Application of random pore model for synthesis gas production by nickel oxide reduction with methane

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ABSTRACT

Recently, there is a great interest in the noncatalytic gas–solid reactions between methane, as an environmentally friendly reducing agent, and metal oxides to yield synthesis gas and the related metal at low temperatures. In the present work, reduction of nickel oxide with methane was investigated. It has been proven that it is possible to produce metallic nickel and synthesis gas, simultaneously. The thermogravimetry measurements and instantaneous mass spectrometry analysis of the gaseous products have been performed for the $NiO + CH_4$ reaction. In addition, the complete mathematical model was developed by applying the random pore model to predict the conversion–time profiles at the temperature range of 600–750 °C. Some important parameters such as concentration dependency, external mass transfer resistance, solid structural changes, product layer resistance, and pore size distribution have been considered in this sophisticated mathematical model. In addition, the random pore model has been modified for consideration of the bulk flow effect. Results obtained from this kinetic study indicate that the model performs well in predicting the experimental data. However by neglecting the bulk flow effect, there are lower predicted rate constants for this reaction. The analysis of the gaseous products showed that the synthesis gas could be produced with a H_2/CO ratio near two.

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1. Introduction

Natural gas is the basic raw material for manufacturing various petrochemical products. The main component of most natural gases is methane. Methane is a stable molecule and, therefore, petrochemical products must be prepared from methane via an intermediate material (synthesis gas path). Synthesis gas is directly used for production of methanol, hydrogen, acetaldehyde, acetic acid, ammonia, ethylene glycol and vinyl acetate. On the other hand, ammonia is used for production of ammonium nitrate and urea. Methanol is also a material for the production of dimethyl ether, methyl butyl ether, formaldehyde, acetic acid, methyl acetate and acetic anhydride. Moreover, synthesis gas can be used to produce liquid hydrocarbons ranging from naphtha to gas oil by Fischer–Tropsch reaction [1,2].

There are different processes for obtaining synthesis gas. It can be produced by steam reforming, partial oxidation, autothermal reforming, and dry reforming [3,4]. The catalyst of these processes is very sensitive to the coke formation. In general, excess steam is used to decrease the coke formation, but a lot of energy is needed [5]. In addition, the required heat of steam reforming reaction must

be supplied from furnaces, which produce a great amount of greenhouse gas. Finally, the H_2/CO ratio of steam reforming is very high (about five). The partial oxidation process has not yet been used commercially, since it involves premixing of CH_4 and O_2 which can be flammable or even explosive under elevated pressures and temperatures. This means that hotspots form near the beginning of the catalyst bed, due to highly exothermic oxidation reaction and create severe problems of safety and stability for the catalyst [6]. However, the H_2/CO ratio of this process is two, which is desirable for methanol production and Fischer–Tropsch reaction. In the autothermal method, there is an advantage of producing the required heat for endothermic steam reforming reaction internally by partial oxidation. Nevertheless, the oxygen separation unit from air is a costly plant. In the dry reforming reaction, the catalyst is deactivated more rapidly by coke deposition due to the absence of steam [7]. Coke may form on the catalyst surface and leads to the catalyst deactivation via pore blockage which is one of the major problems associated with dry reforming [8]. This reaction is more endothermic than steam reforming, and the H_2/CO ratio of this process is very low (lower than unity). However, the main advantage of the dry reforming method is the possibility for converting CO_2 greenhouse gas into petrochemical products.

Recently, there is a great interest in the noncatalytic gas–solid reactions between methane, as reducing agent, and metal oxides to yield synthesis gas and the related metal. In other words, the

Nomenclature

$a = C_A/C_{Ab}$ dimensionless gas concentration
$b = C_B/C_{B0}$ dimensionless solid concentration
C total gas concentration in the pellet (kmol/m^3)
C_A gas concentration in the pellet (kmol/m^3)
C_{Ab} bulk gas concentration (kmol/m^3)
C_B solid reactant concentration (kmol/m^3)
$C_{B0} = \rho_B/M_B$ initial solid reactant concentration (kmol/m^3)
D_{AK} Knudsen diffusivity (m^2/s)
D_{AM} molecular diffusivity of gas A in the pellet (m^2/s)
D_e effective diffusivity of gas A in the pellet (m^2/s)
D_{e0} initial effective diffusivity of gas A in the pellet (m^2/s)
D_p effective diffusivity of gas A in the product layer (m^2/s)
I the left hand side of Eq. (25) (where $I = \frac{C_{B0}(1-\varepsilon_0)}{S_0 \int_0^1 F(\eta)d\eta} \left[\frac{dX}{dt}\right]_{t\to 0}$)
k_m external mass-transfer coefficient (m/s)
k_s surface rate constant (m/s)
K equilibrium constant
K_{ad} adsorption constant (m^3/kmols)
L thickness of the pellet (m)
L_0 pore length per unit volume (1/m^2)
M_B molecular weight of solid reactant (kg/kmol)
M_D molecular weight of solid product (kg/kmol)
n reaction order
r pore radius (m)
$\bar{r}$ average pore radius of the pellet (m)
R^2 correlation coefficient

R_g gas constant (J/mol K)
S_0 reaction surface area per unit volume (1/m)
$Sh = k_m L/2D_{AM}$ Sherwood number for external mass transfer
$Sh^* = Sh(D_{AM}/D_{e0})$ modified Sherwood number
t time (s)
$\upsilon_0(r)$ pore volume distribution function (m^2/kg)
V_p total pore volume (m^3/kg)
$X(\theta)$ solid conversion at each time
z distance from the center of the pellet (m)
Z ratio of molar volume of solid product to solid reactant
$\alpha = v_C - 1$ bulk flow parameter
$\beta = 2k_s(1 - \varepsilon_0)/(v_B D_p S_0)$ product layer resistance
$\theta = k_s S_0 C_{Ab}^n t/[C_{B0}(1-\varepsilon_0)] = t/\tau$ dimensionless time
ε pellet porosity
ε_0 initial pellet porosity
$\delta = D_e/D_{e0}$ variation ratio of the pore diffusion
μ_g viscosity of the gas mixture (kg/m s)
$\eta = 2z/L$ dimensionless position in the pellet
v_B stoichiometric coefficient of the solid reactant
v_D stoichiometric coefficient of the solid product
ρ_B true density of the solid reactant (kg/m^3)
ρ_D true density of the solid product (kg/m^3)
$\phi = (L/2)(k_s S_0 C_{Ab}^{n-1}/v_B D_{e0})^{1/2}$ Thiele modulus for the pellet
ψ random-pore model parameter

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reduction of metal oxides by methane shows the potential for a new green technology of synthesis gas production without using any catalyst and its deactivation problem. Moreover, this process provides other advantages over the conventional coal-based technologies for metal oxides reduction. These preferences are the reduction of operating temperatures, decreasing the greenhouse gas production and, therefore, promoting environmentally friendly technologies [9]. For instance, the operating temperature of zinc oxide reduction can be decreased from about 1200 °C (industrial furnaces with coke) to about 900 °C with methane [10]. The process of using methane as a reducing agent for zinc oxide to produce metallic zinc and synthesis gas has been reported in recent works [10–12].

The gas–solid reaction between methane and the oxygen of the zinc oxide to yield synthesis gas is conducted at a relatively high temperature (about 900 °C), and therefore, it needs a large amount of energy [13]. To carry out the reduction at relatively lower temperatures, nickel oxide has been proposed. Nickel oxide is reduced at a lower temperature than other metal oxides like zinc oxide and iron oxide [14].

The produced metal from the above mentioned noncatalytic gas–solid reactions can be used directly, or in a looping system as an energy carrier. In a chemical-looping system, the oxygen carrier circulates between two reactors. In the air reactor, the metal is oxidized with O$_2$ from the combustion air and it produces heat, whereas there is not any greenhouse gas. In the fuel reactor, the metal oxide is reduced by methane as a fuel [15]. The reduction can be complete to produce CO$_2$ and H$_2$O in a chemical-looping combustion (CLC) process, where CO$_2$ is separated simply after cooling. On the other hand, the main goal in the partial reduction or chemical-looping reforming (CLR) system is production of CO and H$_2$ or synthesis gas.

An important aspect to be considered in a chemical-looping reforming system is the heat balance. The oxidation reaction of the metal oxide is very exothermic; however, the reduction reactions are endothermic. Therefore, the heat for the endothermic reduction reactions is given by the hot circulating solids coming from the air reactor at higher temperatures. The heat generated in the air reactor is enough to fulfill the heat balance in the system [16]. In this case, NiO as the oxygen carrier appears more interesting than other alternatives for looping systems due to its high reaction rate, good selectivity, and cyclic reaction ability [17,18].

Because of the special significance of noncatalytic gas–solid reactions, the accurate prediction of their behavior can provide a basic knowledge for a proper reactor design. Many models have been used to describe the conversion–time profiles of noncatalytic gas–solid reactions in the literature. These models consist of shrinking unreacted core model for nonporous solids, and volume reaction model, grain model, modified grain model, and random pore model (RPM) for the porous solids [19].

The ratio between molar volumes of the solid product and the solid reactant is an important parameter and is expressed as *Z*. Since in many gas–solid reactions *Z* is not equal to unity, significant structural changes occur during the reaction [20]. Among the mentioned models, the modified grain model and RPM can consider this important structural effect. On the other hand, the modified grain model does not take into account the pore size distribution of the solid reactant, whereas in the RPM, a parameter is defined based on the pore size distribution function which is directly used in the differential equations [21,22].

Many works have been performed to determine the kinetics of supported nickel oxide reduction by methane in the area of chemical looping. The reduction of Ni–NiO supported on NiAl$_2$O$_4$ as oxygen carrier and methane as the fuel (reducing agents) has been investigated by Readman et al. [23]. Based on their research, the reduction started rapidly. When most of the NiO has been reduced to nickel, the rate of reduction levels off due to diffusion restriction that becomes the rate-limiting factor. The reaction order observed in this study was slightly less than unity.