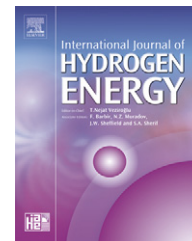


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Some issues in modelling methane catalytic decomposition in fluidized bed reactors

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ARTICLE INFO

Article history:

Received 29 March 2007

Received in revised form

4 January 2008

Accepted 23 March 2008

Available online 12 May 2008

Keywords:

Methane catalytic decomposition

Fluidized bed reactor

Hydrogen production

Attrition phenomena

ABSTRACT

This paper reports a model of fluidized bed thermo-catalytic decomposition (TCD) of methane. The novelty of the model consists of taking into account the occurrence of different competitive phenomena: methane catalytic decomposition, catalyst deactivation due to carbon deposition on the catalyst particles and their reactivation by means of carbon attrition. Comparison between theoretical and experimental data shows the capability of the present model to predict methane conversion and deactivation time during the process. The model demonstrates to be also a useful tool to investigate the role played by operative parameters such as fluidizing gas velocity, temperature, size and type of the catalyst. In particular, the model results have been finalized to characterize the attrition phenomena as a novel strategy in catalyst regeneration.

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1. Introduction

The thermo-catalytic decomposition (TCD) of methane is an attractive process towards the production of hydrogen with reduced CO₂ emissions [1–3]. The use of a catalyst is extremely advantageous since the non-catalytic thermal decomposition would require elevated process temperatures, i.e. above 1200 °C [1,2]. Fluidized beds have been indicated in the last years as an efficient reactor solution for TCD process compared to fixed bed reactors [1–5]. Consequently, new criteria have to be taken into account for catalyst design. In particular, a suitable catalyst should be characterized by a low propensity to attrition in addition to the requirements of high thermal stability and conversion efficiency [6].

Catalytic systems containing Ni [7,8] and Fe [9,10] have been largely tested in the past. The Ni-based catalysts have a maximum operative temperature of 600 °C. As a consequence, methane conversion being thermodynamically limited at this temperature, concentrated hydrogen streams (H₂ > 60%) can-

not be obtained using nickel-based catalysts [6]. On the contrary, Fe-based catalysts are more stable at higher temperatures in the order of 700–1000 °C, but deactivation occurs upon repeated cycles, resulting in a short lifetime [6]. In addition, whatever the catalyst, deposited carbon generally has a filamentous shape, i.e. nanofibres or nanotubes, with metal particles on their tips. This is an undesirable feature with reference to applications in fluidized bed reactors where attrition is likely to remove the active metal phase away from the support, resulting in a decrease in hydrogen production and in an increase in consumption of metals [2].

Muradov et al. [1–3] have investigated the feasibility of using both activated carbon and carbon black as catalysts for methane decomposition in fluidized beds. They pointed out that the process is more advantageous than that involving a metal catalyst: low cost, high temperature resistance and tolerance to potentially harmful compounds. On the other hand, the drawbacks are: (i) the poor catalytic activity of carbon in comparison with metal catalyst; (ii) the carbon

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| Nomenclature | | | |
|--------------|--|-----------------------|---|
| a | catalyst specific surface area, m^2/g | S_2^i | internal catalyst surface occupied by deposited carbon, m^2 |
| c_o | inlet methane concentration, mol/m^3 | t | time, s |
| c_b | methane concentration in the bubble phase, mol/m^3 | t_d | deactivation time, s |
| c_e | methane concentration in the dense phase, mol/m^3 | T | temperature, K |
| d_{b0} | bubble diameter just above the distributor, m | U | fluidizing gas velocity, m/s |
| d_{bm} | maximum bubble diameter, m | U_b | rise velocity of bubbles through the bed, m/s |
| d_b^* | effective bubble diameter at x^* , m | U_{br} | rise velocity of isolated bubbles, m/s |
| d_c | catalyst particle diameter, m | U_{mf} | minimum fluidization velocity, m/s |
| d_p | mean pore diameter of a catalyst particle, nm | v | generic input variable, a.u. |
| D | mean methane diffusivity, m^2/s | V_c | volume of a catalyst particle, m^3 |
| D_{CH_4} | methane diffusivity, m^2/s | W_c | amount of carbon deposited on the external surface of all bed particles, g |
| D_{eff} | methane bulk diffusivity, m^2/s | w_c^e | amount of carbon deposited on the external surface of a catalyst particle, g |
| D_k | methane Knudsen diffusivity, m^2/s | w_c^i | amount of carbon deposited on the internal surface of a catalyst particle, g |
| D_r | bed diameter, m | x | distance above the distributor, m |
| E_1 | catalyst activation energy, J/mol | x^* | distance above the distributor corresponding to the calculation of d_b^* , m |
| E_2 | deposited carbon activation energy, J/mol | y_{Cu} | copper mass fraction of catalyst particles, g/g |
| E_c | carbon elutriation rate, g/s | z | generic output variable, a.u. |
| h_{cd} | thickness of the carbon deposits, nm | | |
| H | bubbling fluidized bed height, m | | |
| H_{mf} | static bed height, m | | |
| k_1 | surface intrinsic kinetic constant of the catalyst, $m^3/(m^2s)$ | Greek symbols | |
| k_1^0 | catalyst frequency factor, $m^3/(m^2s)$ | ε | fractional change in volume of the system between no conversion and complete conversion of methane, – |
| k_2 | surface intrinsic kinetic constant of the deposited carbon, $m^3/(m^2s)$ | ε_c | porosity factor of a catalyst particle, – |
| k_2^0 | deposited carbon frequency factor, $m^3/(m^2s)$ | ε_{mf} | void fraction in the bed at minimum fluidization condition, – |
| k_a | carbon attrition constant, m^{-1} | ρ_b | bulk density of bed of catalyst particles, g/m^3 |
| k_g | mass transfer coefficient outside the particle, m/s | ρ_c | apparent catalyst density, g/m^3 |
| k_p | apparent reaction constant per volume of catalyst particle, s^{-1} | τ | tortuosity factor of a catalyst particle, – |
| k_p^e | apparent external reaction constant per volume of catalyst particle, s^{-1} | τ_g | mean gas residence time, s |
| k_p^i | apparent internal reaction constant per volume of catalyst particle, s^{-1} | Dimensionless numbers | |
| K_{be} | overall coefficient of gas interchange between bubble and dense phase, s^{-1} | Da | Damköhler number |
| K_{bc} | coefficient of gas interchange between bubble and cloud-wake region, s^{-1} | e_{td} | model relative error of deactivation time |
| K_{ce} | coefficient of gas interchange between cloud-wake region and dense phase, s^{-1} | e_{x_i} | model relative error of initial methane conversion |
| M_C | carbon molecular weight, g/mol | e_{x_r} | model relative error of residual methane conversion |
| M_{Cu} | copper molecular weight, g/mol | Re_{mf} | Reynolds number at minimum fluidization condition |
| M_{CH_4} | methane molecular weight, g/mol | Sc | Schmidt number |
| M_{H_2} | hydrogen molecular weight, g/mol | Sh | Sherwood number |
| N_c | number of catalyst particles, – | S_z | sensitivity of a generic output variable |
| P_C | carbon production rate, g/s | X | methane conversion |
| P_{H_2} | hydrogen production rate, g/s | X_{be} | index of gas exchange between bubbles and dense phase |
| S_{cd} | surface of catalyst particle occupied by deposited carbon per carbon mass, m^2/g | X_i | initial methane conversion |
| S^e | total external surface of a catalyst particle, m^2 | X_r | residual methane conversion |
| S^i | total internal surface of a catalyst particle, m^2 | β | fluidization velocity excess with respect to the fluidizing gas velocity |
| S_1^e | external active surface of a catalyst particle, m^2 | Θ | Thiele number |
| S_1^i | internal active surface of a catalyst particle, m^2 | η | effectiveness factor of a catalyst particle |
| S_2^e | external catalyst surface occupied by deposited carbon, m^2 | | |

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