

## Optimal conditions for partial oxidation of propane over ceria-promoted nickel/calcium hydroxyapatite

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**Abstract**—In order to produce hydrogen for application to fuel cells, the optimal conditions for partial oxidation of propane were studied in this research. Ceria-promoted nickel-calcium hydroxyapatite catalysts ( $\text{Ce}_x\text{Ni}_{2.5}\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ ;  $x=0.1-0.3$ ) were investigated for determination of the optimal content of ceria and ratio of  $\text{O}_2/\text{C}_3\text{H}_8$ . With  $\text{O}_2/\text{C}_3\text{H}_8=1.5$  (ideal reaction), ceria-promoted catalysts did not exhibit higher hydrogen yield than the unpromoted catalyst. However, as the  $\text{O}_2/\text{C}_3\text{H}_8$  ratio was increased to 2.0 and higher, ceria-promoted catalysts exhibited higher hydrogen yield and lower hydrocarbon by-product selectivities. The optimal conditions were determined to be content of ceria ( $x$ ) of 0.1 and  $\text{O}_2/\text{C}_3\text{H}_8$  ratio of 2.0.

Key words: Calcium Hydroxyapatite, Ceria, Nickel, Partial Oxidation, Propane

### INTRODUCTION

Fuel cells are a viable alternative for clean energy generation and a variety of fuel cells for different applications are under development [1]. Hydrogen is an ideal fuel for various fuel cells because it is clean and more efficient than other fuels such as methanol and thus simplifies the system integration. However, since no hydrogen infrastructure currently exists, hydrogen supply for fuel cells is directed at developing a fuel processor producing hydrogen from hydrocarbons, and the successful application of fuel cells is dependent on the development of the fuel processor [2].

The production of hydrogen by reforming of methane is a well-established process that has long been studied [3]. In these days, propane, supplied as LPG as the feedstock for hydrogen production offers an alternative way to fuel cells. Propane is a cheap fuel with high power density. It can be transported easily and stored in liquid form in pressure vessels with typical contents ranging from 45 g for small gas canisters up to several tens of kilograms for mobile and portable use [4,5].

Common methods of converting propane to hydrogen include steam reforming (SR), autothermal reforming (ATR), and partial oxidation (POX). SR, the most common method, is an endothermic reaction suited for steady-state operation and can deliver relatively high concentration of hydrogen. But it suffers from poor transient operation and requires external heating. Compared with SR, POX, an exothermic reaction, can offer several other advantages such as compactness, rapid start-up, and good dynamic response. ATR, combining the exothermic (POX) and endothermic (SR) reactions to maintain the required temperature without external heating, is an adiabatic process, but it is hard to control the reaction conditions. Even though POX delivers lower conversion efficiency, the advantages of POX offer promising aspects for processing a hydrocarbon fuel.

In recent studies, noble metal catalysts were applied to POX of propane, such as Rh foam [6], Rh/ $\text{Al}_2\text{O}_3$ /Fecralloy [7], and Ru- $\text{CeO}_2$  [8]. These catalysts showed good stability under strong oxidation condition for long time. The product gas mixture contained hydrocarbons such as methane, ethylene, ethane and propylene, and even ethyne and traces of  $\text{C}_4$  compounds under certain conditions [4,7]. Noble metal catalysts have high activity and low carbon deposition, but the price is too expensive. The Ni catalyst, relatively active and stable at high temperature, is suitable for POX of propane in respect of the price and commercialization [9-11]. Compared with POX of methane [12-14], studies on POX of propane, especially by using Ni catalysts, have seldom been reported so far. The propane POX process still needs stable and active Ni-catalysts, which are not well developed at the present time [15].

A ceria-promoted nickel-calcium hydroxyapatite catalyst, which had recently been studied in our laboratory, showed high activity and selectivity for partial oxidation of methane [16]. We expect that this catalyst would show good activity for producing hydrogen from propane as well. The objective of this research is to find an effective catalyst and reaction conditions for partial oxidation of propane. This work focuses on the promotional effect of ceria and optimal conditions of  $\text{O}_2/\text{C}_3\text{H}_8$  molar feed ratio and temperature. Durability tests were also carried out with a fixed feed composition at 1,023 K.

### EXPERIMENTAL

Reagents used for preparing nickel-calcium hydroxyapatite catalysts ( $\text{Ni}_{2.5}/\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ ) were as follows: calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , Junsei Chemical, minimum 98%), dibasic ammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ , Shinyo Pure Chemical, minimum 98.5%), nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Shinyo Pure Chemical, minimum 97.0%), aqueous ammonia ( $\text{NH}_4\text{OH}$ , Yakuri Pure Chemical, above 28%), and cerium nitrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Yakuri Pure Chemical, minimum 98.0%).

The catalysts were prepared by following the same procedure as described in a previous study [17,18]. Nearly saturated aqueous solu-

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tions of calcium nitrate, dibasic ammonium phosphate and nickel nitrate were prepared separately by dissolving each reagent in distilled water. The solution of nickel nitrate was added slowly to the solution of dibasic ammonium phosphate while stirring, and aqueous ammonia was added to adjust pH to around 11. This mixed solution was added to the solution of calcium nitrate and the pH was adjusted to 11 by adding aqueous ammonia for the precipitation of the phosphate. The resulting mixture was heated in a water bath of a temperature between 333 K and 353 K and then dried in an oven at 383 K for 50 hours. The dried solid was calcined at 1,023 K for 2 hours. The resulting catalyst was crushed and sieved, and particles of 40 to 80 mesh size were used. The molar ratio of Ca/PO<sub>4</sub> was set to 10/6 (the ratio is same as that of apatite) and the molar ratio of Ni/Ca to 2.5/10. These are the optimal ratios determined in a previous work [13]. This catalyst without a promoter was named Ni<sub>2.5</sub>Ca<sub>10</sub>.

Ceria-promoted catalysts were prepared by following the same procedure as described above except the addition of an aqueous solution of cerium nitrate before drying. The molar ratio of Ce/Ni was varied from 0.1/2.5 to 0.3/2.5. Ceria-promoted catalysts were named Ce<sub>a</sub>Ni<sub>2.5</sub>Ca<sub>10</sub>, where subscript "a", which is (Ce/Ni)×2.5, indicates the content of ceria in the catalyst.

The reaction experiments were carried out in a conventional quartz-tube fixed bed flow reactor containing 0.05 g of fresh catalyst with 0.15 g of quartz powder (40-80 mesh). A 10-mm outside diameter (OD) quartz tube, narrowed to 6 mm OD in the middle, was used as the reactor. The reactor was mounted vertically inside a furnace (Lindberg Blue M) and a small amount of quartz wool was packed at the narrowed position. A K-type thermocouple was inserted in the middle of the catalyst bed.

The feed gas including the reactants (i.e., propane, oxygen) and the diluent gas (argon) was introduced to the reactor. The partial pressure of propane was fixed at 0.10 atm, while oxygen was varied depending on O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> molar ratio (1.5-2.5). Argon was used as balance to set the total flow rate 100 cm<sup>3</sup>(STP)/min. The first run was performed at 1,023 K without hydrogen pre-reduction since this temperature had been found to be sufficiently high for the activation of the catalyst by the reactant gas only [13]. The subsequent reaction experiments were carried out by changing the temperature to 1,073 K, 973 K and then decreasing the temperature in 50 K intervals down to 823 K. During the reaction, the exit gas was flowed via a CaCl<sub>2</sub> trap to the analysis section, consisting of two on-line gas chromatographs (GC, Younglin M600D) in parallel. H<sub>2</sub>, CO, CH<sub>4</sub>, and CO<sub>2</sub> were analyzed by the first GC equipped with 1/8 inch Carboxen<sup>TM</sup> 1004 column (Supelco) with Ar carrier and a thermal conductivity detector (TCD). CO<sub>2</sub>, CH<sub>4</sub>, and other hydrocarbons were analyzed in the second GC, equipped with Hayesep<sup>TM</sup> Q column (Supelco) with He carrier and a TCD. Since the concentration of CH<sub>4</sub> was relatively high, CH<sub>4</sub> was detected by both GC's. By comparing the two CH<sub>4</sub> areas, quantitative analysis of the other components was determined. The mass balances for carbon, hydrogen and oxygen were generally within ±5%. A durability test was carried out at 1,023 K with the O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> ratio of 2.0.

## RESULTS AND DISCUSSION

In this study, characterizations of the catalysts were not carried

out, for various characterization results for the catalysts have been presented in previous works [16,18].

Selectivity, defined by Eq. (1), is based on carbon balance; therefore, the sum of the selectivities of the carbon-containing compounds is 100%.

Selectivity of A (%)

$$\begin{aligned} &= \frac{\text{moles of C}_3\text{H}_8 \text{ converted A}}{\text{total moles of C}_3\text{H}_8 \text{ converted}} \times 100 \\ &= \frac{(\text{moles of A produced}) \times (\# \text{ of carbon in 1 molecule of A})}{3(\text{total moles of C}_3\text{H}_8 \text{ converted})} \\ &\times 100 \end{aligned} \quad (1)$$

The hydrogen yield was calculated by dividing moles of produced H<sub>2</sub> with 4 times of total moles of propane fed:

$$\text{H}_2 \text{ yield (\%)} = \frac{\text{moles of H}_2 \text{ produced}}{4(\text{total moles of C}_3\text{H}_8 \text{ fed})} \times 100$$

### 1. Conversion and Selectivities with O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> Ratio of 1.5

The C<sub>3</sub>H<sub>8</sub> conversion is shown as a function of the temperature in Fig. 1, and the product selectivities are presented in Figs. 2-6. Representative product distributions are given in Tables 1 and 2 in more detail. When the reactant gas was fed with the ideal stoichiometric ratio (O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>=1.5 : C<sub>3</sub>H<sub>8</sub>+1.5O<sub>2</sub>→3CO+4H<sub>2</sub>), more than 80% of propane was converted at 923 K and almost complete conversion was attained at 1,023 K. All the catalysts, except for Ce<sub>0.3</sub>Ni<sub>2.5</sub>Ca<sub>10</sub> at 873 K, showed similar trends in conversion and selectivity. At 823 and 873 K for the three catalysts except Ce<sub>0.3</sub>Ni<sub>2.5</sub>Ca<sub>10</sub>, the conversions were considerably lower (25-38%) and the selectivities of the hydrocarbon products (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub>) were very low. Therefore, from the CO and CO<sub>2</sub> selectivities shown in Fig. 2, it can be said that approximately half of the converted propane was consumed by the complete combustion and the remain-

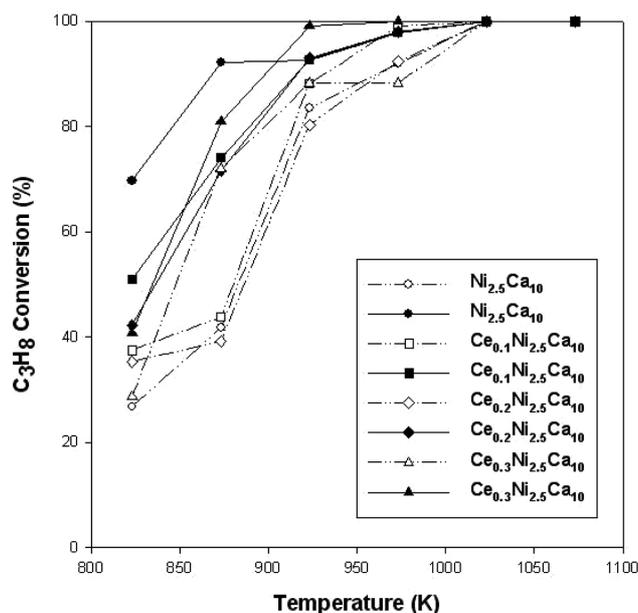


Fig. 1. C<sub>3</sub>H<sub>8</sub> conversion vs. temperature over ceria promoted catalysts with different ceria contents (catalyst charge=0.05 g, VHSV=120,000 cm<sup>3</sup>/g-cat·h, open symbols: O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>=1.5, closed symbols: O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>=2.0).

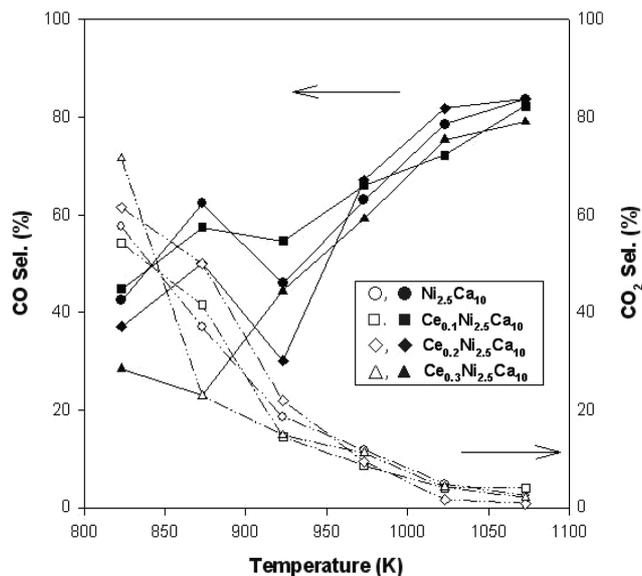


Fig. 2. CO & CO<sub>2</sub> selectivity vs. temperature over ceria promoted catalysts with different ceria contents ( $O_2/C_3H_8=1.5$ , catalyst charge=0.05 g, VHSV=120,000 cm<sup>3</sup>/g-cat-h, closed symbols & solid lines: CO selectivity, open symbols & dotted lines: CO<sub>2</sub> selectivity).

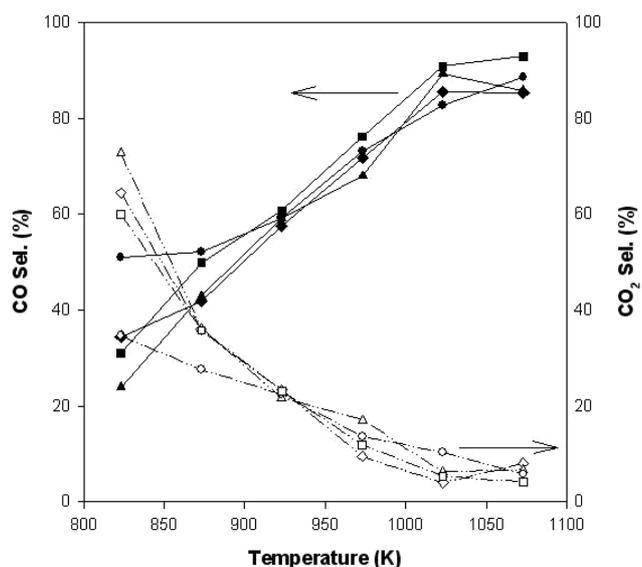


Fig. 3. CO & CO<sub>2</sub> selectivity vs. temperature over ceria promoted catalysts with different ceria contents ( $O_2/C_3H_8=2.0$ , catalyst charge=0.05 g, VHSV=120,000 cm<sup>3</sup>/g-cat-h; legends are the same as Fig. 2).

ing half by the partial oxidation.

At 923 K and above, the CH<sub>4</sub> selectivities lay in a range between 12 and 20%, and did not change much with the temperature; in this temperature range, CO<sub>2</sub> selectivities decreased rapidly while CO gradually increased with temperature. At 923 K, the (C<sub>2</sub>+C<sub>3</sub>) selectivities (where (C<sub>2</sub>+C<sub>3</sub>) means C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub>) were the highest and C<sub>2</sub>H<sub>4</sub> was the major product. As the temperature was raised, the (C<sub>2</sub>+C<sub>3</sub>) selectivities decreased rapidly and the amount of C<sub>3</sub>H<sub>6</sub> was negligible. As a result, the H<sub>2</sub> yield increased steeply in the tem-

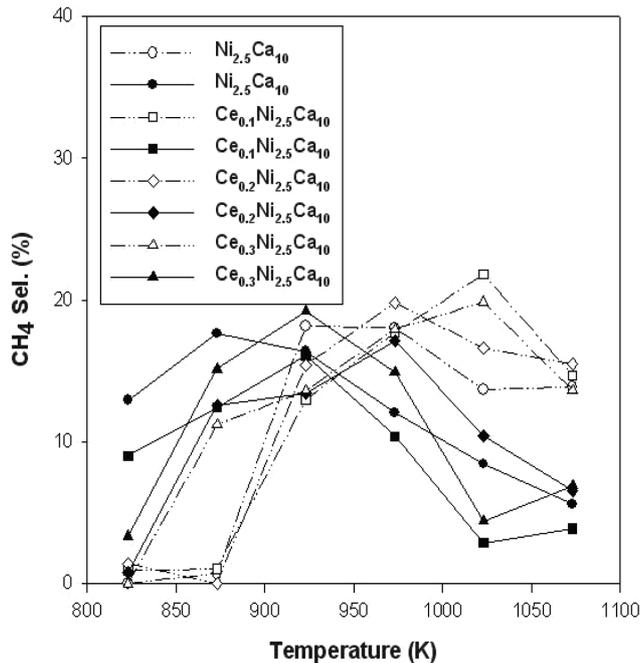


Fig. 4. CH<sub>4</sub> selectivity vs. temperature over ceria promoted catalysts with different ceria contents (catalyst charge=0.05 g, VHSV=120,000 cm<sup>3</sup>/g-cat-h, open symbols:  $O_2/C_3H_8=1.5$ , closed symbols:  $O_2/C_3H_8=2.0$ ).

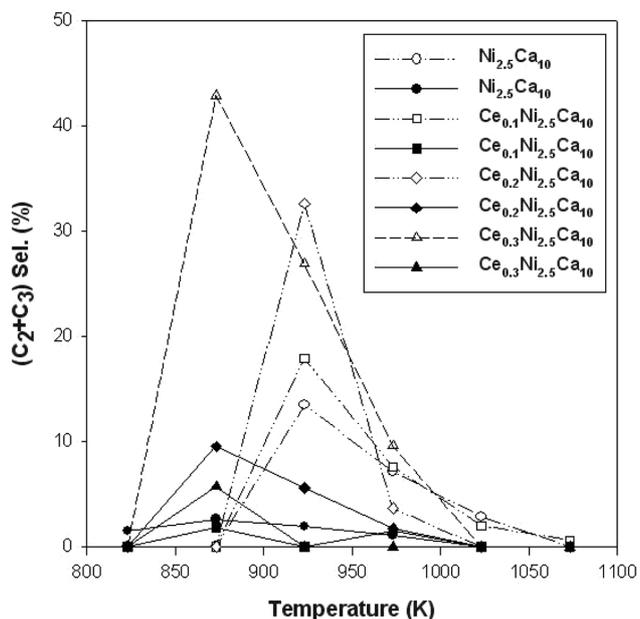
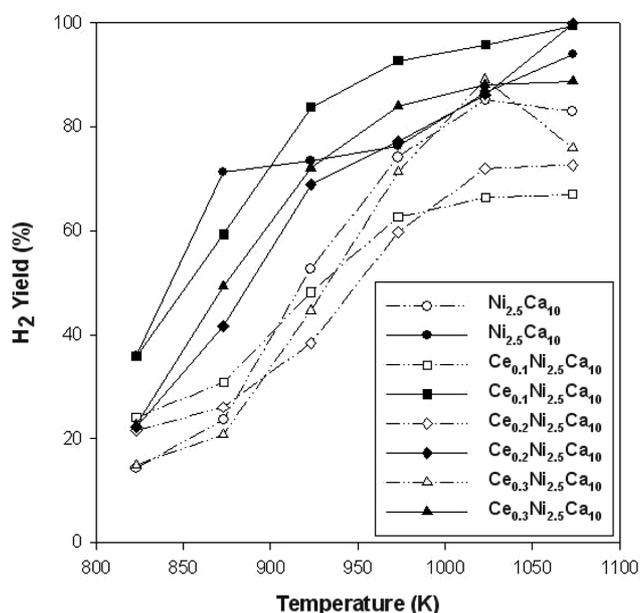


Fig. 5. (C<sub>2</sub>+C<sub>3</sub>) selectivity vs. temperature over ceria promoted catalysts with different ceria contents (catalyst charge=0.05 g, VHSV=120,000 cm<sup>3</sup>/g-cat-h, open symbols:  $O_2/C_3H_8=1.5$ , closed symbols:  $O_2/C_3H_8=2.0$ ).

perature range from 923 K and 1,023 K. Considering the H<sub>2</sub> yield by and large, the highest H<sub>2</sub> yield was obtained over the Ni<sub>2.5</sub>Ca<sub>10</sub> catalyst (Table 1 and Fig. 6).

Ce<sub>0.3</sub>Ni<sub>2.5</sub>Ca<sub>10</sub> showed a different result compared with the other three catalysts, especially at 873 K. Although C<sub>3</sub>H<sub>8</sub> conversion was

high at this temperature, ( $C_1+C_2+C_3$ ) selectivities were high: the selectivities of  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$  and  $C_3H_6$  were 10.6, 27.4, 2.0 and



**Fig. 6.**  $H_2$  yield vs. temperature over ceria promoted catalysts with different ceria contents (catalyst charge=0.05 g, VHSV=120,000  $cm^3/g\cdot cat\cdot h$ , open symbols:  $O_2/C_3H_8=1.5$ , closed symbols:  $O_2/C_3H_8=2.0$ ).

14.2%, respectively, and hence  $H_2$  yield was low (Table 2). The reason is considered to be that too large an amount of ceria would cover a significant portion of the metal active sites on the catalyst surface, which gives rise to lower oxidation activity [1]. In the other words, the decomposition of propane ( $C_3H_8 \rightarrow CH_4 + C_2H_4$ ) or oxidative dehydrogenation ( $C_3H_8 + 1/2O_2 \rightarrow C_3H_6 + H_2O$ ) would have occurred preferentially instead of partial oxidation (Table 2).

## 2. Conversion and Selectivities with Higher $O_2/C_3H_8$ Feed Ratio

Since significant amounts of hydrocarbon products were observed with the  $O_2/C_3H_8$  molar ratio of 1.5, the molar ratio of  $O_2/C_3H_8$  was increased to 2.0 in order to decrease the hydrocarbons by converting them to CO and  $H_2$  by partial oxidation. Compared with the case of  $O_2/C_3H_8=1.5$ , the  $C_3H_8$  conversion became higher in the whole temperature range over all the catalysts: above 923 K, the conversions were over 90% and  $Ce_{0.3}Ni_{2.5}Ca_{10}$  showed the best conversion (Fig. 1). The CO selectivities increased significantly while the  $CO_2$  selectivities were nearly the same or slightly higher when compared with the case of  $O_2/C_3H_8=1.5$  (Figs. 2 and 3). The  $CH_4$  selectivity with  $O_2/C_3H_8=2.0$ , was the highest in the temperature range of 873-973 K, but at 1,023 K and above it became much lower when compared with the case of  $O_2/C_3H_8=1.5$  (Fig. 4). Fig. 5 shows the remarkable effect of excess oxygen on ( $C_2+C_3$ ) selectivity. Compared with the case of  $O_2/C_3H_8=1.5$ , the ( $C_2+C_3$ ) selectivity with  $O_2/C_3H_8=2.0$  decreased drastically, and at 1,023 K it became practically zero. These results clearly show that hydrocarbon products ( $C_1 - C_3$ ) were more readily converted to CO and  $H_2$  when excess oxygen was fed, and hence the  $H_2$  yield improved significantly in the

**Table 1.**  $C_3H_8$  conversion, selectivities,  $H_2/CO$  ratio and  $H_2$  yield in POX of propane over  $Ni_{2.5}Ca_{10}$  catalyst ( $O_2/C_3H_8=1.5$ , VHSV=120,000  $cm^3/g\cdot h$ )

Temperature (K)		823	873	923	973	1,023	1,073
$C_3H_8$ conversion (%)		26.79	41.83	83.61	91.86	100	100
Selectivities (%)	CO	42.46	62.35	45.92	63.00	78.57	83.66
	$CO_2$	57.54	36.97	18.64	11.85	4.88	2.47
	$CH_4$	0	0.69	18.71	18.02	13.69	3.87
	$C_2H_4$	0	0	10.88	4.45	1.45	0
	$C_2H_6$	0	0	2.60	2.68	1.40	0
	$C_3H_6$	0	0	3.79	0	0	0
$H_2/CO$ ratio		1.68	1.21	1.83	1.71	1.45	1.32
$H_2$ yield (%)		14.31	23.59	52.67	74.17	85.24	82.98

**Table 2.**  $C_3H_8$  conversion, selectivities,  $H_2/CO$  ratio and  $H_2$  yield in POX of propane over  $Ce_{0.3}Ni_{2.5}Ca_{10}$  catalyst ( $O_2/C_3H_8=1.5$ , VHSV=120,000  $cm^3/g\cdot h$ )

Temperature (K)		823	873	923	973	1,023	1,073
$C_3H_8$ conversion (%)		28.65	72.02	88.24	88.29	100	100
Selectivities (%)	CO	28.42	22.72	44.43	59.18	83.36	77.84
	$CO_2$	71.58	23.10	14.80	11.12	3.01	2.51
	$CH_4$	0	10.62	13.61	17.94	13.63	19.65
	$C_2H_4$	0	27.42	19.01	6.45	0	0
	$C_2H_6$	0	2.01	2.86	3.45	0	0
	$C_3H_6$	0	14.16	5.28	1.86	0	0
$H_2/CO$ ratio		2.44	1.44	1.52	1.82	1.43	1.28
$H_2$ yield (%)		14.92	17.67	44.65	71.31	89.12	74.42

whole temperature range, as shown in Fig. 6. Although  $\text{Ni}_{2.5}\text{Ca}_{10}$  showed higher  $\text{H}_2$  yields at and below 873 K, ceria promoted catalysts showed higher  $\text{H}_2$  yields above 923 K, and  $\text{Ce}_{0.1}\text{Ni}_{2.5}\text{Ca}_{10}$  showed the highest  $\text{H}_2$  yields (83% at 923 K and 94% at 1,023 K, respectively).

The experiments were subsequently carried out with higher  $\text{O}_2/\text{C}_3\text{H}_8$  ratios (2.25 and 2.5). With these high  $\text{O}_2/\text{C}_3\text{H}_8$  ratios, ( $\text{C}_2+\text{C}_3$ )

hydrocarbons were not detected in the whole temperature range because excess oxygen enhanced partial or complete oxidation of hydrocarbons. Compared with the case of  $\text{O}_2/\text{C}_3\text{H}_8=2.0$ , the  $\text{CO}_2$  selectivity increased and the  $\text{H}_2$  yield decreased slightly. In order to compare the effects of the  $\text{O}_2/\text{C}_3\text{H}_8$  ratio together with three of the ceria content, representative results at 1,023 K are presented in Figs. 7-9. This temperature was chosen for comparison purpose because the

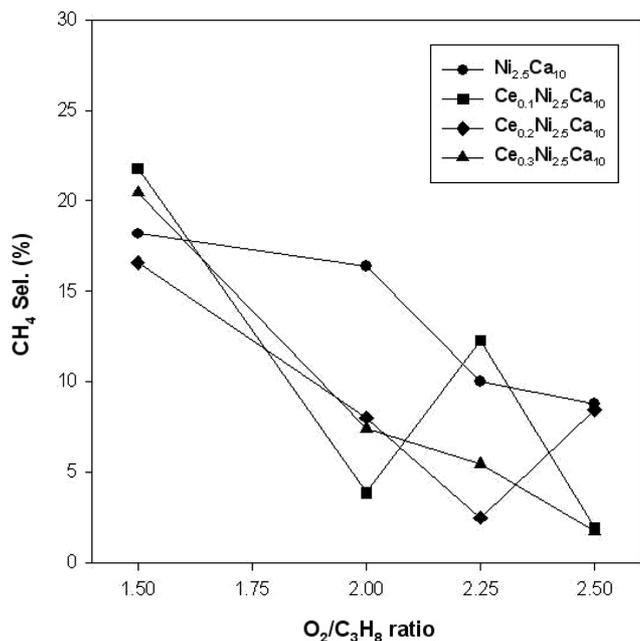


Fig. 7.  $\text{CH}_4$  selectivity vs.  $\text{O}_2/\text{C}_3\text{H}_8$  ratio over ceria promoted catalysts with different ceria contents at 1,023 K (catalyst charge = 0.05 g, VHSV = 120,000  $\text{cm}^3/\text{g}\cdot\text{cat}\cdot\text{h}$ ).

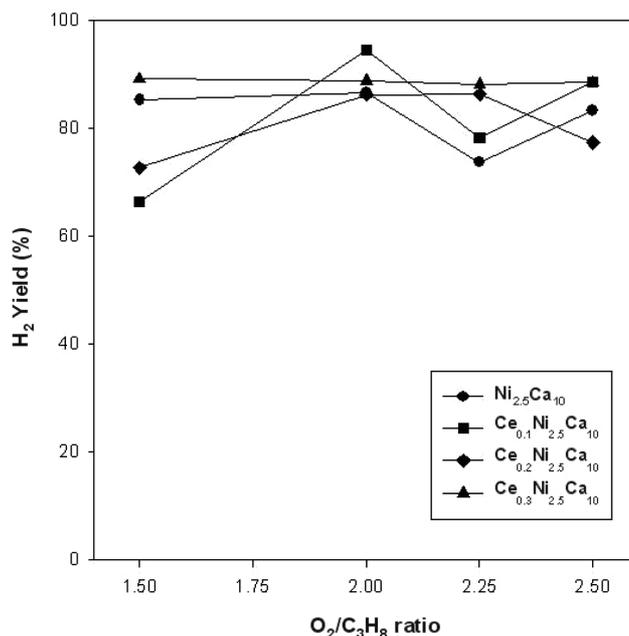


Fig. 9.  $\text{H}_2$  yield vs.  $\text{O}_2/\text{C}_3\text{H}_8$  ratio over ceria promoted catalysts with different ceria contents at 1,023 K (catalyst charge = 0.05 g, VHSV = 120,000  $\text{cm}^3/\text{g}\cdot\text{cat}\cdot\text{h}$ ).

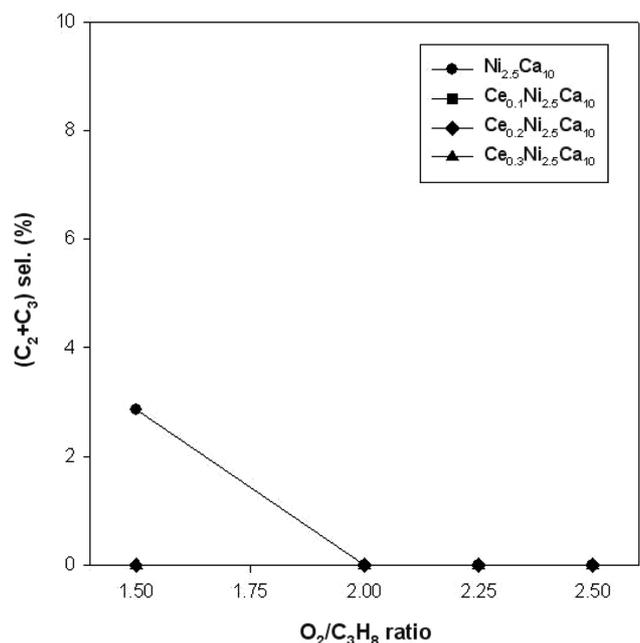


Fig. 8. ( $\text{C}_2+\text{C}_3$ ) selectivity vs.  $\text{O}_2/\text{C}_3\text{H}_8$  ratio over ceria promoted catalysts with different ceria contents at 1,023 K (catalyst charge = 0.05 g, VHSV = 120,000  $\text{cm}^3/\text{g}\cdot\text{cat}\cdot\text{h}$ ).

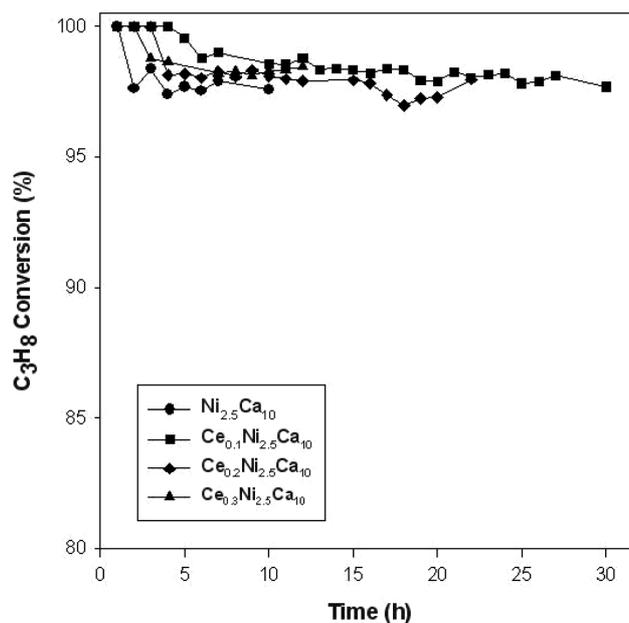


Fig. 10.  $\text{C}_3\text{H}_8$  conversion of durability test over ceria promoted catalysts with different ceria contents at 1,023 K (catalyst charge = 0.05 g,  $\text{O}_2/\text{C}_3\text{H}_8=2.0$ , VHSV = 120,000  $\text{cm}^3/\text{g}\cdot\text{h}$ ).

H<sub>2</sub> yield was almost the maximum and hydrocarbon selectivities were almost the minimum. Among the catalysts tested, ceria-promoted catalysts showed better performance than the unpromoted catalyst with the O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> ratio of 2.0 or higher. This indicates that excess oxygen played a key role by utilizing oxygen storage capacity of ceria [14,18,19], which promotes the partial oxidation of hydrocarbons.

### 3. Durability Test

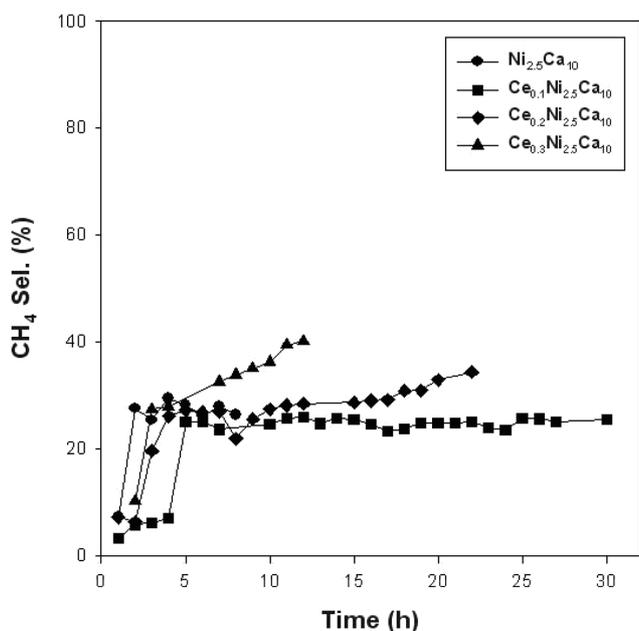


Fig. 11. CH<sub>4</sub> selectivity of durability test over ceria promoted catalysts with different ceria contents at 1,023 K (catalyst charge=0.05 g, O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>=2.0, VHSV=120,000 cm<sup>3</sup>/g·h).

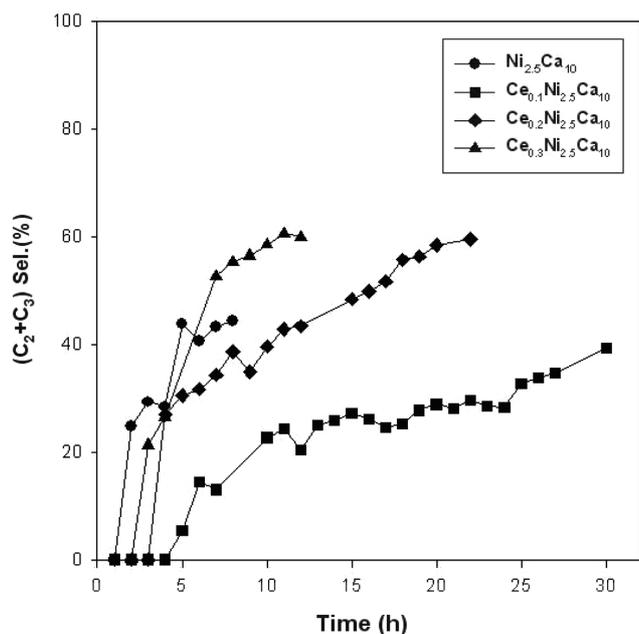


Fig. 12. (C<sub>2</sub>+C<sub>3</sub>) selectivity of durability test over ceria promoted catalysts with different ceria contents at 1,023 K (catalyst charge=0.05 g, O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>=2.0, VHSV=120,000 cm<sup>3</sup>/g·h).

As observed for the four catalysts tested, the optimal O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> ratio may be taken to be 2.0 on average and no (C<sub>2</sub>+C<sub>3</sub>) were produced at 1,023 K. Therefore, durability tests were carried out under these fixed conditions.

As shown in Fig. 10, all the catalysts exhibited C<sub>3</sub>H<sub>8</sub> conversion above 97%. The experiment over Ni<sub>2.5</sub>Ca<sub>10</sub> was stopped at 9 hours due to carbon deposition, which resulted in pressure build-up in the reactor (0.35 kgf/cm<sup>2</sup> gauge). In the case of Ce<sub>0.3</sub>Ni<sub>2.5</sub>Ca<sub>10</sub> it lasted only for 12 hours, because the H<sub>2</sub> yield was so low although the pressure in the reactor was not high.

Fig. 11 shows that the CH<sub>4</sub> selectivity over Ce<sub>0.2</sub>Ni<sub>2.5</sub>Ca<sub>10</sub> and Ce<sub>0.3</sub>Ni<sub>2.5</sub>Ca<sub>10</sub> increased with time more rapidly than that over the Ce<sub>0.1</sub>Ni<sub>2.5</sub>Ca<sub>10</sub>. Ce<sub>0.1</sub>Ni<sub>2.5</sub>Ca<sub>10</sub> exhibited constant CH<sub>4</sub> selectivity after a sudden increase at around 5 hours. Fig. 12 shows (C<sub>2</sub>+C<sub>3</sub>) selectivities increased quite rapidly over all the catalysts. However, the (C<sub>2</sub>+C<sub>3</sub>) selectivity over Ce<sub>0.1</sub>Ni<sub>2.5</sub>Ca<sub>10</sub> showed the slowest increase, reaching 40% at 30 hours. As shown in Fig. 13, Ce<sub>0.1</sub>Ni<sub>2.5</sub>Ca<sub>10</sub> showed the highest H<sub>2</sub> yield during the entire period of the test.

In the case of Ce<sub>0.1</sub>Ni<sub>2.5</sub>Ca<sub>10</sub>, the (C<sub>1</sub>+C<sub>2</sub>+C<sub>3</sub>) selectivity was low within 5 hours. However, it increased suddenly at 5 hours onstream and increased slowly after 5 hours. This shows that the partial oxidation was dominant during the initial 5 hours, but carbon deposition seemed to occur rapidly at this time. The reason for this sudden change is considered to be that when a certain critical portion of the active metal surface was covered with deposited carbon and became inactive, the removal of adsorbed carbon by oxidation (e.g., C(ad)+O(ad)→CO(ad)) was greatly inhibited and the carbon deposition was triggered and accelerated. As the deposited carbon blocked the active metal surface, thermal decomposition became dominant and produced more and more (C<sub>1</sub>+C<sub>2</sub>+C<sub>3</sub>). The other ceria-promoted catalysts showed high (C<sub>1</sub>+C<sub>2</sub>+C<sub>3</sub>) selectivity from 2 or 3 hours onstream. More rapid deactivation of these catalysts may be due to

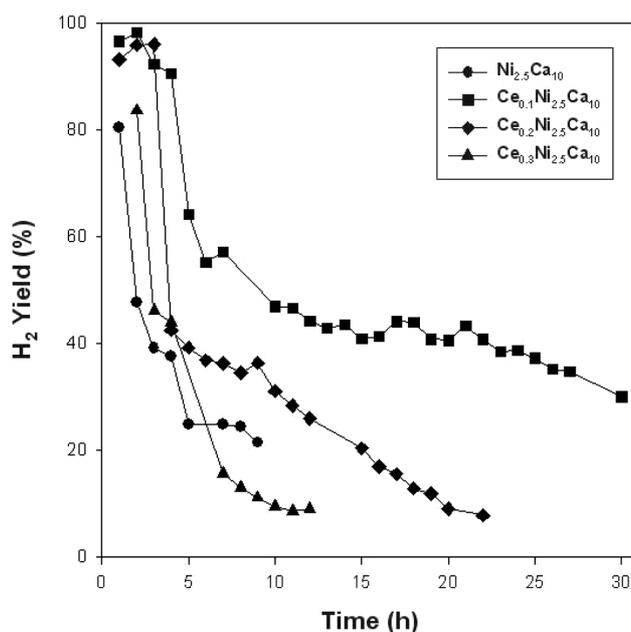


Fig. 13. H<sub>2</sub> yield of durability test over ceria promoted catalysts with different ceria contents at 1,023 K (catalyst charge=0.05 g, O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>=2.0, VHSV=120,000 cm<sup>3</sup>/g·h).

that the active metal surface area was originally smaller than that of  $Ce_{0.1}Ni_{2.5}Ca_{10}$ . When compared with POX of methane, propane is more prone to induce carbon deposition. Further improvement of the catalyst, especially for stability, may be required. Nevertheless, from the lower ( $C_1+C_2+C_3$ ) selectivity and higher  $H_2$  yield,  $Ce_{0.1}Ni_{2.5}Ca_{10}$  has the best stability in regard to activity and against carbon deposition among the catalysts investigated in this work.

### CONCLUSIONS

For partial oxidation of propane with ideal stoichiometric  $O_2/C_3H_8$  ratio of 1.5, the activity of  $Ni_{2.5}Ca_{10}$  was similar to or slightly better than that of the ceria-promoted catalysts. When more oxygen was fed, the  $C_3H_8$  conversion increased and the ( $C_1+C_2+C_3$ ) selectivity decreased, and thus the  $H_2$  yield was improved. Especially, the improvement by the ceria promoter was remarkable. Catalyst durability was also improved by ceria. The optimal  $O_2/C_3H_8$  ratio and ceria content (x) were determined to be 2.0 and 0.1, respectively. With the higher  $O_2/C_3H_8$  ratio, complete oxidation occurred to a greater extent, resulting in lower hydrogen yield. With the higher ceria content, the number of exposed active metal sites became less, resulting in lower partial oxidation activity and poorer durability.

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