Partial Oxidation of Methane to Syngas over Nickel Monolithic Catalysts

Yunhua Li, Yaquan Wang, Xuebin Hong, and Zhaoguang Zhang
Key Laboratory of Green Chemical & Technology, School of Chemical Engineering and Technology,
Tianjin University, Tianjin 300072, P.R. of China

Zhiping Fang, Yu Pan, Yanbo Lu, and Zhongqi Han
Science & Technology Development Center, China Petroleum & Chemical Corporation (SINOPEC),
Beijing 100029, P.R. of China

DOI 10.1002/aic.11016

Keywords: metallic nickel monolithic catalysts, methane, partial oxidation, ceria, zirconia

Introduction

In recent years, catalytic partial oxidation of methane (POM) has widely been investigated as a potential alternative process to steam reforming since the instantaneous reaction is mildly exothermic and can lead to the formation of synthesis gas with hydrogen to carbon monoxide ratio suitable for Fischer-Tropsch, methanol synthesis, and so forth.[1–6] Up to now, most laboratory studies on POM have been conducted in fixed-bed microreactors. In these processes, hot-spot formation can lead to severe catalyst deactivation. Schmidt and coworkers studied a novel monolithic reactor.[4,5] Using this kind of reactor, the reaction can be operated at high gas hourly space velocity (GHSV) and autothermally with no external furnace being required. The results showed that the monoliths coated with Pt, Rh, and Ir were very active and selective for POM reaction. Ni coated monolith showed similar conversion and selectivities to Rh, but rapid deactivation occurred due to carbon deposition and/or metal loss at high temperature.[5]

Supported Ni catalysts, such as Ni/Al_2O_3[7] and Ni/TiO_2,[8] have high catalytic activity at high GHSV in the fixed-bed reactor. However, deactivation occurs quickly. Recently, it has been reported that the incorporation of zirconia into ceria as the support for Pt and Ni catalysts not only significantly improved the stability of the catalyst, but also increased the methane oxidation rate due to its redox properties.[9,10]

We studied the methane partial oxidation over metallic Ni monolith prepared with nickel spheres at high GHSV.[11,12] The results showed that the metallic Ni monolith catalysts can avoid suffering from the disadvantages of supported nickel or nickel coated monolithic catalysts, but the catalytic activity and selectivity were low and far away from thermodynamic equilibrium values.

In the present work, we prepared a metallic Ni monolith with nickel sponge, followed by acid treatment to increase the specific surface area, and further promoted it with ceria and zirconia. The purpose of the present work is to obtain catalysts that are stable and, at the same time, have high conversion of methane and high selectivities to hydrogen and carbon monoxide, with the values being near to those of thermodynamic equilibrium.

Experimental

Catalyst preparation

The Ni monolith was prepared as follows: Ni metallic sponge (80% porosity, Changsha Liyuan Material Co., Ltd.) was cut into 40-60 mesh and packed in an i.d. 10 mm quartz tube with α-Al_2O_3 foams at the front and back. In the presence of hydrogen, the temperature was increased at 1 K/min from ambient temperature to 1473 K, kept at the final temperature for 6 h, and then cooled down to ambient temperature. The monolith obtained was treated with a mixture of 500 cm^3 0.01 wt. % HCl and 500 cm^3 0.2 wt. % H_2SO_4 for 24 h, then thoroughly washed with distilled water and dried. The physical properties of the Ni monolith are listed in Table1.

For the ceria and zirconia promoted Ni monolith, the Ni monolith prepared as above was impregnated with appropriate amounts of $Ce(NO_3)_3$ and $Zr(NO_3)_3$. The catalyst was dried overnight in an oven at 398 K and calcined in a muffle

---

Correspondence concerning this article should be addressed to Y. Wang at yqwang@tju.edu.cn.

Table 1. Summary of Physical Properties of Catalysts

Catalysts	BET Surface Area (m^2/g)	Packing Density (g/cm^3)	Pore Size (μm)	Weight Loading[a] (wt.%) Ce	Zr
Ni monolith	0.20	1.10	40–100	0	0
Ce-Zr/Ni monolith	4.27	1.00	4–100	0.9	1.8

[a] Analyzed by ICP.

furnace at 873 K for 5 h. This catalyst is referred to as Ce-Zr/Ni monolith. The physical properties of the Ce-Zr/Ni monolith are also listed in Table 1.

Experimental procedures

The partial oxidation reaction was conducted at atmospheric pressure in a quartz reactor inside an electric furnace, which could be moved to different positions. The monolith, with diameter of 10 mm and length of 7 mm together with two extruded ceramic monoliths with straight channels at the front and back, was sealed in the reactor by silica alumina cloth. A chromel-alumel thermocouple in a thermocouple well was introduced through the front ceramic monolith to the front edge of the monolith to measure the inlet temperature. When the reactant gases of CH_4 (99.8%) and O_2 (99.9%), controlled by mass flow controllers, were passed through the reactor, the reaction was lighted off with the electric furnace. Then the furnace was moved to the front of the reactor to control the inlet temperature of the gas stream, and the outside of the monolithic catalyst was wrapped with temperature insulation materials to prevent heat loss.

Reaction products were analyzed by a 3420 Gas Chromatograph with two columns, one for the separation of H_2, O_2, CH_4, and CO, another for the separation of CO_2, and a TCD detector. Quantification of the species in the effluent was performed by injection of a gas mixture with known composition for calibration.

Results and Discussion

Changes of CH_4 conversions and H_2 and CO selectivities on the Ni monolith and Ce-Zr/Ni monolith with the CH_4/O_2 ratios, GHSV, and inlet temperatures are shown in Figures 1, 2, and 3, respectively. Methane conversion decreased while selectivities to hydrogen and carbon monoxide increased slightly with the increase of the CH_4/O_2 ratio on both the Ni monolith and the Ce-Zr/Ni monolith, as shown in Figure 1. It is generally accepted that the partial oxidation of methane on nickel catalysts proceeds through an indirect reaction mechanism, that is, total oxidation of a portion of methane followed by steam and CO_2 reforming of the remaining methane.[10,13,14] The decrease of the oxygen content in the feed leads to the combustion of less methane, but leaves relatively more methane for the reforming reactions. Therefore, the conversion of methane drops, but the selectivities to syngas rise with the increase of the CH_4/O_2 ratio. Methane conversion and selectivities to syngas, especially the selectivity to H_2, on the Ce-Zr/Ni monolith are much higher than those on the Ni monolith under the same reaction conditions. For example, on the Ce-Zr/Ni monolith, at inlet temperature 1123 K, GHSV 1.0×10^5 h^{-1}, and CH_4/O_2 ratio 2.0, the conversion of methane and the selectivities to hydrogen and carbon monoxide are 94%, 98%, and 96%, respectively, much higher than those on the Ni monolith catalyst, which are 84%, 92%, and 94%, respectively.

Methane conversion and selectivities to syngas did not change appreciably with the increase of GHSV on both the Ni monolith and the Ce-Zr/Ni monolith, as shown in Figure 2. With the increase of GHSV, the reactants increased in the feed. However, the methane conversion would not decrease because all the oxygen was consumed, that is, no oxygen breakthrough was found in the range of the GHSV studied. At the same time, the total oxidation of more methane at high GHSV released more heat and could cause more reformings of the remaining methane. That might be why the methane conversion and the selectivities to syngas did not change appreciably with the increase of GHSV. On the Ce-Zr/Ni monolith catalyst, the methane conversion and the selectivities to H_2 and CO are higher than those on the Ni monolith, as shown in Figure 2. This will be explained below.

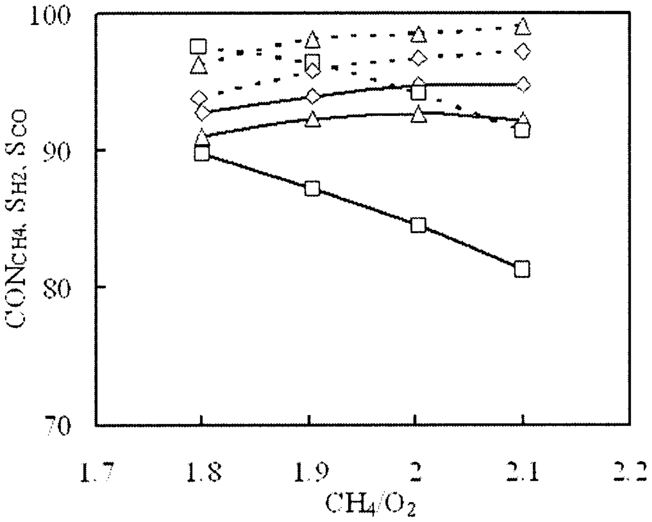

Figure 1. Comparison of CH_4 conversions and H_2 and CO selectivities between Ni monolith and Ce-Zr/Ni monolith at different CH_4/O_2 ratios.

(□) methane conversion; (Δ) H_2 selectivity; (◇) CO selectivity; (solid lines) the Ni monolith and (dashed lines) Ce-Zr/Ni monolith. Reaction conditions: Temperature = 1123K, GHSV = $1.0 \times 10^5 h^{-1}$.

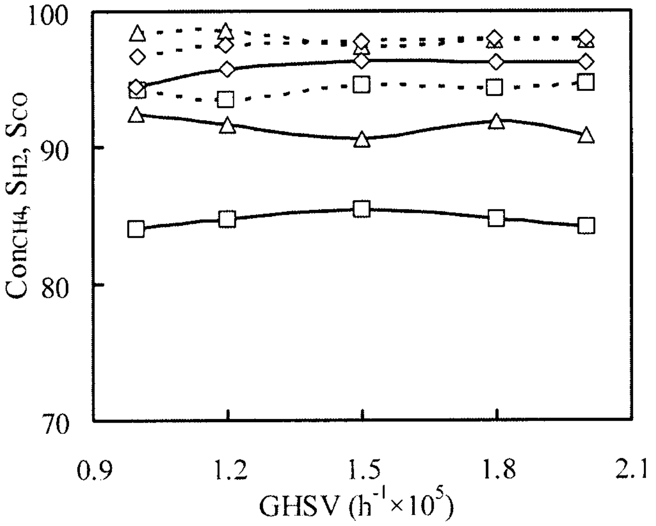

Figure 2. Comparison of CH_4 conversions and H_2 and CO selectivities between Ni monolith and Ce-Zr/Ni monolith at different GHSV.

(□) methane conversion; (Δ) H_2 selectivity; (◇) CO selectivity; (solid lines) the Ni monolith and (dashed lines) Ce-Zr/Ni monolith. Reaction conditions: Temperature = 1123K, $CH_4/O_2 = 2.0$.

Methane conversion as well as selectivities to syngas increased with the increase of temperature over both the Ni monolith and the Ce-Zr/Ni monolith (Figure 3). The increase of the reaction temperature promoted both the methane combustion and the methane reforming reactions. However, it has more effect on the latter endothermic reactions. Hence, the methane conversion and the selectivities to syngas increased with the increase of the temperature. The tendency of the increases in conversion and selectivities was more pronounced on the Ni monolith than on the Ce-Zr/Ni monolith (Figure 3). For example, when the temperature rose from 973 K to 1173 K, methane conversion increased from 76% to 88% on the Ni monolith, while it increased from 90% to 95% on the Ce-Zr/Ni monolith.

In the studies of supported Ni or Ni coated monolithic catalysts, porous materials with high surface area, such as Al_2O_3, were used as supports to increase the specific surface area of the catalysts.[15,16] In this work, nickel sponge was used to prepare the Ni monolith, followed by acid treatment to increase the surface area of the Ni monolith. This is why the catalyst is more active and selective than the nickel monolithic catalyst prepared with nickel spheres.[12] Although the specific surface area of the monolith is still much lower than oxide supported nickel catalysts, it is high enough to achieve the high conversion and selectivities because this reaction is a very fast one, which does not need very high specific surface area.

In the studies of supported nickel catalysts, Pengpanich et al.[10] and Takeguchi et al.[13] found that addition of CeO_2-ZrO_2 solid solution increased both the conversion of methane and the selectivities to H_2 and CO. Takeguchi et al.[13] also found that the catalytic activities for POM increased with an increase in the oxygen storage capacity of the support and, therefore, inferred that the reaction proceeded through a redox mechanism. Kundakovic and Flytzani-Stephanopoulos[17] also found that the solid solution of ceria and zirconia could promote the total oxidation of methane through this mechanism. However, the effect of the solid solution of ceria and zirconia on the increase of the selectivities has not been further elucidated in the literature. In the present work, the addition of CeO_2-ZrO_2 on the Ni monolith also promoted both the conversion of methane and the selectivities to H_2 and CO. We infer that the reaction might proceed through the redox mechanism, that is, the storage of oxygen on the catalyst promoted the combustion of methane. At the same time, we also infer that the total oxidation of more methane in the first step releases more heat, resulting in more reformings of the remaining methane. Therefore, methane conversion and the selectivities to syngas on the Ce-Zr/Ni monolith are higher than those on the Ni monolith.

On the Ce-Zr/Ni monolith, the conversion and the selectivities are very high, that is, 94%, 98%, and 96%, respectively, at the inlet temperature 1123 K, CH_4/O_2 ratio 2.0, and GHSV 1.0 × 10^5 h^{-1}. These values approach those on the supported nickel catalysts, for example, 15% $Ni/Ce_{0.75}Zr_{0.25}O_2$[10] and 13.6 wt. % NiO-5.1 wt.% MgO/silica-alumina[1] under similar conditions, and are near to the thermodynamic equilibrium values, which are 95%, 98%, and 98%, respectively.

Figure 4 shows the results of a long duration test of 30 h on the Ce-Zr/Ni monolith at inlet temperature 1123 K, GHSV 1.0 × 10^5 h^{-1}, and CH_4/O_2 ratio 2.0. Methane conversion and selectivities to H_2 and CO remained almost unchanged during 30 h of reaction. The reaction on the Ni monolith also showed similar stability (not shown). In contrast, the nickel coated alumina monolith lost all the activity

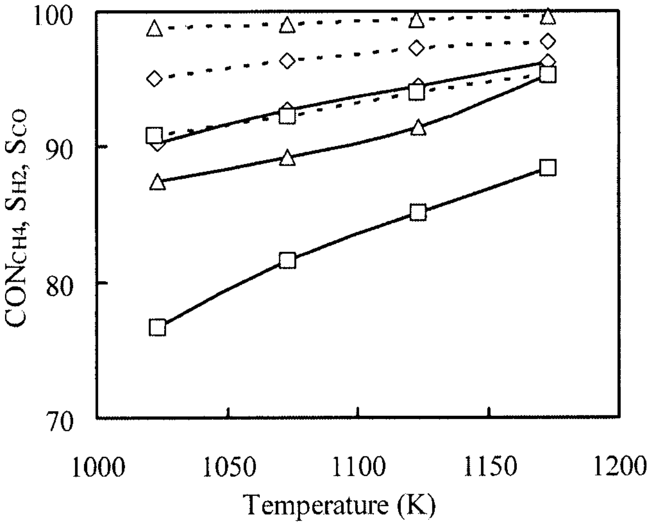

Figure 3. Comparison of CH_4 conversions and H_2 and CO selectivities between Ni monolith and Ce-Zr/Ni monolith at different temperatures.

(□) methane conversion; (Δ) H_2 selectivity; (◇) CO selectivity; (solid lines) the Ni monolith and (dashed lines) Ce-Zr/Ni monolith. Reaction conditions: GHSV = 1.0 × $10^5 h^{-1}$, $CH_4/O_2 = 2.0$.

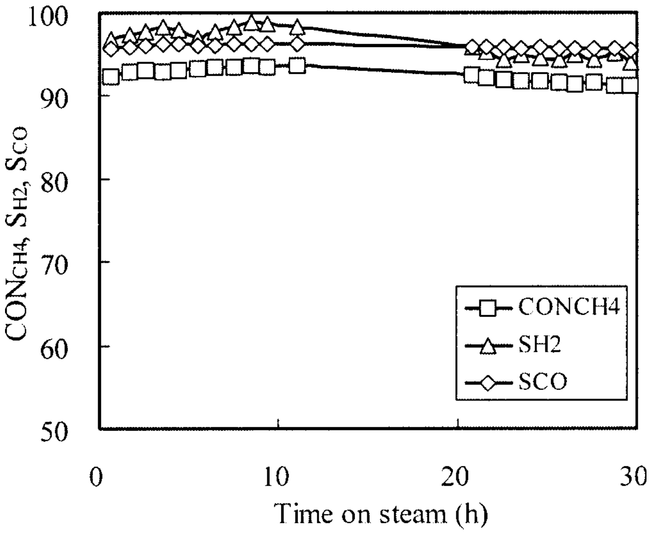

Figure 4. CH_4 conversion and CO and H_2 selectivities as a function of time on stream over Ce-Zr/Ni monolith.

Temperature = 1123 K, GHSV = 1.0×10^5 h^{-1}, CH_4/O_2 = 2.0.

in a few hours.[5] In the supported nickel catalysts or nickel coated alumina monolith, the fine nickel particles tend to aggregate at high temperature and lose the activity. Metal oxides were added in catalysts to create metal-oxide interaction, which may stabilize the activity and prevent carbon deposition to some extent.[1,10] In this work, the nickel acts as both active component and the support, so it would not aggregate further. That might be why the Ni monolith and the Ce-Zr/Ni monolith show very high stability.

Conclusions

The metallic Ni monolith, prepared with nickel sponge, followed by acid treatment, and the Ni monolith promoted with solid solution of ceria and zirconia, Ce-Zr/Ni monolith, showed very high conversion of methane and high selectivities to hydrogen and carbon monoxide in the partial oxidation of methane. For example, at inlet temperature 1123 K, GHSV 1.0×10^5 h^{-1}, and CH_4/O_2 ratio 2.0, methane conversion and selectivities to hydrogen and carbon monoxide are 94%, 98%, and 96%, respectively, on the Ce-Zr/Ni monolith. These values approach those on supported nickel catalysts and are near to the thermodynamic equilibrium ones.

The metallic Ni monolith, either in the absence or presence of solid solution of ceria and zirconia, showed very high stability. After 30 h testing, the methane conversion and the selectivities to H_2 and CO remained almost unchanged. This catalyst system is promising for the conversion of natural gas to syngas or the production of hydrogen.

Acknowledgments

Financial support by the Science & Technology Development Center, SINOPEC, China, and Program of Introducing Talents of Discipline to Universities (No B06006), is gratefully acknowledged. One of the authors (YW) would like to thank Professor Schmidt, Minnesota University, for his invitation, which enabled YW to work in his Group for three months. It is the experience gained in his laboratory that made the authors set up the apparatus quickly and do the work well.

Literature Cited

1. Choudhary VR, Mamman AS. Oxidative conversion of methane to syngas over NiO/MgO solid solution supported on low surface area catalyst carrier. *Fuel Process Technol.* 1999;60:203–211.
2. Choudhary VR, Mamman AS, Uphade BS. Steam and oxysteam reforming of methane to syngas over $Co_xNi_{1-x}O$ supported on MgO precoated SA-5205. *AIChE J.* 2001;47:1632–1638.
3. Claridge JB, York APE, Brungs AJ, Marquez-Alvarez C, Sloan J, Tsang SC, Green MLH. New catalysts for the conversion of methane to synthesis gas: molybdenum and tungsten carbide. *J Catal.* 1998; 180:85–100.
4. Hickman DA, Schmidt LD. Production of syngas by direct catalytic oxidation of methane. *Science.* 1993;259:343–346.
5. Torniainen PM, Chu X, Schmidt LD. Comparison of monolith-supported metals for the direct oxidation of methane to syngas. *J Catal.* 1994;146:1-10.
6. Li ZH, Zhang XY, He F, Xu GH. Catalytic stability of Ni catalyst for partial oxidation of methane to syngas, *Preprint of ACS Fuel Symposia.* 2002;47:335–336.
7. Kim P, Kim Y, Kim H, Song IK, Yi J. Synthesis and characterization of mesoporous alumina with nickel incorporated for use in the partial oxidation of methane into synthesis gas. *Appl Catal A: Gen.* 2004;272:157–166.
8. Wu T, Yan Q, Wan H. Partial oxidation of methane to hydrogen and carbon monoxide over a Ni/TiO_2 catalyst. *J Mol Catal A: Chem.* 2005;226:41–48.
9. Passos FB, De Oliveira ER, Mattos LV, Noronha FB. Partial oxidation of methane to synthesis gas on Pt/$Ce_xZr_{1-x}O_2$ catalysts: the effect of the support reducibility and of the metal dispersion on the stability of the catalysts. *Catal Today.* 2005;101:23–30.
10. Pengpanich S, Meeyoo V, Rirksomboon T. Methane partial oxidation over Ni/CeO_2-ZrO_2 mixed oxide solid solution catalysts. *Catal Today.* 2004;93–95:95–105.
11. Wang YQ. *Autothermal Oxidation of Natural Gas into Syngas at High GHSV.* Chinese Patent ZL. 2003:03101191.8.
12. Wang YQ, Hou YJ, Qi ST. Partial oxidation of methane over monolithic to syngas autothermally catalysts. *J Combustion Sci Techn.* 2001; 7:105–109.
13. Takeguchi T, Furukawa S, Inoue M. Hydrogen spillover from NiO to the large surface area CeO_2-ZrO_2 solid solutions and activity of the NiO/CeO_2-ZrO_2 catalysts for partial oxidation of methane. *J Catal.* 2001;202:14–24.
14. Guo C, Zhang J, Li W, Zhang P, Wang Y. Partial oxidation of methane to syngas over $BaTi_{1-x}Ni_xO_3$ catalysts. *Catal Today.* 2004;98:583–587.
15. Sahli N, Petit C, Roger AC, Kiennemann A, Libs S, Bettahar M. M. Ni catalysts from $NiAl_2O_4$ spinel for CO_2 reforming of methane. *Catal Today.* 2006;113:187–193.
16. Verykios XE. Catalytic dry reforming of natural gas for the production of chemicals and hydrogen. *Int J Hydrogen Energy.* 2003;28:1045–1063.
17. Kundakovic LJ, Flytzani-Stephanopoulos M. Cu- and Ag-modified cerium oxide catalysts for methane oxidation. *J Catal.* 1998;179:203–221.

Manuscript received Apr. 11, 2006, and revision received Aug. 29, 2006.