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Structured reactor with a monolith catalyst fragment for kinetic studies The case of CH_4 partial oxidation on LaNiPt-catalyst

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ABSTRACT

Analysis of the behavior of a structured reactor of small scale has been fulfilled at millisecond contact times and high temperatures. A single channel fragment of corundum honeycomb substrate with supported LaNiPt active component has been tested in partial oxidation of methane as a model reaction at high gas velocities. Rather high rates of mass transfer are achieved for the conditions under study and the regions are defined with the operation mode where chemical kinetics is rate-controlling. The numerical analysis allows contribution of the direct route of methane oxidation into synthesis gas to be evaluated and some kinetic parameters of main reactions to be estimated.

Suggested design of the lab-scale reactor with separate one-channel structural element of a real monolithic catalyst is shown to be promising for kinetic studies under severe conditions.

1. Introduction

Development of gas-to-liquid technologies and use of fuel cells for the energy generation require elaboration of safe and efficient catalytic processes such as hydrocarbons transformation into the synthesis gas (syngas). The catalytic partial oxidation of methane (POM) could be used for the small-scale and distributed production of syngas in the stationary and mobile fuel processing units [1–3]. This process can also be integrated into the stage combustors of methane for gas turbines wherein methane is partially oxidized in a fuel-rich combustor followed by a fuel-lean combustion [4]. In view of such applications, realization of the process at high gas velocities and contact times less than 0.1 s is a promising route to miniaturize the reactors, which determines the use of monolithic catalysts with a high surface to volume ratio and a low pressure drop [5–7].

Among the challenging problems for developing new catalytic systems and their engineering implementation, the investigation of process kinetics under relevant experimental conditions is one of the main issues due to diffusional limitations and noticeable temperature gradients. Investigating very fast and energy-intensive processes such as catalytic combustion of methane and POM, researchers encounter serious problems related to laboratory fixed-bed reactors wherein the large pressure gradients prevent the use of high flow rates. Under relevant conditions, the external mass transfer limitations and marked temperature gradients can hardly be avoided (see review by Groppi et al. [8]).

The kinetic study of very fast processes realized at high temperatures over monolithic catalysts is rather complicated task which demands elaboration of special structured reactors of small scale operating at high flow velocities with a minimum impact of mass transfer, pressure drop, and temperature gradients along the catalyst length.

Many studies were performed to solve these problems. Previous studies of POM were carried out over the multichannel samples of honeycomb monolithic catalysts [9–12]. For example, the POM kinetic study was performed over the Pt- or Rh-supported monoliths of 9 mm diameter when only four channels were exposed to the gas stream [9,10]. Nickel-supported honeycomb catalysts of 16 mm diameter with 52–64 cells/cm^2 were studied by Lezaun et al. [11]. The experimental and numerical study of the transient behavior of POM was carried out on Rh/α-Al_2O_3 monolith with diameter of 10 mm composed of 24 channels with triangular cross-section [12]. However, only application of different types of microchannel catalytic reactors allows studying the reaction kinetics of fast and strongly exothermic reactions (POM, CH_4 combustion) at short contact times under relevant conditions [1,8,13–18].

A laboratory reactor with flat thin Pt gauze was developed for studying the reactions involved into POM at millisecond contact times [1]. To deal with the problems of kinetic studies at high temperatures and flow rates, a structured annular micro-reactor

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Nomenclature

c_i, c_i^s	current concentration of the ith component of the reaction mixture and on the catalyst surface, volume fraction
c_{i0}	concentration of the ith component of the reaction mixture at the channel inlet, volume fraction
D_m	molecular diffusivity of methane (cm^2/s)
d	hydraulic diameter of the channel (cm)
E_j	activation energy of the jth reaction (J/mol)
k_j	constant of the jth reaction rate (s^{-1})
k_{j0}	pre-exponent of the jth reaction rate constant (s^{-1})
$K_{eq,j}$	equilibrium constant of the jth reaction
l	axial coordinate along the channel length (cm)
r_j	rate of the jth reaction ($mol/(cm^3 s)$)
r_i^c	rate of the ith component transformation ($mol/(cm^3 s)$)
R	the universal gas constant (J/(mol K))
S_{sp}	special outer surface of the channel (cm^2/cm^3)
Sh	local Sherwood number
T	temperature (K)
U	superficial gas velocity (cm/s)
z^*	dimensionless axial coordinate

Greek letter

β	local mass transfer coefficient at the channel wall (cm/s)

Subscripts

i	number of the compound of the reaction mixture (i = 1 corresponds to methane; 2, oxygen; 3, carbon oxide; 4, hydrogen; 5, carbon dioxide; and 6, water)
j	number of the reaction, j = 1,2,3,4
∞	asymptotic value at the infinity

consisting of a ceramic tube coated with a small amount of a catalyst was developed [13]. The characterization of the behavior of annular reactor for kinetic measurements was done in [8,14] addressing a deeper understanding of the reactor potentialities. Detailed theoretical and experimental studies of the annular reactor performance demonstrated its adequacy for kinetic investigation of ultra-fast catalytic reactions such as CH_4 partial oxidation and methane or CO combustion [15–17].

Recently, we have studied POM at millisecond contact times on the catalysts based on mixed $MeCeZrO_x$ solid solution promoted by Pt and/or Ni and supported on separate structured elements of the monolithic substrates of different types such as the fragments of ceramic honeycomb monolith with one triangular channel, the gauze rolls, and the wire spiral placed into a thin quartz tube reactor [18,19].

This work aims at detailed analysis of the performance features of a structured reactor with a monolithic $LaNiPt/CeZrO_x$-catalyst based on a honeycomb α-Al_2O_3 support with triangular channels. The results of the first stage of experimental and numerical studies of the reaction of methane partial oxidation in the tube reactor with a separate catalytic fragment with one channel at 4–15 ms contact times are reported below. The studies are focused on the resources of lab-scale reactor of suggested design for kinetic measurements. Mass transfer rates are defined and the reactor potentialities for kinetic studies of fast and highly exothermic reactions are shown.

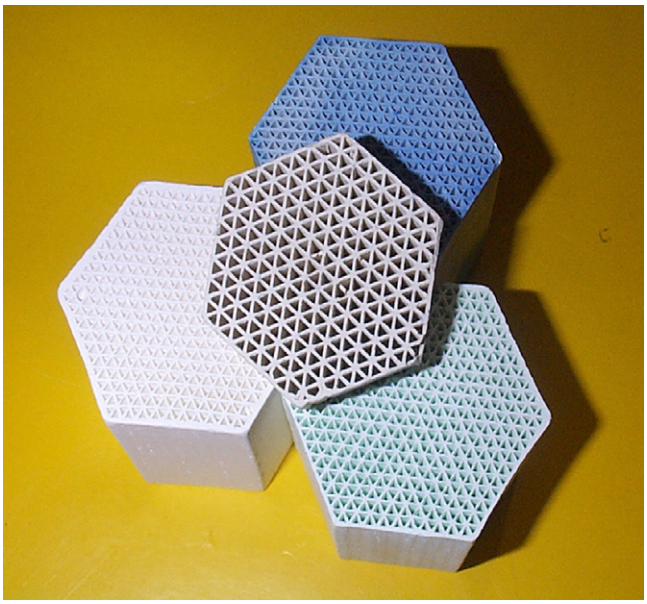

Fig. 1. Samples of monolithic catalyst based on a honeycomb α-Al_2O_3 support with triangular channels.

2. Experimental

2.1. Catalyst preparation

As supports, separate triangular fragments of α-Al_2O_3 monolith (the specific surface area of 3 m^2/g) sintered at 1300 °C, with the wall thickness of 0.2–0.3 mm, the side of the inside triangular channel of 2.3–2.5 mm, and the length of 10–20 mm were used. $Zr_{0.8}Ce_{0.2}O_2$ (10 wt%) and $LaNi_{0.9}Pt_{0.1}O_x$ (7 wt%) were supported by the incipient wetness impregnation first with the mixed solution of $Ce(NO_3)_3$ and $ZrOCl_2$ and then, with the mixed solution of La and Ni nitrates and H_2PtCl_6. After each impregnation, the samples were dried and calcined at 900 °C in air. According to the previous study [20], the $LaNiO_3$ perovskite phase of the hexagonal structure and $Zr_{0.8}Ce_{0.2}O_2$ solid solution are present in the catalysts.

The shape and structure of the catalyst fragments prepared in such a way correspond completely to those for the real catalytic monolith shown in Fig. 1.

2.2. Reactor unit

The testing of the catalysts was carried out in a quartz tube reactor of 4–6 mm inner diameter and 40 cm length. Schematic drawing of the reactor unit is given in Fig. 2. The catalyst fragment with one channel was placed into the quartz tube reactor, and the space between the catalyst and the reactor wall was sealed up with α-Al_2O_3 fiber, so that the reaction mixture went only through the inner channel volume. The quartz tube was placed in the two-zone 30 cm long electric oven. The first part of the oven heated up the gas reactant mixture supplied to the catalyst. The coiled fechraloy gauze was installed in the reactor at 2 cm distance from the channel inlet to provide more effective preheating of the feed. Another part of the oven kept a prescribed reaction temperature. There were two thermocouples to determine the temperature of ovens, and two more thermocouples at the front and rear edges of the channel were used to measure the catalyst temperature. To decrease the heat losses, thin (0.1–0.2 mm diameter) chromel–alumel thermocouples were used. The temperatures of the catalyst and the oven were controlled and continuously monitored by an "ADAM" unit.