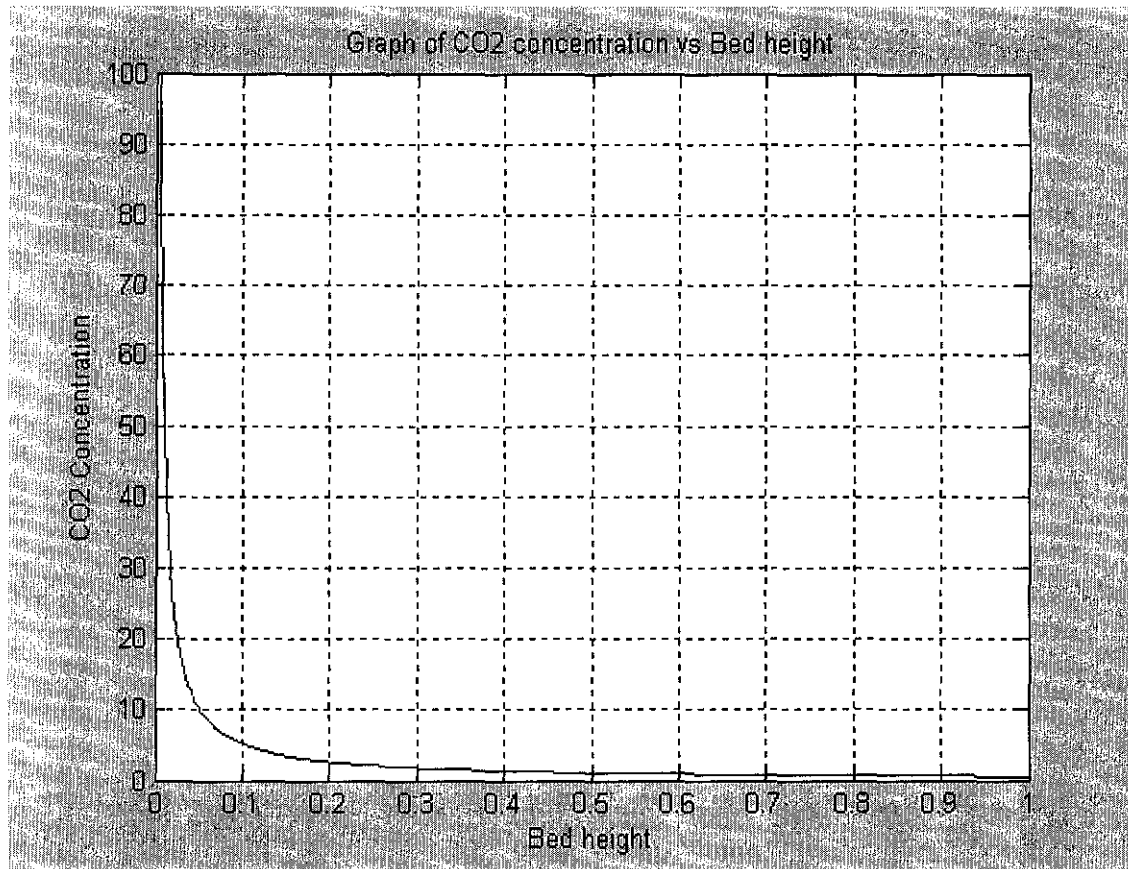

Figure 2: Graph for Carbon dioxide concentration versus bed height

4.6   Other Test

The model equation tested with bigger catalyst particle diameter. It is found that the concentration of carbon dioxide decrease at a faster rate compared to the previous one. Please refer figure 2. The bigger the catalyst might give better reaction rate since the reaction could also occur in the micropores of the catalyst. In the previous experiment,

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the catalyst used was too small that the reaction occurs only at the external surface of the catalyst particle.

Larger size catalyst particle will have reaction at both external and internal surface. Larger catalyst particles will optimize more of its surface area since it can accommodate more active surface area. The only draw back of usage of bigger catalyst diameter is the big pressure drop across the fluidized bed reactor.

The previous experiment was using a catalyst particle diameter of $110\mu m$. this time the particle diameter was replaced with a bigger size, $\rho_s = 1$ mm. The catalytic activity was observed to have a very high reaction rate in very short period of time. Suggested bed height for using the 1 mm diameter is 0.5 cm. This is because addition in catalyst bed would not have a significance conversion of the carbon dioxide.

There was another test that should have been conducted on the reaction model. However the test was not conducted because of time limitation. This test is to study the effect of the limiting reactants. If the concentration of the limiting reactant is to be increased, the product yield will increase. It is proposed that the effect of limiting reactant will give slight different in the concentration profile. Increment in limiting reactant will give higher conversion thus the final concentration of the reactant will be much less.

5   CONCLUSION

The modeling of the carbon dioxide reforming of methane can be said as successful. The objective of the modeling where it is constructed to study catalytic mechanism and activity has been achieved. The analyses of the concentration profile that have been acquired through the Mathlab simulation have been discussed in the discussion part. However the model was not tested to its limit to maximize the outcome that might benefit the writer as well the reader.

There are some problems that have been encountered during the completion of this project. The main problem is time limitation. More time should have been allocated to do the project. Other problem is to find the information source that might assist in completing the subject. However, the writer was able to overcome the problem and came out with the final report of the project.

The study of kinetic analysis of a reaction should be continued as there are still more topics to cover. The reaction model should be given more time to test for different parameters and variables that might give new information regarding the reaction. A real laboratory experiment should be conducted based on the findings through the reaction model. Even it will cost a lot in buying all the equipments, it is the information that will benefit the whole society that counts.

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APPENDICES

Week Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of Project Topic														
Propose topic	█	█												
Topic assigned to student		●												
Prelimary Research Work														
Literature review		█	█	█	█	█	█	█	█	█				
Data Compilation			█	█	█									
Submission of Prelimary Report					●									
Reaction Rate Analysis														
Data analysis					█	█	█	█						
Rate expression					█	█	█	█						
Submission of Progress Report								●						
Development of design expression							█	█	█	█	█			
EDX exhibition											●			
Simulation of Reaction											█	█	█	█
Submission of Interim Report														●

Completed ▉

Milestone ●

Reaction engineering investigations of CO_2 reforming in a fluidized-bed reactor[☆]

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tract

O_2 reforming of methane to synthesis gas over an Ni (1 wt%)/α-Al$_2$O$_3$ catalyst was studied in lab-scale fluidized-bed reactors = 3,5 cm). In the whole range of reaction conditions (p_{CH4} = p_{CO2} = 25–45 kPa, p_{N2} = 10–50 kPa, T_R = 700–800°C, ⋅ = 3,4,5 cm, $m_{cat}/\dot{V}$ = 2.8–7.3 g s ml^{-1}, u/u_{mf} = 6.5–11.8) a stable isothermal operation was achieved. The catalytic performance ngly depended on the oxidation state of the catalyst. When applying a reduced catalyst initial yields of carbon monoxide and rogen near the thermodynamic equilibrium were obtained. However, a slow decrease of methane conversion and syngas yield ;ed by carbon deposition was observed. The fresh unreduced catalyst exhibited significantly lower activity. The in situ reduced lyst was more active but yielded CH$_4$ and CO$_2$ conversions lower than predicted by the thermodynamic equilibrium. The :tion was not influenced by interphase gas exchange. Based on these results, reaction engineering modeling and simulation yielded ɔbal kinetic model which described the experimental data with an error of less than 10% was developed. © 2000 Elsevier Science . All rights reserved.

ᵥords: CO$_2$-reforming; synthesis gas; fluidized-bed modeling

Introduction

n recent years, considerable attention has been paid to methane which is the main component of natural gas ëedstock for the chemical and petrochemical industry. ᴇ indirect route via synthesis gas (syngas) remains main way to convert natural gas into liquid fuels, thanol, ammonia or oxygenates. Currently, syngas is inly produced by steam reforming of methane (Adris, ıden, Lim & Grace, 1996; Qin, Lapszewicz & Jiang,)4). However, the H$_2$: C$_O$ ratio of 3 : 1 obtained by

steam reforming is higher than that needed for Fischer-Tropsch or methanol synthesis. In turn, further gas make up is necessary in order to obtain syngas which meets the requirements of the down-stream technologies.

$$CH_4 + CO_2 = 2CO + 2H2,$$
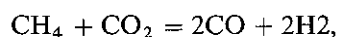
$$\Delta_R H^0_{298\ K} = +247.9\ kJ/mol. \tag{1}$$

Lately carbon dioxide reforming of methane (see Eq. (1)) has gained increasing interest as an alternative process to produce syngas (Edwards, 1995). This process yields the low H$_2$: CO ratio of 1 : 1 which is desirable for synthesis of oxygenated chemicals. CO$_2$ reforming can also be used for producing high-purity CO (Teuner, 1985; Kurz & Teuner, 1990). Furthermore, this reaction is of environmental significance since it consumes two molecules which contribute significantly to the greenhouse effect (Rostrup-Nielsen, 1994). Finally due to the high endothermicity of the reaction it can be used for the chemical energy storage (Wang, Lu & Millar, 1996; Gadalla & Sommer, 1989). Carbon dioxide reforming still has no commercial application by itself (Edwards & Maitra, 1994) but it is used in mixed reforming processes to reduce the H$_2$: CO ratio (Teuner, 1987).

ᴵᴵis paper is dedicated to Prof. Manfred Baerns on the occasion of his ı birthday.

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ɔmenclature

	cross-sectional area of reactor, m^2	N_{orif}	number of distributor holes, dimensionless
$_{j,i}$	concentration of component i in the jth segment of the bubble phase, $mol\,m^{-3}$	NR	number of reactions dimensionless
$_{j,i}$	concentration of component i in the jth segment of the emulsion phase, $mol\,m^{-3}$	m_{cat}	mass of catalyst, g
$_0$	initial bubble diameter, m	η_g	gas viscosity, $Pa\,s^{-1}$
$_j$	local bubble diameter in j^{th} segment, m	p	partial pressure, kPa
	particle diameter, μm, m	$Q_{P,l}$	reaction quotient of reaction l ($Q_{P,l} = \Pi p_{i,j}^{v_{i,l}}$), var.
H^0_{298K}	standard reaction enthalpy, $kJ\,mol^{-1}$	r	reaction rate, $mol\,s^{-1}\,kg_{cat}^{-1}$
·	porosity at minimum fluidization condition, dimensionless	$r_{B,j,l}$	rate of reaction l in the jth segment of bubble phase, $mol\,s^{-1}\,kg_{cat}^{-1}$
$_j$	local bubble hold-up in the jth segment, dimensionless	$r_{E,j,l}$	rate of reaction l in j^{th} segment of emulsion phase, $mol\,s^{-1}\,kg_{cat}^{-1}$
	earth acceleration, $m\,s^{-2}$	ρ_{cat}	catalyst density, $kg\,m^{-3}$
	inner diameter, cm	ρ_g	gas density, $kg\,m^{-3}$
	measuring height, cm	ρ_P	particle density, $kg\,m^{-3}$
	height, cm	STP	standard conditions, dimensionless
	component, dimensionless	t	time, min, h
	segment number in the fluidized bed, dimensionless	T	temperature, °C
	adsorption constant of component i, atm^{-1}	T_R	reaction temperature, °C
$_{,l}$	thermodynamic equilibrium constant of reaction l, var.	TOS	time on stream, h
	kinetic constant of reaction l, var.	u	superficial gas velocity, $cm\,s^{-1}$
$_{E,i}$	mass transfer coefficient in the jth segment, s^{-1}	u_j	superficial gas velocity in the jth segment, $cm\,s^{-1}$
	reaction number, dimensionless	u/u_{mf}	fluidization number, dimensionless
	average life time of a bubble, s	$u_{B,j}$	bubble rise velocity in the jth segment, $m\,s^{-1}$
$_{at}$	mass of catalyst, g	$v_{i,l}$	stechiometric coefficient of component i in reaction l, dimensionless
·	at minimum fluidization condition, dimensionless	$\dot{V}$	volume flow, $m^3\,s^{-1}$
$_{i}$	mass of nickel, g	$V_{B,j}$	volume of bubble phase in the jth segment, m^3
$_{nv,BE,i,j}$	convective flow of component between bubble and emulsion phase in the jth segment of the fluidized bed due to increase of total numbers of moles, $mol\,s^{-1}$	$V_{CP,j}$	volume of cloud phase in j^{th} segment, m^3
		$V_{EP,j}$	volume of emulsion phase in j^{th} segment, m^3
		X_i	conversion of component i, %
		X_i^0	initial conversion of component i, %
		Y_i	yield of component i, %

ɪgainst this background numerous works dealing ɪ the investigation of CO_2 reforming in fixed- reactors over supported metal catalysts were re- ted (for a review see Wang et al., 1996). The reaction .peratures applied in these investigations ranged from °C (Masai, Kado, Miyako, Nishiyama & Tsuruya, 8; Erdöhelyi, Cserenyi & Solymosi, 1993) up to 0°C (Yu, Choi, Rosynek & Lunsford, 1993). Among ɛral transition metals which were proposed as active ɪponents, nickel (e.g. Vernon, Green Cheetham Ashcroft, 1992; Gadalla & Sommer, 1989), platinum . Masai et al., 1988; Vernon et al., 1992; Solymosi, tsan & Erdöhelyi, 1991) and rhodium (e.g. Erdöhelyi

et al., 1993; Richardson & Paripatyadar, 1990) have found widest research interest. For several of these cata- lysts yields of CO and H_2 near the thermodynamic equilibrium were reported (e.g. Vernon, Ashcroft & Cheetham, 1991; Richardson & Paripatyadar, 1990). However, catalyst deactivation due to carbon deposition occurred. This deposition limited application of a fixed- bed reactor for this reaction (Rostrup-Nielsen & Bak Hansen, 1993; Seshan, ten Barge, Hally, van Keulen & Ross, 1994; Swaan, Kroll, Martin & Mirodatos, 1994; Au, Hu & Wan, 1994). Furthermore, in this reactor type steep temperature gradients caused by the high endother- micity of the reaction occurred. These, in turn, promoted

bon deposition (Rostrup-Nielsen & Bak Hansen, 3; Zhang & Verykios, 1994).

n order to eliminate these obstacles which impede the nmercialization of the title reaction the application of uidized-bed reactor was proposed (e.g. Olsbye, Wurzel Mleczko, 1997). Excellent heat dissipation originated n the solids mixing in this reactor type can be utilized obtain good temperature control isothermal opera-1. Application of small particles should allow to over-ne the intra-particle mass transfer limitation which iously reduces catalyst efficiency in fixed beds (Adris al., 1996). Until now, only few experimental studies re dealt with the performance of a fluidized-bed reac-for CO_2 reforming (Mirzabekova, Mamedov, Aliev Krylov, 1992; Blom, Dahl, Salgtern, Sortland, Spjel-vik & Tangstad, 1994; Olsbye et al., 1997). The re-rted results show that conversions near thermo-namic equilibrium can be attained although catalyst activation has not been prevented (Blom et al., 1994). ese studies aimed mainly at catalyst testing with re-ct to their catalytic and mechanical stability.

Against this background reaction engineering invest-tions of CO_2 reforming over an Ni/α-Al_2O_3 in a la-ratory-scale fluidized-bed reactor were carried out. e work aimed at the optimization of reaction condi-ns for obtaining high syngas yields as a base for the imation of kinetic parameters. Special attention was id to the influence of hydrodynamic and reaction con-ions on the deactivation of the catalyst.

Method of investigation

. Experimental

!.1. Catalyst

The Ni (1 wt%)/α-Al_2O_3 catalyst was prepared by cipient wetness technique from α-Al_2O_3 (Janssen) with L aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Merck). After ying for 12 h at 100°C the catalyst precursor was cal-ned in air at 470°C for 10 h. Particle diameters in the nge 71–160 μm were used. The experimentally deter-ined minimum fluidization velocity using nitrogen as e fluidizing gas amounted to $u_{mf,800°C} = 0.006$ m/s.

1.2. Catalyst characterization

The fresh unreduced as well as samples of Ni/Al_2O_3 talyst used in different series of experiments were char-terized by applying several surface and bulk tech-ques. Carbon deposits were determined by means of mperature programmed oxidation (TPO). X-ray dif-action (XRD) analysis was performed in order to deter-ine the phase composition of the catalyst samples and correlate the catalytic activity to specific phases. ransmission electron microscopy (TEM) analysis of ifferent samples aimed at the visualization of nickel articles and carbon deposits.

2.1.3. Apparatus

Experiments were carried out at atmospheric pressure in two fluidized-bed reactors made of quartz with inner diameters of ID = 3 cm and 5 cm (see Fig. 1). In the preheating section ($L = 80$ cm, ID = 2 cm) the feed gas was warmed up to 400°C before distributing through a porous quartz plate ($d_{pore} = 40$–90 μm). The bed tem-perature was controlled by heating the catalytic section from outside. In order to reduce particle entrainment a disengaging section and an internal cyclone were located at the top of the reaction zone.

For measuring the bed temperature, thermocouples within a quartz tube were located in three axial positions of the fluidized bed. Reactants (CH_4, CO_2 and N_2 serv-ing as internal standard) and products (H_2 and CO) were analyzed by on-line gas chromatography. The amount of water which was condensed down-stream from the reac-tor was calculated from the oxygen balance. Concentra-tion profiles were measured applying an axial movable sample tube (OD = 0.8 cm). A detailed description of the experimental equipment is given elsewhere (Mleczko, Pannek, Rothaemel & Baerns, 1996a).
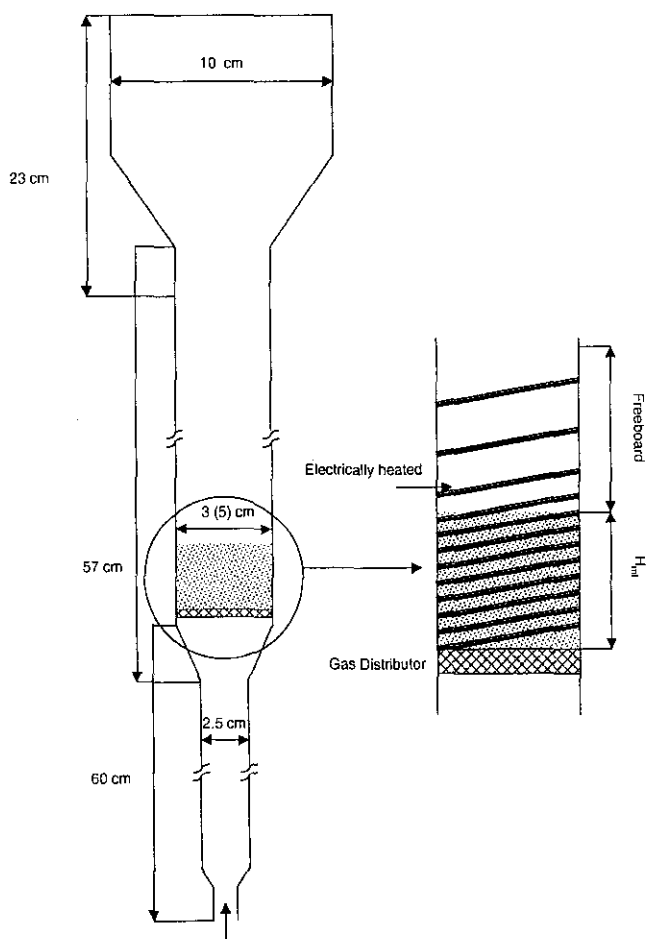

Fig. 1. Schematic sketch of the fluidized-bed reactor applied.

4. Experimental conditions

ı all experiments a $CH_4 : CO_2$ ratio of $1 : 1$ was
lied. Nitrogen-dilution was varied between 10 and
ıPa. The reaction was investigated between 700 and
°C. The reactor was operated in the bubbling regime
$_{mf} = 6.5$–11.8). Catalyst mass was varied between 106
. 177 g. The other experimental conditions are given
he following part.

Modeling

1. Reactor model

¯he hydrodynamics of a fluidized bed was described
a model that originated from the bubble assemblage
del of Kato and Wen (1969). In this model the
dized bed is divided into segments. The height of the
ments corresponds to the local bubble diameter. The
del is based on the two-phase theory of fluidization.
:ording to this theory, the bed is divided into two
ıses, i.e. the emulsion phase and the bubble phase.
:ween the phases exchange of gas takes place; the
:rphase gas exchange coefficient was calculated from
correlation of Kobayashi and Arai (1967). Through
emulsion gas flows with the minimum fluidization
ocity which was calculated from the correlation of
:n and Yu (1966). The excess gas flows in the form of
bbles. The bubble phase consists of particle-free bub-
s that are surrounded by cloud and wake. The cloud
d wake have the same porosity as the emulsion phase
d travel together with bubbles. For describing the
namics of bubbles, i.e. bubble diameter and velocity
: correlation of Werther (1992) was used. The correla-
n of Werther describes growth of bubbles as a result of
alescence and splitting. However, during the reforming
iction local bubble diameter, superficial gas velocity
d the interphase gas exchange are also influenced by
: increase of gas volume due to chemical reaction. The

model equations are given below (Eqs. (2) and (3)). The
correlations used for hydrodynamic modeling are sum-
marized in Table 1 (refer also Mleczko, Ostrowski
& Wurzel, 1996b; Wurzel & Mleczko, 1998).

Model equation for emulsion phase:

$$A_T u_{mf}[c_{E,i,j-1} - c_{E,i,j}] + k_{BE,j}V_{B,j}[c_{B,i,j} - c_{E,i,j}]$$

$$+ \sum_{l=1}^{NR} v_{i,l}r_{E,j,l}(1 - \varepsilon_{mf})\rho_{cat}V_{EP,j} - n_{conv,BE,i,j} = 0. \quad (2)$$

Model equation for bubble phase

$$A_T(u_j - u_{mf})[c_{B,i,j-1} - c_{B,i,j}] - k_{BE,j}V_{B,j}[c_{B,i,j} - c_{E,i,j}]$$

$$+ \sum_{l=1}^{NR} v_{i,l}r_{B,j,l}(1 - \varepsilon_{mf})\rho_{cat}V_{CP,j} + n_{conv,BE,i,j} = 0 \quad (3)$$

2.2.2. Rate equation and estimation of kinetic parameters

Reaction rate of CO_2 reforming was calculated using
a Langmuir–Hinshelwood rate expression. Because
water–gas-shift reaction takes place simultaneously dur-
ing CO_2 reforming (Olsbye et al., 1997) this reaction was
also taken into account to describe the experimental
results. Reaction rate of the water–gas-shift reaction was
calculated by applying first-order rate equation. For
both reactions vanishing reaction rates when approach-
ing equilibrium were taken into account (see Eqs. (4) and
(5)). These rate equations were already applied for de-
scribing kinetics of dry reforming of methane over the
$Ni/La/Al_2O_3$ catalyst (Olsbye et al., 1997).

$$r_{CO_2-Ref} = \frac{k_{CO_2-Ref}p_{CH_4}p_{CO_2}}{(1 + K_1p_{CH_4} + K_2p_{CO})(1 + K_3p_{CO_2})}$$

$$\times \left(1 - \frac{Q_{P,CO_2-Ref}}{K_{P,CO_2-Ref}}\right), \quad (4)$$

ble 1
rrelations used for the calculation of hydrodynamic parameters

rameter	Correlation	Reference
f	$u_{mf} = \eta_g \dfrac{(33.7^2 + 0.0408d_p^3\rho_g(\rho_p - \rho_g)\eta_g^{-2})^{1/2} - 33.7}{(\rho_g d_p)}$	Wen and Yu (1966)
ε,j	$k_{BE,j} = 0.11/d_{B,j}$	Kobayashi and Arai (1967)
0	$d_{B,0} = 1.3[(A_T u_0(N_{orif}A_T)^{-1})^2 g^{-1}]^{0.2}$	Werther, 1992
j	$\dfrac{d}{dh_j}d_{B,j} = \left(\dfrac{2\varepsilon_{B,j}}{9\pi}\right)^{1/3} - \dfrac{d_{B,j}}{3\lambda u_{B,j}}$	Werther (1992)
j	$\varepsilon_{B,j} = 0.8(u_j - u_{mf})/u_{B,j}$	Werther (1992)
	$\lambda_B = 280u_{mf}/g$	Werther (1992)
,j	$u_{B,j} = 0.8(u_j - u_{mf}) + 0.71 \times 3.2\sqrt{gd_{B,j}}$	Werther (1992)

le 2
juency coefficients estimated for CO_2-reforming and water–gas-shift reaction and adsorption constants adapted from Olsbye et al. (1997)

ction	k_0 $(mol\ s^{-1}g_{cat}atm^{-2})$	K_1 (atm^{-1})	K_2 (atm^{-1})	K_3 (atm^{-1})
reforming	0.0150 ± 0.0039	0.52	10	27
er–gas-shift reaction	0.0120 ± 0.0041			

$$s = k_{WGS}P_{CO_2}P_{H_2}\left(1 - \frac{Q_{P,WGS}}{K_{P,WGS}}\right). \qquad (5)$$

ietic parameters were determined by comparing del predictions (using the aforementioned reactor del) with the experimental data reported in this paper ereas adsorption constants were adapted from Olsbye il. (1997) (see Table 2). For the non-linear parameter imization a random search method was applied. In routine the goal function was built as the sum of ares of differences between measured and predicted iversions of methane and carbon dioxide. The details the optimization routine are presented elsewhere insch, Mleczko & Baerns, 1997).

Results and discussion

Reactor operation and catalytic performance

1. Reactor operation

The Ni/α-Al_2O_3 catalyst was mechanically stable and l fluidizable in the whole range of the investigated ction conditions. From the bed with the height of cm ($m_{cat} = 177.2$ g) during 129 h on stream 5.3 g cata- was lost; the average rate of entrainment amounted 0.041 g h^{-1}. The good fluidizability of the catalyst ulted in a good temperature control (see Fig. 2). The bling bed zone showed isothermal behavior. How- r, in the grid zone (0–1 cm) a temperature gradient up 80 K occurred. The temperature drop in the distribu- zone was significantly higher than the one measured he same reactor for the oxidative coupling of methane leczko et al., 1996a) and for the catalytic partial oxida- n of methane to syngas (POx) (Mleczko & Wurzel, 17). This indicates that the temperature drop is not y caused by the cold inlet gases but also by the high lothermicity of the reforming reaction. In the free- ird the temperature increased up to 825°C since this t of the reactor was still heated.

2. Catalytic performance

Highest conversions and syngas yields were achieved the following reaction conditions: $T_R = 800$°C, $f = 5$ cm, $u/u_{mf} = 11.8$, $m_{cat}/\dot{V}_{STP} = 4.7$ g s ml^{-1}, $_4 : p_{CO_2} : p_{N_2} = 1 : 1 : 2$. Methane and carbon dioxide
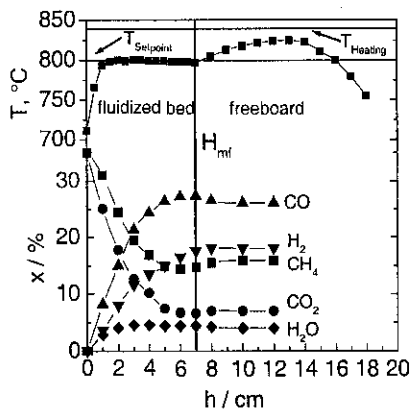

Fig. 2. Axial temperature as well as axial concentration profiles of reactant (CH_4, CO_2) and product (CO, H_2, H_2O) components concentration profile ($CH_4 : CO_2 : N_2 = 1 : 1 : 0.86$, $u/u_{mf} = 8.6$, $H_{mf} = 7$ cm, $T_R = 800$°C).

conversion amounted to 90 and 93%, respectively. Hydrogen and carbon monoxide yield amounted to 81 and 90%, respectively; this corresponds to a $H_2 : CO$ ratio of 0.9.

These results are in line with the published data. In almost all studies conversions near the thermodynamic equilibrium were achieved. No difference between fluidized and fixed beds could be recognized. A comparison between conversions and yields obtained in this work and those reported in the literature is difficult due the differences between reaction conditions and loading of the catalyst with an active component. In order to overcome this obstacle the activity of the investigated catalyst was compared with other systems on the basis of the mass of the active component. This approach is justified by the linear dependency of the catalyst activity on the Ni loading (Goetsch, Say, Vargas & Eberly, 1989). The contact times reported for fixed beds were shorter than the one applied in this work ($m_{Ni}/\dot{V}_{STP} = 0.047$ g s ml^{-1}). Although the contact times for achieving thermodynamic equilibrium are comparable with those reported in the literature, the activity of the catalyst applied in this work was significantly lower than the that of the catalyst prepared by SINTEF (Blom et al., 1994). Finally it should be taken into account that the validity of the linear dependence of the catalytic activity on the Ni loading is limited, e.g. for Ni/NaY–zeolithe catalysts the activity passed

ough a maximum with increasing nickel loading
ang et al., 1996).

since it is generally accepted that reforming reactions
the rate-determining steps during partial oxidation of
:hane to syngas a comparison between CO_2 reform-
and partial oxidation in fluidized beds can be made.
en performing POx over various supported nickel
alysts methane conversions close to the thermodyn-
ic equilibrium were achieved at significantly shorter
tact times than in this work (Bharadwaj & Schmidt,
4; Olsbye, Tangstad & Dahl, 1994; Mleczko & Wur-
1997; Santos, Menendez, Monzon, Santamaria, Miro
.ombardo, 1996). The fact that CO_2 reforming itself is
ver than when it is performed during partial oxidation
iditions was already stated in other works (e.g. Peters,
dolf & Voetter, 1955; Lapszewicz & Xiang, 1992). This
gests that the reforming reactions are promoted when
ie oxygen is present. In order to explain this effect it
. be postulated that carbon deposits which limit the
rall catalytic activity are burnt off easier with oxygen
n with carbon dioxide. Furthermore, it is supposed
t the methane pyrolysis which is assumed to be the
:-determining step of the reforming reactions can be
elerated since hydrogen is withdrawn from adsorbed
thane by adsorbed oxygen.

Parameters influencing catalytic activity and stability

1. Activity of the fresh catalyst

n the fresh (not-pretreated) catalyst nickel is com-
tely oxidized. Therefore, when measuring the initial
ivity of the catalyst the activity of the oxidized NiO
s for CO_2 reforming can be determined. Furthermore,
ct of in situ reduction on catalytic activity during
ction can be analyzed. Moreover, the influence of the
ction conditions on the catalyst state can be observed
determining the course of conversions over time on
:am. In the experiment the methane-to-carbon dioxide
io amounted to 1 : 1. The feed was diluted with nitro-
i (p_{N_2} = 30 kPa). The height of the settled bed and
dization number (u/u_{mf}) amounted to 5 cm (m_{cat} =
'.2 g) and 8.6, respectively.

The fresh catalyst showed a very low activity for CO_2
orming, e.g. the initial conversions of methane and
bon dioxide amounted to 9 and 13%, respectively (see
;. 3). Under reaction conditions activity of the catalyst
reased. The characterization of the catalyst surface
icated that these changes in the catalytic activity can
correlated with the oxidation state of Ni sites. XRD
ilysis showed that the fresh catalyst contained com-
tely oxidized nickel (see Fig. 4a). The low initial con-
sions indicate that oxidized nickel sites exhibit low
alytic activity for CO_2 reforming. Therefore, slow
itinuous reduction of nickel sites by non converted
thane resulted in the increase of conversion. This
lanation is confirmed by XRD (see Fig. 4b) and TEM

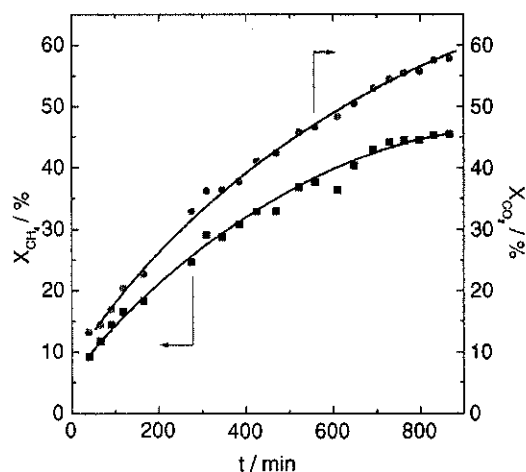Fig. 3. Dependence of methane and carbon dioxide conversions on time on stream applying a fresh catalyst ($CH_4 : CO_2 : N_2 = 1 : 1 : 0.22$, u/u_{mf} = 8.6, T_R = 800°C, H_{mf} = 5 cm).
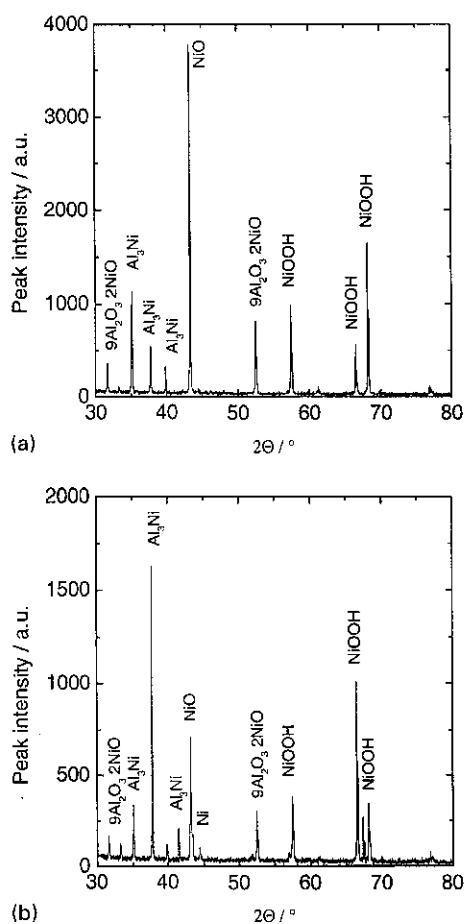

Fig. 4. XRD pattern of the fresh (unreduced) catalyst (a) and (b) of the catalyst used for CO_2 reforming after 120 h on stream ($CH_4 : CO_2 : N_2 = 1 : 1 : 2$, u/u_{mf} = 11.8, H_{mf} = 5 cm, T_R = 800°C).

analysis of the used catalysts (after 120 h on stream)
which showed that during CO_2 reforming metallic Ni
sites were formed. The reduction process is promoted
by increasing conversion since the partial pressure of

lrogen which is a more efficient reducing agent than
:hane increases during the activation period. The pos-
ited explanation for the increase of the activity of fresh
Al_2O_3 catalyst agrees well with published informa-
i; also other investigators reported that an increase of
reduction degree of supported metal catalysts (Ni,
ı resulted in higher conversions when performing dry
l steam reforming (Au et al., 1994; Dissanayake,
synek, Kharas & Lunsford, 1991; Santos et al., 1996).
ıfter a period of 13 h the catalyst attained a stationary
:e; no further substantial changes in conversions of
thane and carbon dioxide occurred. Final conver-
ıs, that amounted to 46% for methane and 58% for
bon dioxide were lower than those calculated for the
rmodynamic equilibrium. In contrast to the results
orted for the catalytic partial oxidation of methane to
thesis gas for which methane conversions near the
rmodynamic equilibrium after an in situ activation of
catalyst were achieved (e. g. Dissanayake et al., 1991;
ıtos et al., 1996), final conversions during CO_2 reform-
were at comparable contact times significantly lower
n those predicted by thermodynamics.

2. Catalyst deactivation

Catalytic stability was investigated by studying two
alysts applied for dry reforming over a period of 60 h
t had exhibited different initial activities. Different
alytic activity was established by treating the first
alyst with O_2/N_2 (1 : 1) for 1 h at 600°C after 60 h on
:am (CO_2 reforming). The second catalyst was not
treated prior to reaction. The bed with the stationary
ght of 5 cm for the first catalyst and 3 cm for the
ond one was fluidized with a gas velocity
: 7.1 cm s^{-1} (u/u_{mf} =11.8). In both experiments the
ction temperature and the methane-to-carbon dioxide
io amounted to 800°C and 1 : 1, respectively. The feed
s diluted with nitrogen (p_{N_2} = 50 kPa). The experi-
nts covered a period of approx. 100 h.
For both catalysts two periods can be recognized (see
ſ. 5). In the first period the activity of the catalyst
ied with TOS. In the second period both catalysts
ained constant catalytic activity. The catalyst that had
ibited high initial activity ($X^0_{CH_4}$ = 90%, $X^0_{CO_2}$ =
%) deactivated; after 50 h on stream conversions drop-
l to 78% for methane and 86% for carbon dioxide.
ıultaneously, yields dropped from 82 to 75% for hy-
ıgen and from 90 to 83% for carbon monoxide. TPO
asurements performed for the Ni/Al_2O_3 catalyst (see
ſ. 6) indicate that during CO_2 reforming continuous
bon deposition occurred, which is assumed to be
ponsible for the loss of activity. After 8 h on stream
ly small amounts of carbon were deposited on the
alyst which could be burnt off at a temperature of
und 680°C. In contrast, the specimen which was taken
the end of the reaction period (approx. 100 h) showed
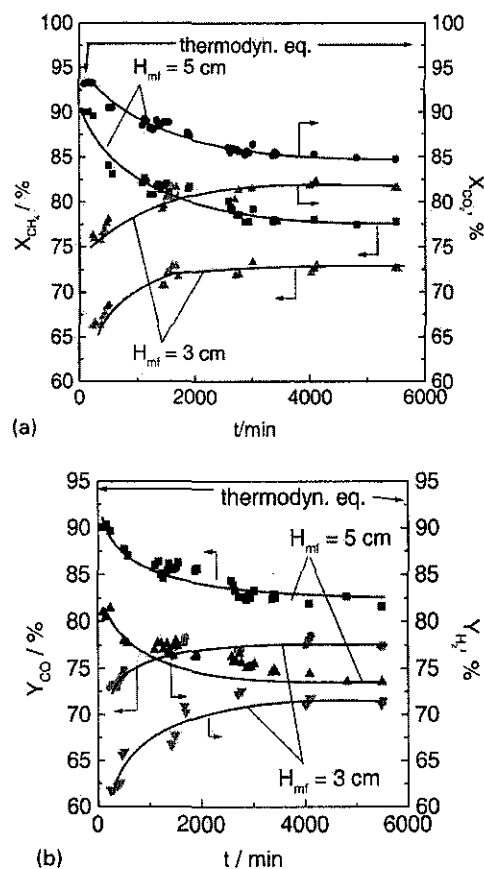substantial larger amount of carbon deposits which

Fig. 5. Dependence of methane and carbon dioxide conversion (a) and
(b) yield on time on stream for a regenerated (H_{mf} = 5 cm) and a non-
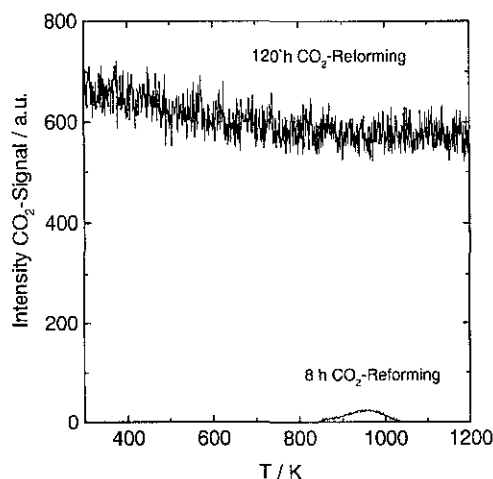regenerated (H_{mf} = 3 cm) catalyst ($CH_4 : CO_2 : N_2 = 1 : 1 : 2$,
u/u_{mf} = 11.8, T_R = 800°C).

Fig. 6. Intensity of the CO_2 signal during TPO for two catalyst samples
differing in time on stream ($CH_4 : CO_2 : N_2 = 1 : 1 : 2$, u/u_{mf} = 11.8,
H_{mf} = 5 cm, T_R = 800°C).

could be burnt off continuously over the whole range of
temperature. Furthermore, a second catalyst phase of
black color was built up. The formation of the carbon
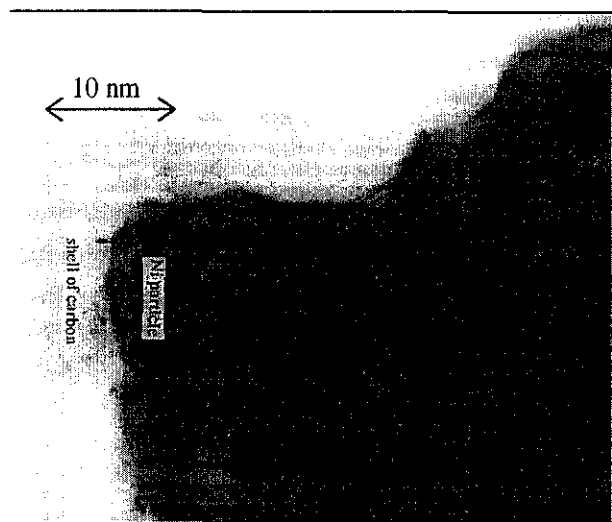deposits on the catalytic surface was also confirmed by

7. TEM photography of the catalyst after 100 h of CO_2 reforming $_4$: CO_2 : N_2 = 1 : 1 : 2, u/u_{mf} = 11.8, H_{mf} = 5 cm, T_R = 800°C).

D and TEM measurements. Furthermore, TEM anal-
. indicates that a shell of carbon was built up around
cel crystallites (see Fig. 7). The blocking of active sites
arbon deposits as the reason for the loss of catalytic
vity during CO_2 reforming was also postulated by
er investigators (e.g. Rostrup-Nielsen & Bak Hansen,
3; Bitter, Hally, Seshan, van Ommen & Lercher, 1996).
'he initial conversions and yields measured over the
alyst that exhibited low initial activity amounted to
% for methane, 76% for carbon dioxide, 62% for
Irogen and 73% for carbon monoxide. For this cata-
. conversions and yields rose in the initial period with
e on stream. Conversions increased to 73% for meth-
: and 82% for carbon dioxide. Simultaneously, yields
e to 72% for hydrogen and 78% for carbon monox-
. The low initial activity of this catalyst charge is
umed to result from the passivation of deposited car-
1 during the off-stream period. The explanation that
aging of carbon deposits can be responsible for the
ay of catalytic activity is supported by the work
formed by Buyevskaya, Wolf & Baerns (1994) in the
P reactor over an Rh catalyst. The initial increase of
iversions and yields observed during the activation
iod can be attributed to the substitution of the pas-
ated carbon by fresh, active carbon deposits during the
ersed Boudouard reaction. When the passivated car-
1 was completely substituted by fresh carbon deposits
itationary state of constant catalytic activity was
ieved.
'he stationary state that was obtained after approx.
h independent of the initial catalyst state is attributed
a dynamic equilibrium between reactions that con-
ne deposited carbon (reversed Boudouard reaction)
l produce carbon deposits (methane pyrolysis). Due to
itinuous catalyst deactivation when performing CO_2

reforming in fixed-bed reactors (e.g. Swaan et al., 1994)
and the steady-state activity in the fluidized-bed the
conclusion is drawn that catalyst deactivation is in-
fluenced by the hydrodynamic conditions in the reactor
type applied. In a fluidized-bed reactor deactivated cata-
lyst particles are transported by means of the solid mix-
ing into the carbon-dioxide-rich distributor zone where
the carbon deposits can be consumed by the reversed
Boudouard reaction. Therefore, a fluidized-bed reactor
seems to be more suitable for performing CO_2-reforming
reaction than a fixed bed not only with respect to temper-
ature control but also due to the slower deactivation of
the catalyst. This is underlined by the different deactiva-
tion rates. For an Ni (6.2 wt%)/Al_2O_3-SiO_2 catalyst the
deactivation rate in a fixed bed amounted to 3.7% h^{-1}
(Swaan et al., 1994) whereas it amounted to 1.5% h^{-1}
(Blom et al., 1994) and 0.6% h^{-1} (this work) in the
fluidized bed.

3.2.3. Effect of water on catalyst regeneration

Since an excess of steam is known to prevent carbon
deposition during the steam-reforming process experi-
ments were conducted in which the catalytic activity with
and without steam addition (p_{H_2O} = 15 kPa) was investi-
gated. In these experiments the deactivated catalyst that
exhibited low initial activity was used. The methane-to-
carbon dioxide ratio was held constant at 1 (p_{CH_4} =
p_{CO_2} = 35 kPa). Nitrogen dilution amounted to 15 and
30 kPa, respectively. The reforming reaction was carried
out at 800°C in a catalytic bed (H_{mf} = 5 cm, m_{cat} = 64 g)
fluidized with a gas velocity u = 5.2 cm s^{-1} (u/u_{mf} = 8.6).

For both investigated feed-gas compositions a similar
dependence of catalytic activity on TOS was observed; in
the first 15 h methane and carbon dioxide conversion
increased followed by constant activity (see Fig. 8). Water
in the feed had no effect on the period of activation.
However, slightly lower conversions were measured
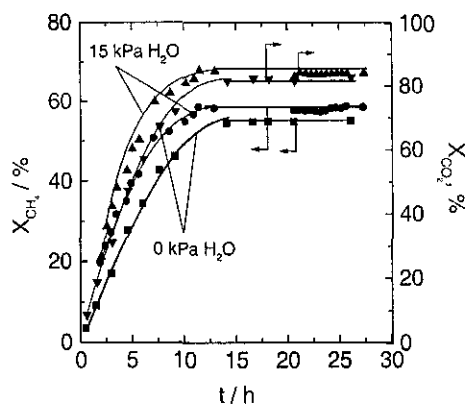when applying the dry feed due to thermodynamic

Fig. 8. Dependence of methane conversion on time on stream with and
without water addition (CH_4 : CO_2 : N_2 = 1 : 1 : 0.86, u/u_{mf} = 8.6,
H_{mf} = 5 cm, T_R = 800°C).

...sons. The addition of water to the feedstock also had significant influence on the catalytic stability of the /α-Al₂O₃ catalyst. This behavior can be explained the stronger oxidation potential of carbon dioxide npared to water. Since the catalyst is continuously nsported in the carbon-dioxide-rich distributor zone bon gasification by carbon dioxide is dominant npared to water.

. Concentration profiles

.n order to elucidate the reaction pathway of CO_2 orming in a fluidized bed axial concentration profiles re measured. In these experiments the minimum bed ght H_{mf} and the $p_{CH_4} : p_{CO_2}$ ratio amounted to 7 cm 1 1 : 1, respectively. Measurements were performed in ped fluidized with a gas velocity of $u = 5.2$ cm s^{-1} $u_{mf} = 8.6$) carrying out the reaction at 800°C.

The measured concentration profiles are presented in g. 2. The most significant changes of the concentrations ik place within the first two centimeters of the fluidized 1. In this region a decrease of the concentrations of the d gases methane and carbon dioxide from 35% at the it to 24.3% for methane and 17.6% for carbon dioxide s observed. Simultaneously, the concentrations of the iducts hydrogen and carbon monoxide increased up 11.4 and 14.8%, respectively. Also in the upper part of : bed, the concentrations of methane and carbon diox-decreased continuously, whereas the concentrations the selective products hydrogen and carbon monoxide reased. However, with increasing distance from the ; distributor the concentration gradients decreased. iter yielded a maximum of 4.4% at a bed height of m followed by a flat decline of 4% at the end of the 1. At the end of the bed a decay of carbon monoxide icentration and an increase of the concentrations of : feed gases methane and carbon dioxide were mea-ied. In the freeboard (8–12 cm) no further changes in icentrations occurred although the temperature is through a maximum in this region. This indicates it the reaction is heteregeneously catalyzed whereas i-phase reactions have no influence on the extent of iction.

In the whole bed, concentration of carbon dioxide was ver than the methane concentration. Also the hydro-1 concentration was always lower than that of carbon inoxide. This indicates that beside the CO_2-reforming iction the water–gas shift reaction also takes place ich results in a H₂/CO ratio below 1. With respect to : reaction rates it can be expected that the one for ter-gas reaction is faster than the one for CO_2-reform-; reaction since even in the distributor zone where the ihest reaction rates for CO_2 reforming occur the differ-ze between the methane and carbon dioxide concentra-n is significant. Simultaneously, formation of water ies place. The product distribution in the bed is also

influenced by the steam-reforming reaction. This would explain the axial increase of the H₂/CO ratio (0.42–0.68) since steam reforming produces more hydrogen than carbon monoxide. However, steam reforming has only minor effect on the methane conversion.

The concentration profiles presented above differ significantly from those measured during partial oxidation of methane for which almost constant gas composition was attained in the distributor zone (Olsbye et al., 1994; Mleczko & Wurzel, 1997). It is therefore assumed that thermodynamic equilibrium for partial oxidation is reached significantly faster compared to CO_2 reforming. As mentioned earlier it is concluded that CO_2 reforming itself is slower compared to its reaction rate during partial oxidation.

3.4. Effect of reaction conditions on catalytic performance

3.4.1. Effect of temperature

Temperature dependence of conversion was studied between 700 and 800°C. The methane : carbon dioxide ratio in the feed gas and the height of the bed amounted to 1 : 1 and $H_{mf} = 3$ cm ($m_{cat} = 106$ g). The partial pressure of nitrogen and the fluidization number amounted to 30 kPa and 7.5, respectively.

Upon increasing temperature from 700 to 800°C the conversions of methane and carbon dioxide rose from 29 to 77% and from 43 to 84% (see Fig. 9). Simultaneously, the yields of the selective products hydrogen and carbon monoxide increased from 25 to 73% for hydrogen and from 40 to 81% for carbon monoxide. In the investigated temperature range conversions and yields predicted by the thermodynamic equilibrium were not achieved. However, the deviations between experimental values and the ones predicted by thermodynamic equilibrium decreased with increasing temperature. At a temperature of 800°C these deviations amounted to 11% for X_{CO_2} and 17% for Y_{H_2}. Hydrogen selectivity also rose with increasing
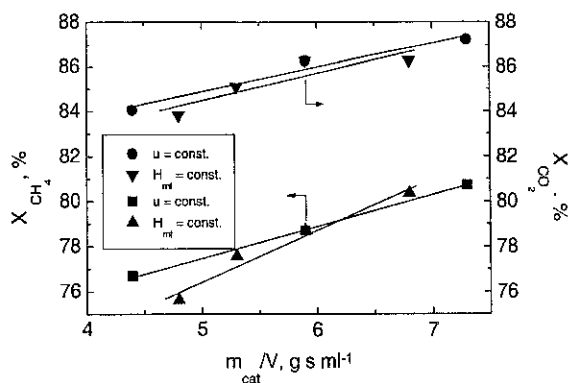
Fig. 9. Dependence of experimental (exp.) methane and carbon dioxide conversions and those predicted by thermodynamic equilibrium (eq.) on reaction temperature ($CH_4 : CO_2:N_2 = 1 : 1 : 0.86$, $u/u_{mf} = 7.5$, $H_{mf} = 3$ cm).

operature. These results indicate that the reaction is
letically controlled in the investigated range of reac-
n conditions.

'.2. Effect of hydrodynamic conditions

In order to investigate the influence of hydrodynamic
conditions on conversions and syngas yields contact time
s varied between 4.4 and 7.3 g s ml^{-1} by changing the
ght of the bed and the gas velocity. Fluidization num-
: was varied between 6.5 and 9.2 and the bed height
tween 3 and 5 cm (106.2–177.2 g cat.). Bed temperature
d methane-to-carbon dioxide ratio at the reactor inlet
counted to 800°C and 1, respectively.

As expected the conversions of methane and carbon
oxide strongly depended on contact time (see Fig. 10).
monotonous growth of conversions and yields was
hieved with increasing contact time. No significant
ference between conversions was observed when in-
:asing contact time by using higher beds or lower gas
locities. However, conversion was slightly less sensitive
changes of the contact time when this parameter was
luenced by varying the mass of catalyst than when
anging gas velocity. An increase of the contact time by
lucing the fluidization number e.g. by changing gas
locity results in smaller bubbles. This, in turn, reduces
: back-mixing of gas and improves mass transport
tween bubbles and the emulsion phase. Since the differ-
ces in the sensitivity of conversions to the changes of
: contact time did not differ significantly it can be
ncluded that in the investigated range of reaction con-
tions CO_2 reforming was not controlled by the inter-
iase gas exchange.

The finding that the reactor performance is not con-
olled by mass transfer limitation is another difference to
e partial oxidation of methane which confirms that the
tes of both reactions are significantly different. How-

ever, with respect to large-scale application mass transfer
limitation may become important. Simulations per-
formed for catalytic partial oxidation (Wurzel &
Mleczko, 1998) indicate that in an industrial-scale reac-
tor the rate of reforming reactions was limited by the
mass exchange between bubbles and the emulsion phase.
In turn, longer contact times are required in order to
achieve the same conversions as in the lab-scale reactor.
This difference was explained by a significant change of
the hydrodynamic conditions due to the formation of
larger bubbles; in the lab-scale reactor bubble size
amounted to approx. 0.5–1 cm (visually observed) where-
as bubble diameters up to 20 cm were calculated for an
industrial unit.

3.5. Simulation results

The conversions of methane measured in the station-
ary state were used for estimation of the frequency coeffi-
cients in the rate equations for the CO_2 reforming and
water–gas-shift reaction. These conversions were com-
pared with the ones by the previously presented model of
the fluidized bed. In this approach the estimated kinetic
parameters are biased by the uncertainty in the descrip-
tion of the bed hydrodynamics, i.e. the back-mixing and
inter-phase gas exchange. Because studies of the effect of
the contact time showed that the measured conversions
were not limited by the inter-phase gas exchange this
approach is justified. Additionally, the correlations used
for prediction of the bubble dynamics were verified in
cold-flow studies with the Ni/Al_2O_3 catalyst (Wurzel
& Mleczko, 1998).

The estimated frequency coefficients and their confi-
dence regions (based on a confidence number of 0.95) are
presented in Table 2. With the developed model the
measured conversions of methane and carbon dioxide
could be reproduced with an error lower than 10% (see
Fig. 11a). It has to be pointed out that all experimental
data points were below those predicted by thermo-
dynamics, i.e. the good accuracy of the model is not due
to the thermodynamic limitations. The validity of the
model was confirmed by good prediction not only of the
integral data but also of the concentration profiles (see
Fig. 11b). The concentrations calculated for the bubble
and emulsion phase follow the experimentally measured
concentrations. In line with the experimental findings
that the inter-phase gas exchange in a lab-scale
fluidized-bed reactor has only small influence on the
conversions the calculated gas composition in the emul-
sion phase differed only slightly from the one in the
bubble phase. Nevertheless, the better agreement of the
values predicted for the bubble phase with the concentra-
tions measured experimentally indicates that the pre-
dicted reaction rates are slightly underestimated. This
conclusion is also in agreement with the results presented
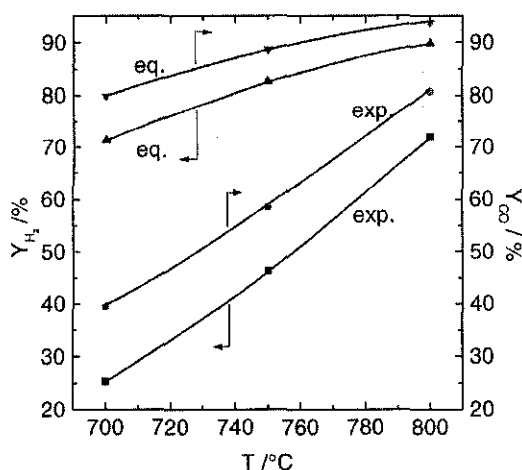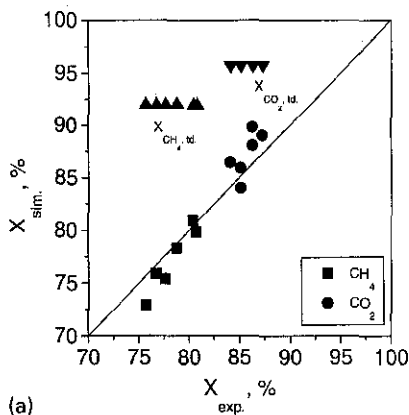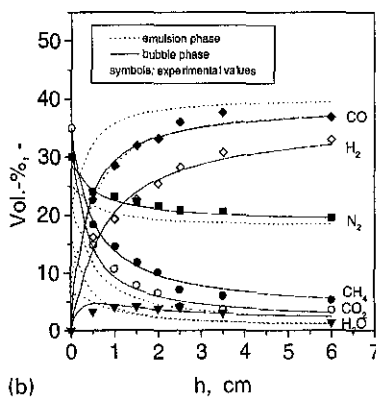in the parity plot. Thus, this model can be used as

g. 10. Effect of hydrodynamic conditions on methane and carbon
oxide conversions ($CH_4 : CO_2 : N_2 = 1 : 1 : 0.86$, $T_R = 800°C$,
$u_{mf} = 6.5$–9.2, $H_{mf} = 3$–5 cm).

(a)

(b)

11. Parity plot of experimental and simulated methane and carbon ide conversion (a) and (b) measured and calculated concentration iles (conditions see Fig. 2) during CO_2 reforming in a fluidized bed.

aluable tool for scaling-up of a fluidized-bed reactor dry reforming of methane.

Conclusions

Carbon dioxide reforming of methane was investigated a laboratory-scale (ID = 3, 5 cm) fluidized-bed reac-. The catalyst was well fluidizable and almost isother-l conditions were obtained over the whole range of ction conditions studied. Highest conversions and gas yields were achieved applying the following ction conditions: $T_R = 800°C$, $H_{mf} = 5$ cm, $u/u_{mf} = 8$, $m_{cat}/V_{STP} = 4.7$ g s ml^{-1}, $p_{CH_4} : p_{CO_2} : p_{N_2} = 1 : 1 : 2$. :thane and carbon dioxide conversion amounted to 90 l 93%, respectively. Hydrogen and carbon monoxide ld amounted to 81 and 90%, respectively; this corres-nds to a $H_2 : CO$ ratio of 0.9. On the basis of experi-ntal results a model of the fluidized-bed reactor for dry orming of methane was developed. This model, that s able to reproduce experimental conversions with an or of less than 10% can be used as a valuable tool for : reaction engineering studies of different reactor con-urations proposed for the title reaction (see e.g. leczko, Malcus & Wurzel, 1997).

It has been shown that the performance of the Ni/α-Al_2O_3 catalyst depended strongly on the oxidation state of the active component. Oxidized nickel sites showed a very low catalytic activity compared to the reduced, metallic ones; applying a reduced catalyst initial yields of carbon monoxide and hydrogen near the thermodyn-amic equilibrium were obtained, whereas the fresh unreduced catalyst exhibited significantly lower activity. With increasing time on stream a slow decrease of meth-ane conversion and syngas yield was observed. Carbon deposition was found to be responsible for the deactiva-tion of a highly active catalyst. After several hours on stream constant level of conversions and yields was achieved. This makes the significant difference in the deactivation behavior of the Ni/Al_2O_3 catalyst in the fixed-bed and the fluidized-bed reactor. Addition of water to the feedstock showed no significant influence either on catalyst regeneration or on conversions.

The in situ reduced catalyst yielded CH_4 and CO_2 conversions lower than predicted by the thermodynamic equilibrium. CO_2 reforming in the laboratory reactor was not influenced by inter-phase gas exchange. This conclusion was also drawn from simulations of the lab-scale unit which resulted in a good reproduction of the experimental data. With respect to the process commer-cialization the fluidized-bed reactor seems to be a suit-able reactor type. However, several serious problems like effect of pressure on the catalyst deactivation has to be investigated. Therefore, in the industrial-scale external catalyst regeneration might be necessary (Mleczko et al., 1997). Furthermore, the problem of metal dusting due to the high CO content in the reformed gas has to be taken into account with respect to the construction of the re-formed gas boiler (Grabke, Krajak, Müller-Lorenz & Strauß, 1996; Hohmann, 1996).

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lass transfer coefficient

atalyst density calculation
pie*(dp/2)^2*h
m/vo

inimum fluidization velocity
=(1/180)*Emf^3*dp^2/(1-Emf)*(ps-pg)*g/vi

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2=0.25 ;
=0.25 ;
2=0.15 ;
0.52 ;
10 ;
27 ;

2=(kco2-pch4*pco2)/(1+k1*pch4+k2*pco)*(1+k3*pco2)

ubble velocity
=0.006 ;
11.8 ;
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02 profile
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4.7 ;
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(1-fb)*gb*rco2/k

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=pie*(dp/2)^2*h
=m/vo

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= 0.237 ;
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emulsion phase
=(1-fb)*gb*rco2/k

 between 0 to 5
(rco2*gb*fb+k*dC)/(Ca*Ub*fb)

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