Catalysis Today 171 (2011) 97–103

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Syngas production from natural gas via catalytic partial oxidation using ceramic monolith catalyst at short contact time and elevated pressure

Shigeru Kado[a,*], Ken-ichi Imagawa[a], Asako Kiryu[a], Fuyuki Yagi[a], Takeshi Minami[a], Hironori Kawai[a], Ken-ichi Kawazuishi[a], Keiichi Tomishige[b,1], Arata Nakamura[c], Yoshifumi Suehiro[d]

[a] Chiyoda Corporation, Moriya-cho, Kanagawa-ku, Yokohama 221-0022, Japan
[b] Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
[c] Inpex Corporation, Minato-ku, Tokyo 107-6332, Japan
[d] Japan Oil, Gas and Metals National Corporation, Chiba, Chiba 261-0025, Japan

ARTICLE INFO

Article history:
Received 31 October 2010
Received in revised form 21 February 2011
Accepted 2 March 2011
Available online 29 March 2011

Keywords:
Catalytic partial oxidation
High pressure
Short contact time
Monolith
Rh
Isotopic exchange

ABSTRACT

The development of the catalyst suitable for the catalytic partial oxidation (CPOX) of natural gas was investigated for the efficient production of synthesis gas. The catalyst of $Rh/CeO_2 + ZrO_2 + MgO$ was found to show higher catalytic performance than Rh/MgO. The additional effect of CeO_2 and ZrO_2 to Rh/MgO on catalytic property was studied by H_2-TPR, isotopic oxygen exchange reaction and DRIFT spectroscopy. And it was revealed that the state of Rh can maintain metallic phase during the CPOX reaction, and that oxygen can be supplied from lattice oxygen, and that adsorbed CO can desorb easily. The application of foam monolith catalyst coated with developed support materials to high pressure and short contact time CPOX reaction has been investigated, and we have succeeded in demonstrating the stable catalytic performance for 2000 h at 1.0 MPa and 500,000 h^{-1} GHSV.

1. Introduction

Gas to Liquid (GTL) processes have received great attention as an effective technology for converting natural gas to ultra clean liquid fuels [1–3] as well as monetizing natural gas [4]. Evolution in Fisher–Tropsch reactor such as circulating fluid-bed reactor development by Sasol brought the growth in the capacity of FT process to tens of thousands of barrels per day of capacity [5]. In order to improve the total energy efficiency of GTL process, the syngas production reactor has been also developed because, in GTL process, the capital cost of syngas production section is considered to the largest portion of the total capital cost [6]. Also, the larger capacity of synthesis gas production section will be desired in order to reduce the capital cost per product [6]. Furthermore, the reduction of greenhouse gas, such as CO_2 emission, is strongly required for the suppression of the global warming. Therefore the development of more compact synthesis gas production processes with high energy efficiency is desired.

Chiyoda Corporation, University of Tsukuba, INPEX Corporation and JOGMEC (Japan Oil, Gas and Metals National Corporation) have jointly developed catalytic partial oxidation (CPOX, $CH_4 + 1/2O_2 \rightarrow CO + 2H_2$) catalyst and process to produce synthesis gas with higher efficiency and less natural gas consumption and CO_2 emission under high throughput conditions (GHSV = 1×10^5 to 1×10^6 h^{-1}). In the GTL process with larger capacity, the autothermal type reforming process is considered to be more economic than steam reformer [6].

As for the catalyst development, Green and co-workers have published that some noble metals like Ru, Rh, Ir could catalyze methane partial oxidation [7]. Hickman and Schmidt demonstrated the extremely short contact time reaction using Rh impregnated foam monolith catalyst and obtained very high syngas selectivity [8]. After this publication, there was a significant increase in publications from academia and industry. Some of them have already demonstrated the high pressure CPOX reaction [9–11] up to 2 MPa [12]. The higher operating pressure is desirable when considering the following synthetic process, such as FT process operated around 3 MPa. Basini et al. from Snamprogetti, energetically developed CPOX catalyst and processes by large scale, and published

* Corresponding author at: Research & Development Center, Chiyoda Corporation, 3-13, Moriya-cho, Kanagawa-ku, Yokohama 221-0022, Japan. Tel.: +81 45 441 9142; fax: +81 45 441 9728.
E-mail address: skado@ykh.chiyoda.co.jp (S. Kado).
[1] Present address: Tohoku University, School of Engineering, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai, 980-8579, Japan.

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.03.009

many reports on both fundamental and practical study [13–16], as well as Shell, ConocoPhillips.

We have been also paid attention to CPOX reaction at short contact time and elevated pressure to reduce the reactor size and capital cost for syngas production drastically. Chiyoda Corporation and University of Tsukuba have studied the catalyst development, which is suitable for CPOX reaction from the viewpoints of Rh modification with other material mainly done by University of Tsukuba, and the effect of support material mainly done by Chiyoda Corporation. Tomishige and co-workers have found that the modification of Rh with Co or CeO_2 was effective to promote CPOX reaction and reduce the highest temperature of the catalyst bed. They also studied the structural characterization in detail and revealed that the strong interaction between Rh and additives [17–20].

On the other hand, Chiyoda Corporation has found that the addition of CeO_2 and ZrO_2 to Rh/MgO as support materials enhanced CPOX reaction [21,22]. The feature of this catalyst is described in this report including fundamental properties and application to the foam monolith catalyst, which is the candidate for the industrial catalyst due to the low pressure drop even at the high space velocity. The monolith foam catalyst has high surface to volume ratio, so that the homogeneous reaction such as complete oxidation at gas phase can be quenched. Surprisingly it is suggested from kinetic study that even over 2 MPa the heterogeneous reaction is still dominant over monolith foam catalyst [23]. But from the detailed chemistry and modeling based on experiments to know gas and solid temperature and mole fraction, mass transport limitation of oxygen is indicated due to the quite fast reaction rate [24]. This transport limitation means the difficulty of reactor design in scaling up, so the demonstration at practical conditions is quite important. We have succeeded in demonstrating the stable catalytic performance at 1.0 MPa and 500,000 h^{-1} GHSV using foam monolith catalyst.

2. Experimental

2.1. Catalyst preparation

A fundamental study such as the effect of support materials on catalytic performance at atmospheric pressure and each characterization was done using granule catalysts. The support material was prepared by physical mixing of each precursor of metal oxide such as CeO_2, ZrO_2 and MgO. The mixture was pressed into disk-shape to make tight contact among metal oxides and then calcined at high temperature. The sintered disk-shape support material was crushed and sieved into desired granule size from 0.36 to 0.43 mm before an aqueous solution of Rh precursor was impregnated by incipient wetness method. Finally, the catalyst was calcined again at moderate temperature after drying completely.

A stability test at high pressure and GHSV was examined over monolith catalyst employing α-Al_2O_3 ceramic foam as substructure. The disk-shape support material prepared by the same way described above was crushed into fine powder using ball mill to prepare water solvent slurry. The ceramic foam was coated with support material by slurry and calcined followed by Rh loading by incipient wetness method.

2.2. Catalytic performance

The catalytic performance at atmospheric pressure was evaluated using fixed bed flow type reactor whose schematic diagram has been already reported [21]. The thermowell for measuring the temperature by thermocouple was installed through the center of catalyst bed. The outlet temperature of the catalyst bed mentioned in the section of results was measured by this thermocouple.

Table 1
Composition of town gas used for catalyst stability test shown in Figs. 10 and 11.

Species	Volume %
CH_4	89
C_2H_6	6
C_3H_8	3
C_4H_{10}	2

The catalyst was reduced by hydrogen around 900 °C before catalytic performance test. After the reduction, the mixture of $CH_4/O_2/Ar = 30/15/55$ was introduced at atmospheric pressure and 400,000 h^{-1} GHSV. The catalyst bed was heated by external heating system for 3 h to confirm the steady state of the reaction, and then the electronic furnace outside the reactor was removed to achieve the autothermal condition.

The stability test at high pressure and GHSV was examined using another bench-scale reactor system by feeding compressed town gas whose contents are listed in Table 1, pure oxygen and steam at almost 1 N m^3/h total flow rate. In this case, the monolith catalyst was employed without thermowell put through the catalyst bed to avoid any possible heat loss. The standard conditions were 1.0 MPa, 500,000 h^{-1} GHSV, $O_2/C = 0.5$ and $H_2O/C = 0.04–0.08$. The experiments were conducted under autothermal condition.

Both reactor systems were equipped with on-line TCD-GC system to detect H_2, CO, CH_4 and CO_2. During every experiment shown in the section of results, no oxygen was detected.

2.3. Characterization

Hydrogen temperature programmed reduction (H_2-TPR) profile of the granule catalyst was measured by introducing 2.5% H_2 diluted with He with increasing temperature from ambient temperature to 850 °C. After the temperature reached 850 °C, it was maintained for 30 min until H_2 consumption was completed. Before H_2-TPR, the sample was pretreated in air for 30 min and then in Ar for 30 min at 500 °C to remove the impurities adsorbed on the surface.

Oxygen isotopic exchange reaction was conducted by pulse method injecting $CH_4/O_2 = 2$ mixture gas with 2.5 μmol/pulse at 900 °C by flowing He carrier gas at 1,000,000 h^{-1} GHSV corresponding flow rate. The loading amount of Rh existing in the pulse reactor was as small as 0.1 μmol, which was much smaller than injection amount, so that the catalytic reaction proceeded under this condition. Before the pulse reaction, the catalyst was pretreated by the continuous flow of $CH_4/^{16}O_2 = 4\%/2\%$ mixture diluted with helium at 900 °C for 1 h to confirm the steady state of CPOX reaction. The effluent gas was monitored by mass spectroscopy.

DRIFT spectra were recorded using Nicolet 6700 (Thermo Fischer Scientific) at a resolution of 4 cm^{-1} by collecting 120 scans in about 80 s. The monolith catalyst was crushed into powder and 30 mg of them was installed in the apparatus and reduced. In the case of CO adsorption, CO was introduced by pulse up to saturation. Desorption property of CO was measured by increasing temperature from ambient temperature to 500 °C, and spectra were recorded at every 50 °C interval. In the case of CPOX reaction, $CH_4/O_2 = 4\%/2\%$ mixture diluted with nitrogen was introduced at 500 cm^3/min at fixed temperature.

3. Results and discussion

3.1. Additive effect of CeO_2 and ZrO_2 to MgO as support materials

The Rh/MgO-based catalyst has been examined in terms of the suitability for CPOX reaction, and the additive effect of CeO_2 and