# Partial Oxidation of Methane over Ni Catalysts Supported on Ce-$ZrO_2$ Mixed Oxide

Hyun-Seog Roh, Wen-Sheng Dong, Ki-Won Jun, and Sang-Eon Park*
*Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology, Taejon 305-600, Korea*

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A novel catalyst, Ni/Ce-$ZrO_2$ exhibits very high catalytic activity and stability in partial oxidation of methane to synthesis gas. It gives 99.6% $CH_4$ conversion at 850 °C and the activity was maintained for 100 h.

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Catalytic partial oxidation of methane (POM) to CO and $H_2$ is of great practical importance in utilization of natural gas. Compared with the conventional highly endothermic catalytic steam reforming of methane, which is well established process for converting hydrocarbons into hydrogen or synthesis gas in industry, the catalytic POM offers the alternatively greatest potential for fast, efficient and economical conversion of methane to hydrogen or synthesis gas, due to being mildly exothermic, high conversion, high selectivity, suitable H/C ratio for the Fischer–Tropsch and methanol synthesis, and very short residence time. In 1990, Green and coworkers[1] reported that some noble metals could catalyze POM to the thermodynamic equilibrium composition of product gases. Recently, Choudhary and coworker[2] have reported that Ni/MgO showed good activity and selectivity in the reaction.

In our previous studies, we have performed the $CO_2$ reforming of methane over Ni/$ZrO_2$ catalysts with more than 10 wt % Ni loading, which showed both high activity and stability in spite of a large amount of carbon deposition.[3] On the basis of these results, we have applied Ni/$ZrO_2$ catalysts to POM and found its fairly good catalytic performance. In the next step, the zirconia support was modified with Ce in order to improve the oxygen storage capacity of the catalysts, thereby to improve catalytic activity and stability. We report here that a novel nickel catalyst system supported on a ceria-doped zirconia exhibited high catalytic performance for POM in comparison with the other supported Ni catalyst systems.

Supports employed in this study were zirconia, ceria, Ce-doped zirconia, magnesium aluminate, α-alumina, and magnesia. Ce-doped zirconia support was prepared by sol–gel method using the mixture of zirconyl chloride and the corresponding salt of Ce. The weight ratio of $ZrO_2$ to $CeO_2$ is 4:1. The modified zirconia support was calcined at 800 °C for 6 h in air. Supported Ni catalysts (with Ni loading of 15 wt%) were prepared by the molten-salt method[4] with $Ni(NO_3)_2 \cdot 6H_2O$. The catalyst samples were calcined at 550 °C for 6 h in air. Activity tests were carried out under atmospheric pressure in a fixed-bed microreactor. 50 mg of each catalyst was loaded into a quartz reactor with inner diameter of 4 mm. The reaction temperature was measured and controlled by a thermocouple inserted directly into the top layer of the catalyst bed. Prior to reaction tests, the catalysts were reduced in 5% $H_2/N_2$ at 700 °C for 3 h. The reactant gas stream consisted of $CH_4$ and $O_2$ with a molar ratio of 1.875:1 — $O_2$ was taken in slight excess over the stoichiometry to compensate its deficiency caused by total combustion. Effluent gases from the reactor were analyzed by an on-line gas chromatograph (Chrompack CP9001) equipped with a capillary column (CarboPLOT P7) and a thermal conductivity detector. The BET surface areas and pore volumes were measured by nitrogen adsorption. XRD patterns were recorded using a Rigaku 2155D6. TPR was carried out in conventional apparatus using 5% $H_2/N_2$ gas with a heating rate of 10 °C/min.

It has been recently reported that Ni/$ZrO_2$ catalysts with more than 10 wt% Ni loading showed high activity at 750 °C for 30 h in the $CO_2$ reforming in spite of giving a birth of a large amount of carbon deposition.[3] The carbon species deposited on the Ni/$ZrO_2$ catalyst at an initial stage of the reaction were characterized to play a role as an active reaction intermediate in the reaction. However, its stable activity can be obtained only under diluted reaction conditions. In POM reaction, coke resistance is as important as that in $CO_2$ reforming. Zirconia has thermal stability at high temperature as well as significant surface area. Furthermore, because it has both basic and weak acidic sites, zirconia can have high resistance to coke formation.[3] In addition to these superior properties, the surface area of zirconia can be increased by the change of its phase from monoclinic to tetragonal using doping of other metals. The modification of a zirconia support with ceria reveals the most profound effect for coke resistance of catalyst.[5]

The supported Ni catalysts mentioned above were tested at 750 °C and space velocity of 55,200 $cm^3/h \cdot g_{cat}$, and activities for $CH_4$ conversion with time on stream are presented in Figure 1. In the case of Ni/$Al_2O_3$ catalyst, the activity decreased gradually with increasing time due to the carbon which was formed during the reaction. Ni/$MgAl_2O_4$, which is generally used as a commercial steam reforming catalyst, showed high initial activity (82% conversion), but the activity decreased by degrees with time due to the coke deposition like Ni/$Al_2O_3$ catalyst.

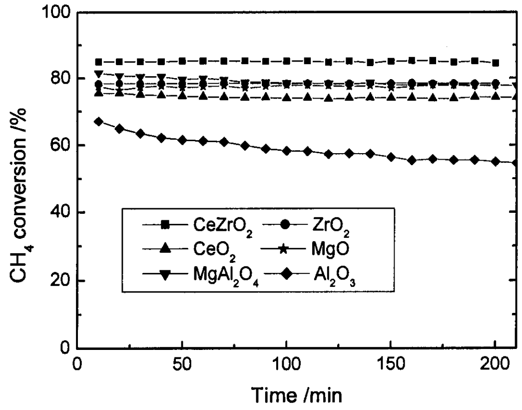

**Figure 1.** $CH_4$ conversion with time on stream over various Ni/support (15 wt% Ni) systems. (Reaction conditions: P = 1 atm, T = 750 ℃, $CH_4/O_2$ = 1.875, GHSV = 55200 $cm^3/h \cdot g_{cat}$).

Ni/MgO showed 78% $CH_4$ conversion and it was maintained. So far, Ni/MgO has been considered as the best catalyst system for POM.[2] Ni/$CeO_2$ showed about 75% $CH_4$ conversion and the activity was maintained during the reaction. Lin and coworkers[6] obtained high activities (about 91% $CH_4$ conversions) using 13% Ni/MgO, Ni/CaO, and Ni/$CeO_2$ at the condition of 750 °C and 56,000 $cm^3/h{\cdot}g_{cat}$. Their results are somewhat different from our results. We obtained 78% and 75% $CH_4$ conversions with 15% Ni/MgO and Ni/$CeO_2$, respectively, at similar temperature and GHSV. These differences are due to the fact that the reaction temperature of our system was directly measured in the top layer of the catalyst bed. According to the experimental results reported by Tsang et al.,[7] the temperature in the top layer of the catalyst bed was found to be about 30 °C higher than that at the other places in the catalyst bed. Lin and coworkers[6] also reported that there was about 35 °C difference in the catalyst bed. By the way, Ni/$ZrO_2$ showed both high activity and stability. Its activity is almost the same as that of Ni/MgO. Furthermore, Ni/Ce-$ZrO_2$ showed the highest activity (85% $CH_4$ conversion) as well as high stability. The activity was maintained during the reaction for 100 h. The activities of Ni/Ce-$ZrO_2$ with various GHSV and temperature were tested. GHSV effect was not so significant. The conversion was almost unchanged without regard to GHSV. But temperature had significant effect on activities. $CH_4$ conversions were 94–98% at 800 °C showing a little change with GHSV, and 96–99.6% at 850 °C.

**Table 1.** $H_2$ selectivity, CO selectivity, and $H_2$/CO ratio over various catalysts. (Reaction conditions: P = 1 atm, T = 750 ℃, $CH_4/O_2$ = 1.875, GHSV = 55200 $cm^3/h{\cdot}g_{cat}$)

| Catalyst | $H_2$ selectivity | CO selectivity | $H_2$/CO ratio |
|---|---|---|---|
| Ni/Ce-$ZrO_2$ | 0.98 | 0.89 | 2.1 |
| Ni/$ZrO_2$ | 0.95 | 0.89 | 2.1 |
| Ni/$CeO_2$ | 0.89 | 0.82 | 2.2 |
| Ni/MgO | 0.97 | 0.85 | 2.3 |
| Ni/$MgAl_2O_4$ | 0.93 | 0.84 | 2.2 |
| Ni/$Al_2O_3$ | 0.75 | 0.65 | 2.3 |

Table 1 shows $H_2$ selectivity, CO selectivity, and $H_2$/CO ratio over the various catalysts. Ni/Ce-$ZrO_2$ showed the highest $H_2$ selectivity (0.98) and CO selectivity (0.89). General trends of both $H_2$ selectivity and CO selectivity were similar to those of $CH_4$ conversion. The higher $CH_4$ conversion was obtained, the higher selectivities of $H_2$ and CO were measured. $H_2$/CO ratios of the catalysts were slightly higher than 2.0, because CO selectivities were below 0.9 resulting from $CO_2$ formation.

This fact that Ni supported on Ce-doped zirconia showed high activity and stability can be explained as following. Ce displays synergistic effect as a modifier of $ZrO_2$ in the POM reaction. The presence of ceria in the catalyst has beneficial effects on the catalyst performance such as improving the catalyst stability and enhancing concentration of the highly mobile oxygen species. The role of ceria in the catalyst is assigned to form a thermally stable solid solution with zirconia and to give high capacity of oxygen storage.[8] This is supported by the temperature programmed reduction results (Figure 2), which indicate that the interaction with zironia leads to the easier reduction of ceria. The reduction of ceria could be done at 880 °C, but it could be achieved at 640 °C when the ceria is located in the solid solution of Ce-$ZrO_2$. This solid solution is identified as a tetragonal phase to have high surface area. Usually POM reaction is carried out over 700 °C, so the easier reducibility of ceria makes it possible to transfer oxygen molecule effectively via redox cycle. The surface area of Ce-doped $ZrO_2$ depends on the calcination temperature, and the support calcined at 800 °C has the surface area of 55 $m^2/g$ which was confirmed by BET analysis. This high surface area is due to the Ce doping effect which makes zirconia tetragonal phase which was confirmed by XRD analysis. In contrast to Ce-doped zirconia support, undoped zirconia has surface area of 18 $m^2/g$. After loading Ni on the support, 15% Ni/Ce-$ZrO_2$ has surface area of 40 $m^2/g$. High oxygen storage capacity of ceria is based on the ability to store and release reversibly a large amount of oxygen, responding to the reaction condition. Ceria in the catalyst is partially reduced under reductive condition and the partially reduced ceria site produces active oxygen species from oxygen molecule, which may react with the deposited carbon or prevent the carbon formation with the help of oxygen spillover from the support onto the Ni sites.

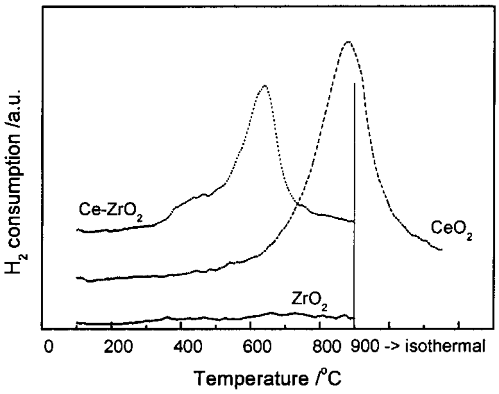

**Figure 2.** TPR patterns of $ZrO_2$, $CeO_2$, and Ce-$ZrO_2$.

In summary, 15% Ni/Ce-$ZrO_2$ catalyst reveals high activity as well as high stability in the POM reaction compared with generally reported catalytic systems such as 15% Ni catalysts supported on MgO, $CeO_2$, and $Al_2O_3$. The high catalyst stability is mainly ascribed to the synergistic effect of Ce modifier resulting from high oxygen storage capacity and high temperature stability.

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