A combination of silicon carbide and zirconia open cell foams coated with 3% Pd/Co_3O_4 as structured catalysts for the lean combustion of methane

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Abstract

Different combinations of ceramic open cell foams (OCF) made of silicon carbide (SiC) and zirconia (Zir) coated with 3 wt.% Pd/Co_3O_4 as the active phase, were studied as structured catalysts for the combustion of CH_4 in lean conditions (inlet CH_4 concentration: 0.5 and 1 vol.%). The catalytic activity of the structured catalysts was tested at different weight hourly space velocities, with an excess of oxygen. Among the various combinations tested, the reactor made of 1.5 cm SiC + 1.5 cm Zir (1.5SiC/1.5Zir) showed the best catalytic performance, thanks to the different thermal conductivity of the OFC used.

Keywords: process intensification; thermal conductivity; methane emissions; catalytic oxidation; low temperature.

1. Introduction

The greenhouse effect is one of the leading causes of global warming.[1] Greenhouse gases (GHG) such as carbon dioxide (CO_2), methane (CH_4), chlorofluorocarbons (CFCs) and nitrous oxide (N_2O) are the main responsible for greatly warming the surface of the Earth.[2] CH_4 is the most powerful GHG after CO_2, and contributes to 14% of the overall GHG emissions.[3] CH_4 emissions come primarily from human activities such as industry, energy, agriculture, and waste process sectors. Even though it occurs in lower concentrations than CO_2 (usually 1 vol.% or lower), CH_4 produces 20 times as much warming as CO_2.[1-3] Reducing CH_4 emissions is a powerful step to slow-down global warming, which can lead to multiple economic and climate change benefits as well as public health and safety.[3]

Catalytic oxidation of CH_4 is one of the most promising technologies to mitigate CH_4 emissions. For this purpose, Pd-based catalysts supported on simple metal oxides, or mixed metal oxides (such as spinels or perovskites), have been extensively studied in form of powder catalysts.[4,5]

Nowadays, there has been an increased interest in the use of ceramic open cell foams (OCF) as supports for catalysts to be used in combustion, reforming, and after-treatment systems for pollutant emissions control, thanks to their remarkable heat and mass transfer characteristics.[5] OCF combine the advantages of foams, such as high porosity (which leads to low pressure drop at high flow velocities) and high geometric surface area (that improves mass transfer properties increasing the effectiveness factors and enhancing radial convection), with the superior thermal and mechanical properties of ceramic materials. These properties lead to important improvements with respect to conventional structured supports (e.g., monoliths and packed beds) for high temperature and exothermic reactions, such as catalytic combustion reactions.[5,6]

2. Experimental

We investigated a combination of a series of ceramic OCF made of silicon carbide (SiC) and zirconia (Zir), 30 pore per inch, as ceramic supports for 3 wt.% Pd/Co_3O_4 used as a catalyst towards the lean combustion of CH_4. The carrier of the catalytic active phase, Co_3O_4, was coated on OCF by solution combustion synthesis (SCS), while the catalytic active phase, Pd, was deposited on the carrier by wetness impregnation (WI). This catalyst was chosen based on our previous studies.[5] Considering the different thermal conductivity values of SiC (0.4 W m^{-1} K^{-1}) and Zir (0.027 W m^{-1} K^{-1}), volumetric heat transfer coefficients across the coated OCF were estimated at different superficial velocities and temperatures. Then, based on the preliminary results obtained testing each single foam-based catalyst, a series of tests towards the combustion of CH_4 in lean conditions was conducted by using a combination of the two supports. Specifically, OCF were placed in the reactor facing SiC at the inlet and Zir at the outlet, and varying the length of each of them, but maintaining constant the overall length at 3 cm (1 cm SiC + 2 cm Zir; 1.5 cm SiC + 1.5 cm Zir; 2 cm SiC + 1 cm Zir). During the tests, the reactor was fed with 100, 200, and 300 NmL min^{-1} (equivalent to a weight hourly space velocity, WHSV, of 30, 60, and 90 NL s^{-1} g_{cat}^{-1}, respectively) of a gaseous mixture containing 1 and 0.5 vol.% CH_4 in nitrogen, with an excess of oxygen (O_2/CH_4 molar ratio of 8).

3. Results and discussion

Heat management is a fundamental aspect of adiabatic or quasi-adiabatic systems, as the system analyzed in this study. Among all the combinations of ceramic OCF made of Zir and SiC (1SiC/2Zir; 1.5SiC/1.5Zir; 2SiC/1Zir), the best catalytic performance toward CH_4 combustion was obtained for the 1.5SiC/1.5Zir combination, whose T_{50} (temperature of 50% CH_4 conversion) varied from 190 to 373 °C from 30 to 90 WHSV, feeding 1 vol.% CH_4 as inlet concentration (**Fig. 1A**). Lower T_{50} were recorded feeding 0.5 vol.% CH_4 as inlet concentration. With the other SiC/Zir reactor combinations (**Fig. 1B**), the recorded T_{50} worsen at all WHSV. The presence of SiC OCF in the right length at the inlet of the reactor, where the reaction starts and the heat produced is still negligible because of the low conversion of CH_4, helps to retain the heat of reaction and consequently provide the necessary energy for boosting the ignition of the first reacting molecules on the surface of the OCF.[7] While Zir OCF at the outlet of the reactor, where the conversion of CH_4 close to its maximum, maintains a stable thermal behavior, thanks to the low thermal conductivity value, favoring the removal of the heat of reaction by convection, without influencing the thermodynamics of the exothermic reaction of combustion.

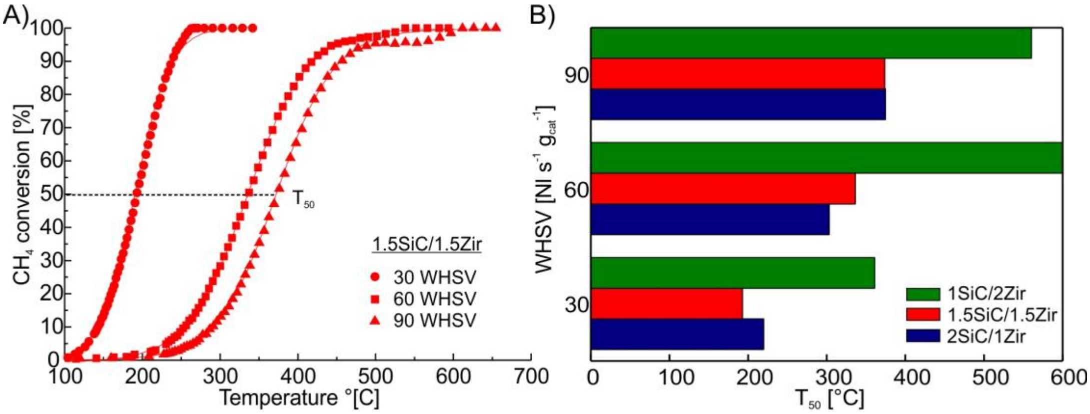

Figure 1. **A)** CH_4 conversion for the reactor combination 1.5SiC/1.5Zir, tested at three different WHSV. **B)** T_{50} of the three reactor combinations, tested at three different WHSV (1 vol.% CH_4 as inlet concentration).

4. Conclusions

The aim of this work is to arrange an optimal catalytic system towards the lean combustion of methane able to work at low temperature. The best results were obtained by placing first a catalytic SiC OCF at the beginning of the reactor (to favor the ignition of the reaction, that is, the kinetics, especially at high WHSV), followed by a catalytic Zir OCF to favor then the thermodynamics of the reaction.

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