

Promotion effects of ceria in partial oxidation of methane over Ni-calcium hydroxyapatite

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Abstract—Effects of ceria added as a promoter to a nickel-calcium hydroxyapatite catalyst, which has recently been reported to exhibit high activity and selectivity in partial oxidation of methane, were investigated. The ceria-promoted catalyst exhibited higher activity and stability than the unpromoted one. This is considered due to the oxygen storage capacity of ceria, which promotes easier removal of the deposited carbon. The optimum content of ceria was determined to lie in the range of the Ce/Ni ratio from 0.1/2.5 to 0.2/2.5.

Key words: Calcium Hydroxyapatite, Ceria, Methane Partial Oxidation, Nickel, Promoter

INTRODUCTION

Catalytic partial oxidation of methane (POM) for synthesis gas and hydrogen production has been an active research subject in recent years, because it is mildly exothermic and does not require high operating pressures and hence is more energy efficient than the well established steam reforming of methane [Au and Wang, 1997; Choudhary et al., 1997; Diskin and Ormerod, 2000; Dissanayake et al., 1991; Dissanayake et al., 1993; Hayakawa et al., 1997; Liu et al., 2002a, b; Takehira, 2002; Tornaiainen et al., 1994; van Looij and Geus, 1997].

There have been numerous studies on POM over various metal catalysts such as Ni, Rh, Pt and Pd. Among these, Ni is the most extensively studied catalyst because it is effective as well as cheap. Ni is usually supported on alumina and silica, but it is susceptible to the formation of inactive nickel aluminate and silicate. Sintering of Ni and the supports and coke formation are other problems. Several attempts have been reported to overcome these problems, as described in earlier works, such as precoating of alumina with MgO or Ce-ZrO₂ [Choudhary et al., 1997; Liu et al., 2002a, b] and use of perovskite or Al-Mg oxide supports [Hayakawa et al., 1997; Takehira, 2002].

In recent works from our laboratory, it has been reported that other new types of catalyst, nickel-strontium phosphate, nickel-calcium phosphate and nickel-calcium hydroxyapatite, exhibit high activity and selectivity in POM [Jun et al., 2003, 2004a, b; Lee and Yoon, 2001; Lee et al., 2002]. No refractory oxide support was used in these catalysts. It was found that these catalysts could be activated by the reacting gases only (methane+oxygen) at around 850 K or 723 K. In these catalysts, very fine nickel particles of several nanometers were observed, and these are believed to come out from the calcium (or strontium) nickel phosphate and hydroxyapatite structure under reducing environment during the reaction. Among these catalysts, nickel-calcium hydroxyapatite was more active than the others. However, this catalyst showed slow deactivation during a long-term test, primarily due to carbon deposition [Jun et al., 2004a].

Therefore, improvement of the catalyst in this respect may be needed.

Several reports show that ceria is effective for elimination of deposited carbon during POM, steam reforming or CO₂ reforming of methane [Asami et al., 2003; Dong et al., 2002; Mattos et al., 2002; Stagg-Williams et al., 2000]. Ceria is also reported to be effective in enhancing the activity [Craciun et al., 2002; Dong et al., 2002; Kusakabe et al., 2004; Mattos et al., 2002; Sharma et al., 2000]. These promotion effects of ceria are believed to originate from its oxygen storage capacity. In this work, ceria was added as a promoter to a nickel-calcium hydroxyapatite catalyst in order to improve the catalyst. Its effects on the activity and stability in POM were investigated and its optimum content was determined.

EXPERIMENTAL

The catalysts were prepared by following the same procedure as described in a previous work [Jun et al., 2004b]. Aqueous solutions of calcium nitrate, nickel nitrate and dibasic ammonium phosphate, after adjusting their pH to 10-11 by ammonia water, were mixed at room temperature with vigorous stirring for 1 h. The water was evaporated to get a thick paste and a cerium nitrate solution was added. Then the mixture was dried at 383 K overnight and finally heat-treated in air at 1,073 K for 2 h to obtain the catalyst. The solid catalyst was crushed and sieved, and particles of 40- to 80-mesh size were used for the test. The mole ratio of Ca/PO₄ employed was fixed at 10/6, which corresponds to that in calcium hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂), and Ni/PO₄ mole ratio was also fixed at 2.5/6, which was reported to be in the optimum range in the previous work [Jun et al., 2004a]. The mole ratio of Ce/Ni was varied from 0.05/2.5 to 0.5/2.5. The ceria-promoted catalyst was designated to be Ce_aNi_{2.5}Ca₁₀, where a denotes (Ce/Ni)×2.5, and the unpromoted catalyst was designated to be Ni_{2.5}Ca₁₀.

The catalyst performance was tested by a conventional method using an 8 mm i.d. quartz-tube flow reactor as described in the previous work [Jun et al., 2004b]. The following experimental conditions were employed. The partial pressures of methane and oxygen were 16.2 and 8.1 kPa (0.16 and 0.08 atm), respectively. Ar was used as the diluent gas and the total flow rate was 100 cm³(STP)/min. The catalyst charge was 0.03 g, and this was mixed with inert

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quartz powder to make the catalyst bed 0.2 g (the volume hourly space velocity (VHSV) was $200,000 \text{ cm}^3(\text{STP})/\text{g-cat}\cdot\text{h}$). For each catalyst, the first run was performed at a reaction temperature of 1,023 K without employing the hydrogen pretreatment since this temperature had been found to be sufficiently high for the activation [Jun et al., 2004b], and then the temperature was adjusted to the desired temperature. The product gas was analyzed by two gas chromatographs using Carboxen 1004 columns (Supelco); one used Ar as the carrier gas and the other used He. The latter was needed especially when the concentration of produced CO_2 was too low to detect by using the Ar carrier gas. The H_2 yield is defined here as (moles of H_2 produced)/[2×(moles of CH_4 fed)].

RESULTS AND DISCUSSION

Various characterization results for the unpromoted catalyst were presented in the previous work [Jun et al., 2004b]. However, since the common characterization results for the ceria-promoted catalysts did not give us useful or meaningful information, the detailed data are not presented here. For instance, the XRD patterns were almost the same due to the small amount of ceria. The BET surface area was quite low (ca. $10\text{--}17 \text{ m}^2/\text{g}$). The XPS spectra showed only that the cerium was in the state of Ce^{4+} and no quantitative analysis was possible. In particular, the amount of H_2 chemisorption was so low (percentage exposed of Ni was less than about 0.2%, which is almost in the error range of the usual measuring apparatus) that its variation upon ceria addition was hardly distinguishable.

As a preliminary performance test, the catalysts with the Ce/Ni molar ratio up to 0.5/2.5 were examined in the temperature range from 673 to 1,073 K. All the ceria-promoted catalysts exhibited higher activity, CO selectivity and H_2 yield than the unpromoted catalyst, indicating that ceria is effective in promoting the activity and selectivity. Among the promoted catalysts, the catalyst having a Ce/Ni

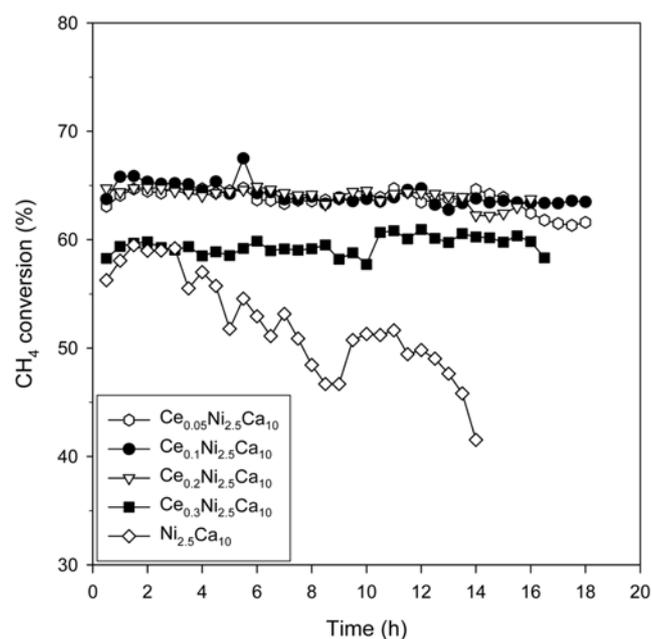


Fig. 1. Catalyst activity and stability test (CH_4 conversion) in POM at 873 K (VHSV= $200,000 \text{ cm}^3/\text{g-cat}\cdot\text{h}$).

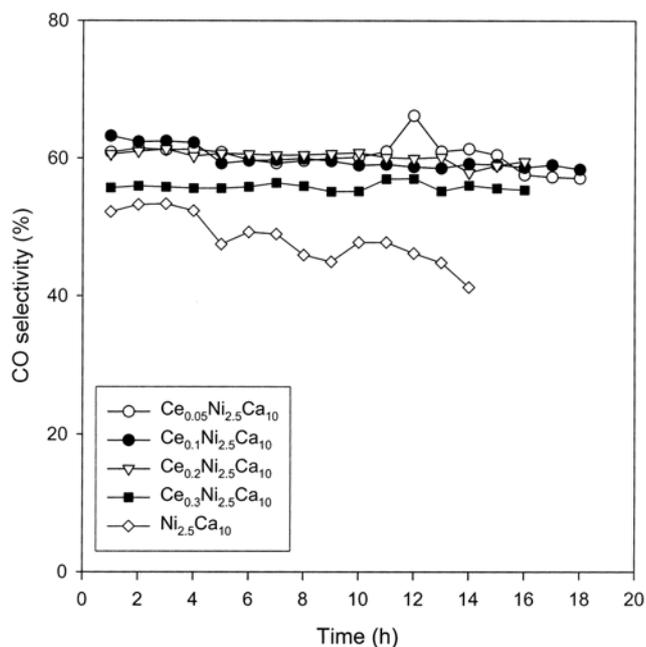


Fig. 2. Catalyst stability test on CO selectivity in POM at 873 K (VHSV= $200,000 \text{ cm}^3/\text{g-cat}\cdot\text{h}$).

ratio around 0.1/2.5 appeared to be the most active. However, all the data were close to the equilibrium and hence the distinction is not so pronounced.

For better comparison, a performance test was carried out at 873 K with a high VHSV. This temperature was chosen because from the thermodynamic equilibrium analysis the carbon deposition could occur to a greater extent at this temperature than at higher temperatures such as above 1,000 K. The results are shown in Figs. 1-3. The catalysts with the Ce/Ni ratio from 0.05/2.5 to 0.2/2.5 showed

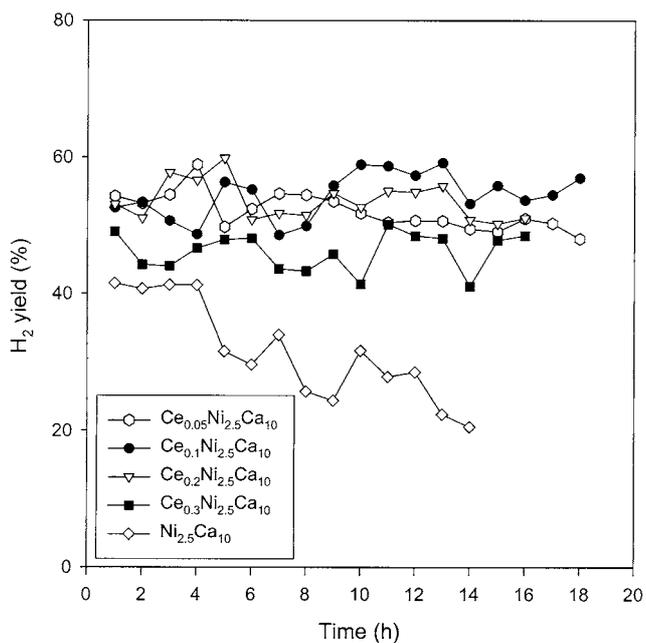


Fig. 3. Catalyst stability test on H_2 yield in POM at 873 K (VHSV= $200,000 \text{ cm}^3/\text{g-cat}\cdot\text{h}$).

significantly higher conversion, CO selectivity, H₂ yield and stability than the unpromoted catalyst. These three promoted catalysts exhibited almost the same performance to one another. However, Ce_{0.05}Ni_{2.5}Ca₁₀ showed slightly poorer stability since it exhibited slightly lower CH₄ conversion and H₂ yield after about 15 h on-stream than Ce_{0.1}Ni_{2.5}Ca₁₀ and Ce_{0.2}Ni_{2.5}Ca₁₀. Ce_{0.3}Ni_{2.5}Ca₁₀ showed somewhat lower performance than the other promoted catalysts, but it was also very stable and more active than the unpromoted catalyst. The relatively lower activity of this catalyst may be due to an excessive amount of ceria, which physically covers the active nickel surface to a greater extent. Therefore, it can be said that the optimum content of ceria lies in the range of Ce/Ni ratio from 0.1/2.5 to 0.2/2.5. In contrast with the ceria-promoted catalysts, the unpromoted catalyst deactivated rapidly. From scanning electron microscopy for the catalyst samples after the reaction, many carbon fibers or nanotubes, whose diameters ranged from 60 to 130 nm, were observed on the unpromoted catalyst while they were hardly seen on the ceria-promoted catalysts.

A long-term test was carried out at 1,023 K for Ce_{0.2}Ni_{2.5}Ca₁₀. As shown in Fig. 4, the catalyst deactivated gradually. For comparison, the data for a Ni_{2.5}Ca_{9.5} catalyst (having the Ni : Ca : PO₄ molar ratio of 2.5 : 9.5 : 6.0) reported in the previous work [Jun et al., 2004a] were also included in the figure. But this catalyst had been tested with a considerably lower VHSV of 30,000 cm³/g-cat·h, or a 6.7 times more amount of catalyst. When taking account of this, one can say that the ceria-promoted catalyst is more stable than the unpromoted one. After 71 and 85 h of operation for each, the catalysts were treated with a gas having 10% O₂ in Ar for 1 h in order to burn out the deposited carbon. When the reaction was resumed, the activity was restored considerably. This indicates that carbon deposition is the major cause of the deactivation. Rapid deactivation

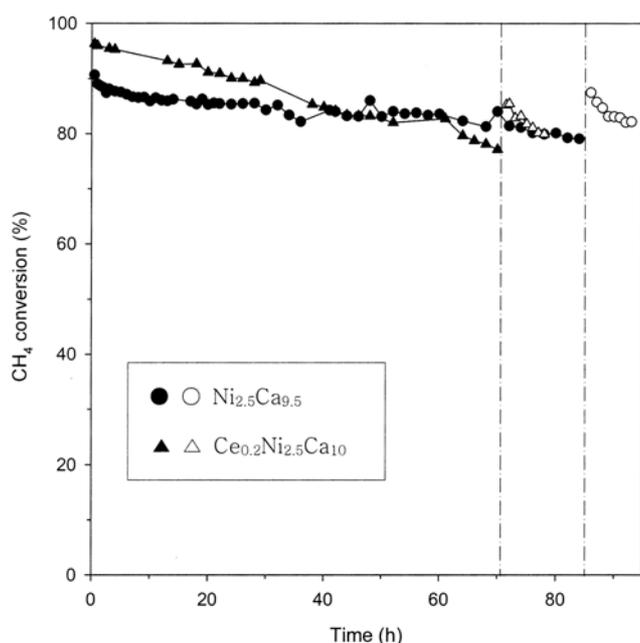


Fig. 4. Long-term tests of Ce_{0.2}Ni_{2.5}Ca₁₀ (VHSV=200,000 cm³/g-cat·h) and Ni_{2.5}Ca_{9.5} (VHSV=30,000 cm³/g-cat·h; data from Jun et al., 2004a) at 1,023 K. Open symbols: after oxidation for 1 h.

for a few hours right after the catalyst restoration is considered due to rapid carbon deposition on clean, highly active Ni metal surface.

For the effects of ceria, several researchers have observed that it enhances the catalyst stability as well as the activity, as mentioned in the introduction. They all agree that the promotion effects come from the oxygen storage capacity or high reducibility of ceria. To summarize their suggestions, the carbon deposited on the active metal surface migrates to the metal-ceria interface and reacts with the lattice oxygen in ceria to produce CO, which maintains the metal surface clean and promotes adsorption of methane. As a result of this, ceria enhances the stability and activity. Re-oxidation of the reduced ceria by taking oxygen adsorbed on the metal may control the deep oxidation on the metal to CO₂ and H₂O, resulting in higher CO selectivity and H₂ yield. The results obtained in this work are also in agreement with the above explanation.

CONCLUSIONS

It was found that ceria added to a nickel-calcium hydroxyapatite catalyst promotes the stability, activity, CO selectivity and H₂ yield in POM. The carbon deposition was effectively suppressed in the presence of ceria. It is considered that the promotion effects of ceria originate from its oxygen storage capacity. The optimum content of ceria was determined to lie in the range of the Ce/Ni ratio from 0.1/2.5 to 0.2/2.5.

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