

Partial Oxidation of Methane over Ni/CeZrO₂ Mixed Oxide Solid Solution Catalysts

A. S. Larimi and S. M. Alavi

Abstract—In this study, nickel catalysts over the CeO₂–ZrO₂ solid solution were prepared by the co-precipitation method for partial oxidation of methane. The structures of the catalysts were systematically examined by N₂ adsorption, X-ray diffraction (XRD) and H₂-TPR techniques. The catalytic performance was investigated for partial oxidation of methane as well. The results showed that the Ni/CeO₂–ZrO₂ catalysts had a large BET area. The Ni/CeO₂–ZrO₂ catalysts showed high activity and 5%Ni/Ce_{0.25}Zr_{0.75}O₂ was reported to exhibit the highest BET surface area, activity, stability, and H₂ and CO selectivity for partial oxidation of methane.

Index Terms—Methane partial oxidation, Ni/Ce_(1-x)Zr_xO₂, nickel catalysts, solid solution.

I. INTRODUCTION

Natural gas is the cleanest fossil fuel and the most desirable feedstock for chemicals production. Steam reforming of natural gas is widely used to produce synthesis gas for various chemicals. In recent years, a catalytic partial oxidation of methane to synthesis gas: CO and H₂ has been widely investigated [1–9] as an attractive alternative process to steam reforming since the reaction is mildly exothermic and can produce H₂/CO ratio of 2 which is suitable for methanol or Fischer–Tropsch synthesis. Many catalysts containing transition metals (Ni, Co and Fe) [1–3], the noble metals (Ru, Rh, Pd, Pt, Ir) [4–6] and metal oxides [7–9] have been reported as active catalysts for the partial oxidation of methane. Among those, Ni-based catalyst shows an excellent catalytic activity in this reaction when compared to noble metal catalysts due to its low cost [10]. However, several problems such as deactivation of these catalysts by coke formation and/or metal sintering remain to be solved. Recent studies have focused on developing a highly active and stable catalyst for partial oxidation. Ceria has been studied for various reactions utilizing its redox properties, which can be further enhanced in the presence of a metal or metal oxide [10]. It is well known that CeO₂–ZrO₂ solid solutions also have a high oxygen storage capacity which plays the important role of enhancing catalytic activity under reducing and oxidizing conditions [11]. Moreover, zirconia improves the thermal stability of ceria by decreasing the rate of the crystallite growth process [12]. In this study, we report on the

activity, selectivity and stability of Ni/Ce_(1-x)Zr_xO₂ (x=0.25, 0.5 and 0.75) catalysts for methane partial oxidation to synthesis gas over the temperature range of 450–850°C at atmospheric pressure.

II. EXPERIMENTAL

A. Catalyst Preparation

5wt%Ni/Ce_(1-x)Zr_xO₂ (x=0.25, 0.5 and 0.75) catalysts were prepared by the co-precipitation method. Ce(NO₃)₃·6H₂O (98.5% Merck), ZrOCl₂·8H₂O (99% Merck) and Ni(NO₃)₂·6H₂O (99% Merck) solids were dissolved in distilled water in a ratio corresponding to the desired final composition. NaOH aqueous solution was added slowly under stirring until the PH of mixture reached 11. The precipitate was washed with distilled hot water, dried in an oven at 90 °C for 24 hours and calcinated in air at 750 °C for 4 hours. Also, X%Ni/Ce_{0.25}Zr_{0.75}O₂ (X=0, 5, 10, 15 and 20) catalysts were prepared by the same method.

B. Catalyst Characterization

BET surface area was determined by N₂ adsorption at 300 °C (a three point Brunaur-Emmett-Teller (BET) method using a Quantachrome Corporation Autosorb). Samples were pre-treated at 250 °C for 5 h. X-ray diffraction (XRD) profiles were recorded on a Philips PW1800 diffractometer by using Cu Kα radiation and a power of 40kV ×30mA.

C. Catalytic Reaction

Catalytic tests were carried out in a fixed-bed flow reactor, operated isothermally at atmospheric pressure. The reactor was made with a quartz tube of 4 mm inner diameter. The reactor was heated with an electric oven equipped with temperature controller. About 300 mg of each catalyst was loaded into a reactor. The catalyst was tableted, pulverized into 25–45 mesh, set in the reactor, and then *in situ* pretreated in a pure H₂ stream at 700 °C for 2 h. After the catalyst was cooled, the reactant gas mixture containing CH₄ and O₂ with the molar ratio of 2 and 17 mol% N₂ was allowed to flow at GHSV=149000 h⁻¹. The product gases were analyzed by an on-line Teif gostar 101-B chromatograph equipped with a molecular sieve and propack q columns and a TCD, and using Him with flow of 15 ml/min as carrier.

The methane conversion and selectivities reported in this work were calculated in the following way:

$$CH_4 \text{ Conversion} : \% X_{CH_4} = \frac{CH_4^{in} - CH_4^{out}}{CH_4^{in}} \times 100 \quad (1)$$

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$$H_2 \text{ Selectivity } : \%S_{H_2} = \frac{H_2^{out}}{2(CH_4^{in} - CH_4^{out})} \times 100 \quad (2)$$

$$CO \text{ Selectivity } : \%S_{CO} = \frac{CO^{out}}{CH_4^{in} - CH_4^{out}} \times 100 \quad (3)$$

III. RESULTS AND DISCUSSION

A. BET Surface Area

Table I summarizes BET surface areas for all synthesized samples. It was noticed that the BET surface areas of catalysts increase with increasing Zr content. This might be due to the substitution of a Zr^{+4} (0.86 Å) ion, which has a smaller cationic radius, in the Ce^{+4} (1.09 Å) lattice location. A decrease of crystal size would usually be expected to accompany an increase in surface area [12]. Ceria has low thermal stability and is sinter during the calcinations process. Since sintering occurs due to the crystallite growth [12], it could be said that ZrO_2 improves thermal stability of ceria by decreasing the rate of the crystallite growth process. BET results are higher than those reported by Xu et al. [13]. By using $ZrOCl_2 \cdot 8H_2O$ instead of ZrO_2 as a starting metal salt, more gasses will release during the calcination process, so porosity will increase and it is resulted in increasing BET surface area. It can be observed that the BET surface area of the catalysts decreased with an increase in Ni loading. This can be explained considering that Ni sites behave as centers promoting the sintering during the calcination stage.

TABLE I: THE RESULTS OF BET SURFACE AREA.

Catalyst	BET Surface area (m ² /g)
Ni/Ce _{0.25} Zr _{0.75} O ₂	160
Ni/Ce _{0.5} Zr _{0.5} O ₂	128
Ni/Ce _{0.75} Zr _{0.25} O ₂	112
10%Ni/CeZrO ₂	136
20%Ni/CeZrO ₂	110

B. XRD

Fig. 1 presents XRD patterns of calcined catalysts. No evidence for extra peaks due to non-incorporated ZrO_2 was observed in any XRD patterns of $Ni/Ce_{(1-x)}Zr_xO_2$ (x=0.25, 0.5 and 0.75) catalysts. This suggests that ZrO_2 will be incorporated into the CeO_2 lattice to form a solid solution.

It should be noted that the diffraction peaks were shifted to higher degrees with the increasing amounts of ZrO_2 .

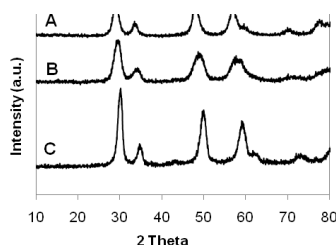


Fig. 1. X-ray diffraction profiles for $Ni/Ce_{0.25}Zr_{0.75}O_2$ (A), $Ni/Ce_{0.5}Zr_{0.5}O_2$ (B), $Ni/Ce_{0.75}Zr_{0.25}O_2$ (C).

This observation was attributed to shrinkage of lattice due to the replacement of Ce^{+4} (1.09Å) with a smaller cation

radius Zr^{+4} (0.86Å). The results are similar to those observed by Xu et al. [13], Pengpanich et al. [14] and Alifanti [15].

C. Catalytic Activity for Methane Partial Oxidation

Fig. 2 presents the effect of temperature on the catalytic activity of the catalysts. The conversion values were taken after 1h of reaction at each temperature. The catalytic activity of the catalysts increased with an increase in Zr loading. The results are similar to those observed by Xu et al. [13] and Pengpanich et al. [14].

H_2 and CO selectivities are presented in Figs. 3 (a) and (b), respectively. The catalytic activity of all catalysts increases with an increase in reaction temperature, resulting in increasing H_2 and CO selectivities. It can be observed that the order of both H_2 and CO selectivity is: $Ni/Ce_{0.25}Zr_{0.75}O_2 > Ni/Ce_{0.5}Zr_{0.5}O_2 > Ni/Ce_{0.75}Zr_{0.25}O_2$

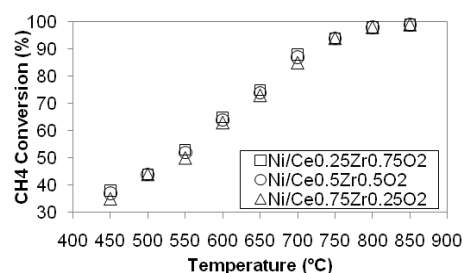


Fig. 2. CH_4 conversion over $Ni/Ce_{(1-x)}Zr_xO_2$ catalysts. (Reaction conditions: $P=1$ atm, $CH_4/O_2=2$, GHSV=106000 h^{-1})

Fig. 4 shows the H_2 selectivity in comparison with the CO selectivity for $Ni/Ce_{0.5}Zr_{0.5}O_2$ catalyst.

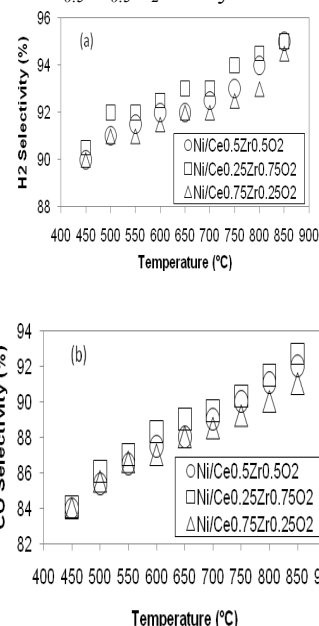


Fig. 3. (a) H_2 selectivity and (b) CO selectivity, during partial oxidation of methane for $Ni/Ce_{(1-x)}Zr_xO_2$ catalysts.

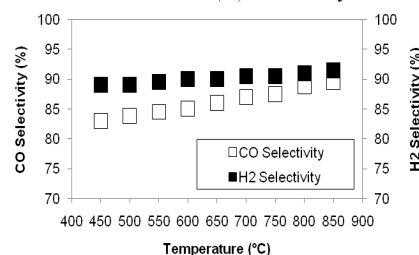


Fig. 4. H_2 and CO selectivities during partial oxidation of methane for Ni/CeO_2 catalyst. ($CH_4/O_2=2$)

At temperatures below 650°C, catalysts behave as total oxidation catalysts, producing more CO_2 and less CO, therefore CO selectivity decreases with a larger gradient than H_2 selectivity.

D. Catalytic Stability

Fig. 5 shows the variations of CH_4 conversion over various catalysts at 700 °C as a function of time-on-stream.

It is shown that the CH_4 conversion for these catalysts was almost unchanged over a 7 h period. This stability is due to the strong metal-support interaction of catalysts. The results are similar to that observed by Pengpanich et al. [14].

Since catalyst deactivation is mainly due to the carbon deposition [16], [17], [18], not sintering, no coke formation was seen on the catalysts.

H_2 and CO selectivities are shown in Fig. 6 (a) and (b), respectively. All catalysts have a high selectivity for H_2 and CO, indicating low carbon deposition. $Ni/Ce_{0.25}Zr_{0.75}O_2$ catalyst has the highest selectivity. The results are similar to that observed by Pengpanich et al. [14].

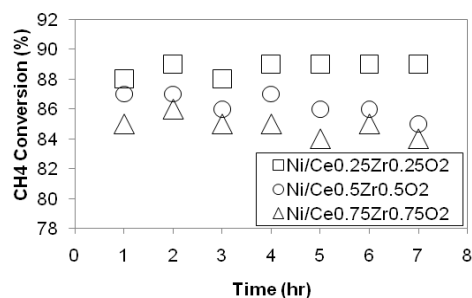


Fig. 5. CH_4 conversion over various catalysts at 700 °C

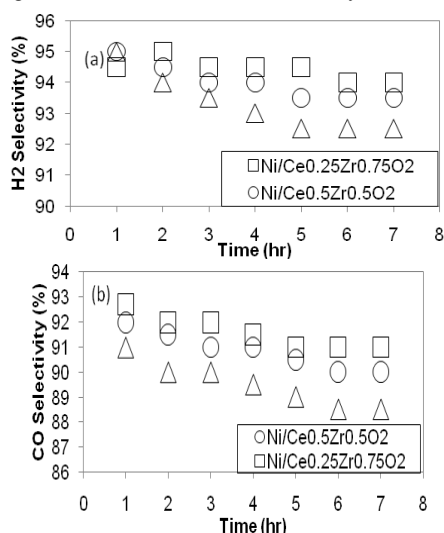


Fig. 6. (a) H_2 selectivity and (b) CO selectivity for $Ni/Ce_{(1-x)}Zr_xO_2$ catalysts at 700 °C

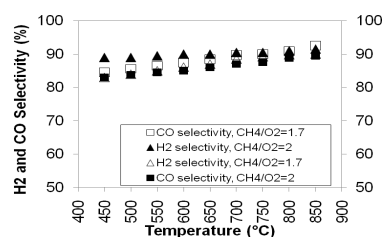


Fig. 7. H_2 and CO selectivities during partial oxidation of methane for $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst.

E. Effect of Feed Ratio on Catalytic Activity

The CH_4/O_2 ratio also affects the catalytic activity of the catalysts. An increase in oxygen content in the feed stream ($CH_4/O_2=1.7$), resulted in increasing CH_4 conversion because both partial and total oxidation occurs. Also, CO selectivity increased and H_2 selectivity decreased for all catalysts. This is due to the fact that a sufficient amount of oxygen is available to convert CO and H_2 to CO_2 and H_2O , respectively (Fig. 7). The results are similar to that observed by Pengpanich et al. [14].

In the case of insufficient oxygen ($CH_4/O_2=2.5$), the CH_4 conversion was found to remain unchanged for $Ni/Ce_{(1-x)}Zr_xO_2$ ($x=0.25, 0.5$ and 0.75) catalysts. It can be concluded that this is because these catalysts have considerable oxygen storage ability due to the presence of CeO_2 (Fig. 8).

A decrease in oxygen content in the feed stream ($CH_4/O_2=2.5$) resulted in decreasing CO selectivity and increasing H_2 selectivity. This is due to the lack of oxygen, so CO and H_2 are not able to convert to CO_2 and H_2O , respectively (Fig. 9). The results are similar to that observed by Pengpanich et al. [14].

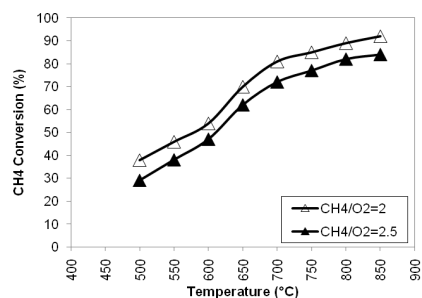


Fig. 8. CH_4 conversion for $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst

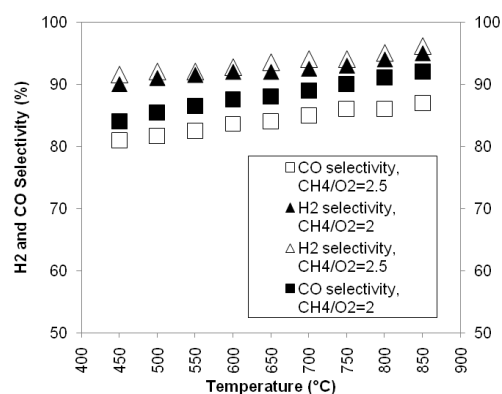


Fig. 9. H_2 and CO selectivities during partial oxidation of methane for $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst.

IV. CONCLUSIONS

All catalysts have shown high surface area. XRD patterns show that ZrO_2 was incorporated into the CeO_2 lattice and form a solid solution in $Ni/Ce_{(1-x)}Zr_xO_2$ ($x=0.25, 0.5$ and 0.75) catalysts. It can be concluded that reaction over $Ni/Ce_{(1-x)}Zr_xO_2$ ($x=0.25, 0.5$ and 0.75) catalysts could be carried out even at low temperatures. The catalytic activity of the $Ni/Ce_{(1-x)}Zr_xO_2$ catalysts increased with an increase in Zr loading. The order of both H_2 and CO selectivities were $Ni/Ce_{0.25}Zr_{0.75}O_2 > Ni/Ce_{0.5}Zr_{0.5}O_2 > Ni/Ce_{0.75}Zr_{0.25}O_2$.

An increase in oxygen content in the feed stream resulted in increasing CH₄ conversion and CO selectivity, but decreasing H₂ selectivity. In the case of insufficient oxygen the CH₄ conversion was found to decrease for Ni/ZrO₂ catalyst while it remained unchanged for Ni/Ce_(1-x)Zr_xO₂ (x=0.25, 0.5 and 0.75) catalysts.

REFERENCES

- [1] C. T. Au, H. Y. Wang, and H. L. Wan, *Mechanistic studies of CH₄/O₂ conversion over SiO₂-supported nickel and copper catalysts*. J. Catal.; 158:343-348. 1996.
- [2] Y. H. H u and E. Ruckenstein, *Transient kinetic studies of partial oxidation of CH₄*. J. Catal; 158:260-266. 1996.
- [3] P. Pantu and G. R. Gavalas. *Methane partial oxidation on Pt/CeO₂ and Pt/Al₂O₃ catalysts*. Appl. Catal. A; 223: 253-260. 2002.
- [4] P. Pantu, and K. Kim, Gavalas G.R. *Methane partial oxidation on Pt/CeO₂-ZrO₂ in the absence of gaseous oxygen*. Appl. Catal. A; 193:203-214. 2000.
- [5] K. Otsuka, Y. Wang, and M. Nakamura, *Direct conversion of methane to synthesis gas through gas-solid reaction using CeO₂-ZrO₂ solid solution at moderate temperature*. Appl. Catal. A; 183:317-324. 1999.
- [6] E. Ruckenstein and Y. H. Hu, *Methane partial oxidation over NiO/MgO solid solution catalysts*. Appl. Catal. A; 183:85-92. 1999.
- [7] K. Otsuka, Y. Wang, E. Sunada, and I. Yamanaka. *Direct partial oxidation of methane to synthesis gas by cerium oxide*. J. Catal.; 175:152-160. 1998.
- [8] B. Irigoyen, N. Castellani, and A. Juan, *Methane oxidation reactions on MoO₃ (100): A theoretical study*. J. Mol. Catal. A; 129:297-310. 1998.
- [9] K. C. Taylor, *Nitric Oxide Catalysis in Automotive Exhaust Systems*. Catal. Rev.-Sci. Eng.; 35:457-481. 1993.
- [10] H. S. Roh, K. W. Jun, W. S. Dong, J. S. Chang, S. E Park, and Y. Joe, *Highly active and stable Ni/Ce-ZrO₂ catalyst for H₂ production from methane*. J. Mol. Catal. A; 181:137-142. 2002.
- [11] G. ColoAn, F. Valdivieso, M. Pijolat, R. T. Baker, J. J. Calvino, and S. Bernal. *Textural and phase stability of Ce_xZr_{1-x}O₂ mixed oxides under high temperature oxidizing conditions*. Catalysis Today; 50:271-284. 1999.
- [12] S. Pengpanich, V. Meeyoo, T. Riksomboon, and K. Bunyakiat. *Catalytic oxidation of methane over CeO₂-ZrO₂ mixed oxide solid solution catalysts prepared via urea hydrolysis*. Appl. Catal. A; 234:221-233. 2002.
- [13] S. Xu and X. Wang, *Highly active and coking resistant Ni/CeO₂-ZrO₂ catalyst for partial oxidation of methane*. Fuel; 84:563-567. 2005.
- [14] S. Pengpanich, V. Meeyoo, and T. Riksomboon, *Methane partial oxidation over Ni/CeO₂-ZrO₂ mixed oxide solid solutioncatalysts*. Catal. Today; 93-95:95-105. 2004.

- [15] M, Alifanti, B. Baps, N. Blangenois, J. Naud, P. Grange, and B. Delmon, *Chem Mater*;15:395. 2003.
- [16] K. Otsuka, Y. Wang, E. Sunada, and I. Yamanaka. *Direct partial oxidation of methane to synthesis gas by cerium oxide*. J. Catal.; 175:152-160. 1998.
- [17] Fornasiero P, Dimonte R, Rao G. R, Kaspar J, Meriani S, Trovarelli A, Graziani M. *Rh-loaded CeO₂-ZrO₂ solid-solutions as highly efficient oxygen exchangers: Dependence of the reduction behavior and the oxygen storage capacity on the structural-properties*. J. Catal.; 151:168-177. 1995.
- [18] P. Fornasiero, G. Balducci, R. DiMonte, J. Kaspar, V. Sergo, G. Gubitosa, A. Ferrero, and M. Graziani, *Modification of the redox behaviour of CeO₂ induced by structural doping with ZrO₂*. J. Catal.; 164:173-183. 1996.



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