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Partial oxidation of n-butane over ceria-promoted nickel/calcium hydroxyapatite

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Abstract−LPG has good infrastructure and is anticipated to be used for production of hydrogen, and n-butane which constitutes a main component of LPG for vehicles. Partial oxidation (POX) of n-butane is investigated in this research by employing ceria-promoted Ni/calcium hydroxyapatite catalysts ($Ce_xNi_{2.5}/Ca_{10}(OH)_2(PO_4)_6$ x=0.1-0.3) which have recently been reported to exhibit good catalytic performance in POX of methane and propane. The experiments were carried out with changing ceria content, O_2/n-C_4H_{10} ratio and reaction temperature. As the O_2/n-C_4H_{10} ratio increased up to 2.75, the n-C_4H_{10} conversion and H_2 yield increased and the selectivity of methane and other hydrocarbons decreased. But with O_2/n-C_4H_{10}=3.0, the n-C_4H_{10} conversion and H_2 yield decreased. $Ce_{0.1}Ni_{2.5}/Ca_{10}(OH)_2(PO_4)_6$ showed the highest n-C_4H_{10} conversion and H_2 yield on the whole. In durability tests, higher hydrogen yield and better catalyst stability were obtained with the O_2/n-C_4H_{10} ratio of 2.75 than with the ratio of 2.5.

Key words: Butane, Ceria, Hydrogen, Nickel, Partial Oxidation

INTRODUCTION

A fuel cell is an energy conversion device that produces electrical energy with higher conversion efficiency and lower pollutant emissions than combustion processes [1-3]. 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 [4]. Although hydrogen is the ideal fuel for a fuel cell, the use of other fuels such as methane, methanol, ethanol, liquefied petroleum gas (LPG), gasoline and other oil derivatives is also possible via internal or instack reforming [5-7]. Among these fuels, liquefied petroleum gas (LPG) is a commercial gas that is easily transported and has a well-developed infrastructure. The main components of LPG are propane and butane, and the butane has been widely used as fuels for vehicles and portable gas ranges [1,8].

Common methods of converting butane to hydrogen include steam reforming (SR), autothermal reforming (ATR), and partial oxidation (POX). Among these, POX systems have better dynamic response than a steam reforming system since they require minimal external heating and can be heated internally quickly by the exothermic reaction of the fuel. POX processes also attract much attention primarily because of the low energy requirement due to the opposite contribution of the exothermic hydrocarbon oxidation and endothermic steam reforming and also because of the high space velocity compared with the SR process [9].

Ceria-promoted nickel-calcium hydroxyapatite catalysts, which had recently been studied in our laboratory, showed high activity for partial oxidation of methane and propane [4-7,10]. Since the properties of propane and butane are not quite different, the above catalysts are expected to exhibit similar performance to that for the POX of propane. The objectives of this research are to find the optimal ceria content and operating conditions for partial oxidation of n-butane. This work focuses on the promotion effect of ceria and the optimal oxygen/n-butane molar feed ratio. Long-term durability tests were also carried out with fixed feed ratios at 1,023 K.

EXPERIMENTAL

1. Catalyst Preparation

Reagents used for preparing nickel/calcium hydroxyapatite catalysts ($Ni_{2.5}/Ca_{10}(OH)_2(PO_4)_6$) were as follows: calcium nitrate ($Ca(NO_3)_2\cdot H_2O$, Junsei Chemical, minimum 98%), dibasic ammonium phosphate ($(NH_4)_2HPO_4$, Shinyo Pure Chemical, minimum 98.5%), nickel nitrate ($Ni(NO_3)_2\cdot H_2O$, Shinyo Pure Chemical, minimum 97.0%), aqueous ammonia (NH_4OH, Yakuri Pure Chemical, above 28%), and cerium nitrate ($Ce(NO_3)_3\cdot H_2O$, Yakuri Pure Chemical, minimum 98.0%).

The catalysts were prepared by following the same procedure as described in a previous work [10]. Nearly saturated aqueous solutions 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 the 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_4 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 the previous work [10]. This catalyst without a promoter was named as $Ni_{2.5}Ca_{10}$.

Ceria-promoted catalysts were prepared by following the same procedure as described above except addition of the aqueous solu-

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tion 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 $Ce_aNi_{2.5}Ca_{10}$, where subscript "a", which is (Ce/Ni)×2.5, indicates the content of ceria in the catalyst.

2. Reaction Procedure and Apparatus

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) as the diluent. 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., n-butane and oxygen) and the diluents gas (argon) was introduced to the reactor. Due to its low vapor pressure, the butane feed line was maintained at 323 K by a heating coil that was rolled around the line from the gas cylinder to the reactor inlet. The partial pressure of butane was fixed at 0.10 atm, while oxygen was varied depending on O_2/n-C_4H_{10} molar ratio (2.0-3.0). Argon was used as balance to set the total flow rate 100 cm^3 (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 [10]. The subsequent 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 $CaCl_2$ trap to the analysis section, consisted of two on-line gas chromatographs (GC, Younglin M600D) in parallel. H_2, CO, CH_4, and CO_2 were analyzed by the first GC equipped with 1/8 inch Carboxen™ 1004 column (Supelco) with Ar carrier and a thermal conductivity detector (TCD). CO_2, CH_4, and other hydrocarbons were analyzed in the second GC, equipped with Hayesep™ Q column (Supelco) with He carrier and a TCD. Since CO_2 and CH_4 were detected by both the GCs, the component with higher concentration was chosen as the standard of balance. By comparing the two CH_4 or CO_2 areas from both the GCs, the amounts of the other components were determined. The mass balances for carbon, hydrogen and oxygen were generally within ±5%. The durability test was carried out at 1,023 K with the O_2/n-C_4H_{10} ratios of 2.5 and 2.75 for about 30 hours or until the hydrogen yield became below 20%.

RESULTS AND DISCUSSION

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

$$\text{Selectivity of A } (\%) = \frac{\text{moles of n-C}_4\text{H}_{10}\text{ converted to A}}{\text{total moles of n-C}_4\text{H}_{10}\text{ converted}} \times 100$$

$$= \frac{(\text{moles of A produced}) \times (\text{\# of carbon in 1 molecule of A})}{4(\text{total moles of n-C}_4\text{H}_{10}\text{ converted})} \times 100 \qquad (1)$$

The hydrogen yield was calculated by dividing moles of produced H_2 with 5 times of total moles of n-C_4H_{10} fed:

$$H_2 \text{ yield } (\%) = \frac{\text{moles of H}_2\text{ produced}}{5(\text{total moles of n-C}_4\text{H}_{10}\text{ fed})} \times 100 \qquad (2)$$

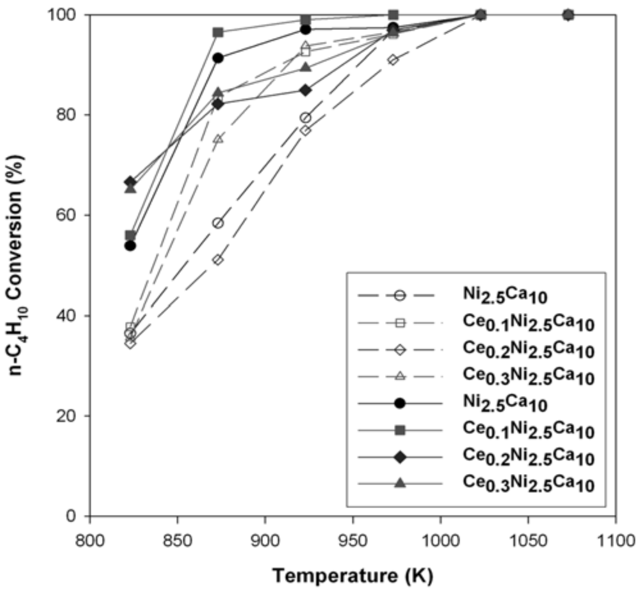

Fig. 1. n-C_4H_{10} conversion vs. temperature over the catalysts with different ceria contents (catalyst charge=0.05 g, VHSV= 120,000 cm^3/g-cat·h, open symbols: O_2/n-C_4H_{10}=2.0, closed symbols: O_2/n-C_4H_{10}=2.75).

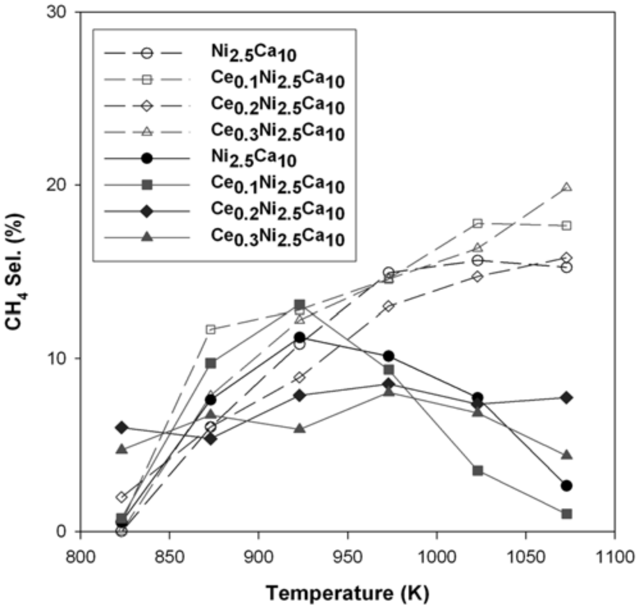

Fig. 2. CH_4 selectivity vs. temperature over the catalysts with different ceria contents (catalyst charge=0.05 g, VHSV=120,000 cm^3/g-cat·h, open symbols: O_2/n-C_4H_{10}=2.0, closed symbols: O_2/n-C_4H_{10}=2.75).

1. Effect of Ceria Content

1-1. Conversion and selectivity with O_2/n-C_4H_{10} feed ratio of 2.0

The n-C_4H_{10} conversions are shown with respect to temperature in Fig. 1, and the product selectivities are presented in Figs. 2-4. 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_2/n-C_4H_{10}=2.0: n-C_4H_{10}+$2O_2$→4CO+$5H_2$), less than 40% of n-butane was converted at 823 K. At 873 and 923 K, the

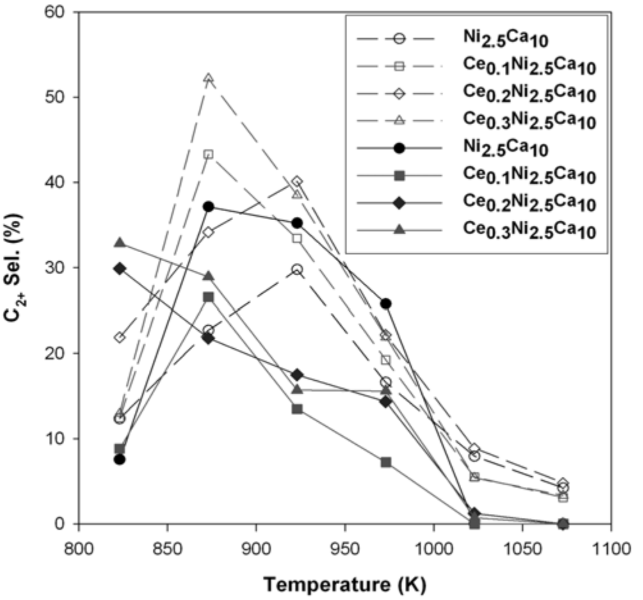

Fig. 3. C_{2+} selectivity vs. temperature over the catalysts with different ceria contents (catalyst charge=0.05 g, VHSV=120,000 cm^3/g-cat·h, open symbols: O_2/n-C_4H_{10}=2.0, closed symbols: O_2/n-C_4H_{10}=2.75).

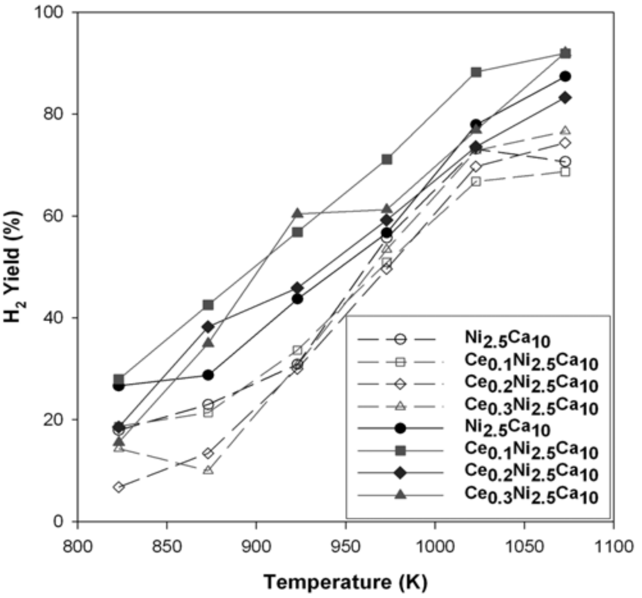

Fig. 4. H_2 yield vs. temperature over the catalysts with different ceria contents (catalyst charge=0.05 g, VHSV=120,000 cm^3/g-cat·h, open symbols: O_2/n-C_4H_{10}=2.0, closed symbols: O_2/n-C_4H_{10}=2.75).

n-butane conversion over $Ce_{0.1}Ni_{2.5}Ca_{10}$ was the highest while that over $Ce_{0.2}Ni_{2.5}Ca_{10}$ was the lowest, and the difference in the conversion was as large as 32%. Above 1,023 K, all the catalysts showed almost complete conversion. CH_4 selectivity gradually increased with temperature over all the catalysts and was the highest in the temperature range of 1,023-1,073 K (Fig. 2). The effect of ceria on the CH_4 selectivity was not pronounced. The C_{2+} (=C_2H_4, C_2H_6, C_3H_6 and 1-C_4H_8) selectivity exhibited highest in the temperature range of 873-923 K (Fig. 3). Among the by-products, C_2H_4 showed the highest selectivity (Tables 1 and 2). Above 923 K, the C_{2+} selectivity rapidly decreased with increasing temperature for all the catalysts. The H_2 yield accordingly increased with temperature, showing the maximum at 1,023-1,073 K (Fig. 4). The hydrocarbon selectivity (for CH_4 plus C_{2+}) was lower over $Ni_{2.5}Ca_{10}$ than over the other three catalysts. When the ceria content was high, the decomposition of n-butane or oxidative dehydrogenation would have occurred preferentially instead of partial oxidation. The reason is considered due to that the ceria would cover a significant portion of metal active sites on the catalyst surface and to that the oxygen was not supplied sufficiently, which gives rise to lower oxidation activity. Moreover, the higher ceria content resulted in lower activity due to covering of more active metal sites. The amount of the exposed active Ni species may be determined by the H_2 chemisorption in order to confirm the covering effect of ceria. However, although the hydrogen chemisorption experiments were performed with a volumemetric adsorption apparatus, the amounts of H_2 chemisorbed were so small that they were in the almost in the error range of the measurement (less than 0.33 cm^3 (STP) H_2/g_{cat} or the percentages exposed of Ni less than 1.2%). Similar results have already been reported in a previous work [14]. Therefore, it was hard to confirm the above suggestion by the H_2 chemisorption experiments, especially for the catalysts in this work.

Table 1. n-C_4H_{10} conversion, selectivities, H_2/CO ratio and H_2 yield in POX of n-butane over $Ni_{2.5}Ca_{10}$ catalyst (O_2/n-C_4H_{10}=2.0, VHSV=120,000 cm^3/g-cat·h)

Temperature (K)		823	873	923	973	1023	1073
C_4H_{10} conversion (%)		36.46	58.38	79.41	96.90	100	100
Selectivities (%)	CO	24.72	38.01	36.07	56.40	70.62	77.81
	CO_2	62.94	33.24	23.34	12.10	5.81	2.77
	CH_4	0	6.03	10.83	14.92	15.63	15.23
	C_2H_4	0	17.26	21.31	13.68	5.71	2.88
	C_2H_6	0	0	2.44	2.91	2.22	1.32
	C_3H_6	12.34	0.75	1.16	0	0	0
	1-C_4H_8	0	4.70	4.86	0	0	0
H_2/CO ratio		2.49	1.29	1.35	1.27	1.29	1.13
H_2 yield (%)		17.92	22.95	30.86	55.71	73.12	70.62

1-2. Conversion and Selectivity with Higher O_2/n-C_4H_{10} Feed Ratio

Since significant amounts of the hydrocarbon products were observed with the O_2/n-C_4H_{10} molar ratio of 2.0, the molar ratio of O_2/n-C_4H_{10} was increased up to 3.0 in order to convert the hydrocarbons to CO and H_2 to a greater extent by partial oxidation. Representative product distributions are given in Tables 3 and 4. Compared with the case of O_2/n-C_4H_{10}=2.0, the n-C_4H_{10} conversion became higher in the whole temperature range over all the catalysts (Fig. 1). In the case of O_2/n-C_4H_{10}=2.75, the conversions over all the catalysts were over 90% above 973 K and $Ce_{0.1}Ni_{2.5}Ca_{10}$ showed the highest conversion. The conversion obtained with the O_2/n-C_4H_{10}=2.5 was similar to that with the ratio of 2.75. Compared with the cases of the O_2/n-C_4H_{10} ratio of 2.5 and 2.75, the conversion obtained with the O_2/n-C_4H_{10}=3.0 was lower particularly at low tem-

Table 2. n-C_4H_{10} conversion, selectivities, H_2/CO ratio and H_2 yield in POX of n-butane over $Ce_{0.1}Ni_{2.5}Ca_{10}$ catalyst (O_2/n-C_4H_{10}=2.0, VHSV=120,000 cm^3/g-cat·h)

Temperature (K)		823	873	923	973	1023	1073
C_4H_{10} conversion (%)		37.80	83.56	92.60	96.13	100	100
Selectivities (%)	CO	24.24	25.38	36.47	53.26	71.32	76.68
	CO_2	62.82	19.65	17.30	12.95	5.42	2.58
	CH_4	0.50	11.68	12.79	14.57	17.77	17.65
	C_2H_4	0.76	32.14	25.37	12.41	2.97	1.74
	C_2H_6	0	2.32	2.80	3.37	2.52	1.35
	C_3H_6	10.54	0.20	0.77	2.68	0	0
	1-C_4H_8	1.15	8.63	4.49	0.77	0	0
H_2/CO ratio		2.54	1.26	1.25	1.24	1.17	1.12
H_2 yield (%)		18.65	21.40	33.65	50.90	66.77	68.69

Table 3. n-C_4H_{10} conversion, selectivities, H_2/CO ratio and H_2 yield in POX of n-butane over $Ni_{2.5}Ca_{10}$ catalyst (O_2/n-C_4H_{10}=2.75, VHSV=120,000 cm^3/g-cat·h)

Temperature (K)		823	873	923	973	1023	1073
C_4H_{10} conversion (%)		53.89	91.35	97.07	97.47	100	100
Selectivities (%)	CO	40.44	23.84	38.45	52.46	76.84	88.59
	CO_2	51.48	31.42	26.33	21.78	15.43	8.77
	CH_4	0.54	7.61	11.21	10.13	7.74	2.64
	C_2H_4	0	17.67	10.57	2.15	0	0
	C_2H_6	0	1.82	1.94	1.46	0	0
	C_3H_6	7.54	17.64	11.5	12.03	0	0
	1-C_4H_8	0	0	0	0	0	0
H_2/CO ratio		1.53	1.65	1.46	1.39	1.27	1.23
H_2 yield (%)		26.65	28.71	43.7	56.66	77.9	87.35

Table 4. n-C_4H_{10} conversion, selectivities, H_2/CO ratio and H_2 yield in POX of n-butane over $Ce_{0.1}Ni_{2.5}Ca_{10}$ catalyst (O_2/n-C_4H_{10}=2.75, VHSV=120,000 cm^3/g-cat·h)

Temperature (K)		823	873	923	973	1023	1073
C_4H_{10} conversion (%)		56	96.51	99	100	100	100
Selectivities(%)	CO	38.15	36.88	48.33	67.47	86.46	90.29
	CO_2	52.27	26.82	25.09	15.94	10.01	8.69
	CH_4	0.77	9.73	13.1	9.36	3.53	1.02
	C_2H_4	0	14.82	2.96	0	0	0
	C_2H_6	0	1.72	1.42	0	0	0
	C_3H_6	8.81	10.02	9.1	7.23	0	0
	1-C_4H_8	0	0	0	0	0	0
H_2/CO ratio		1.63	1.49	1.49	1.32	1.28	1.27
H_2 yield (%)		27.95	42.54	56.85	71.12	88.25	91.92

peratures between 823 and 873 K (the data not shown for brevity). With the O_2/n-C_4H_{10} ratio of 2.75, the CH_4 selectivity increased with temperature up to 923 or 973 K and then decreased at higher temperatures. This is different from the trend observed with the O_2/n-C_4H_{10} ratio of 2.0 where the CH_4 selectivity increased with increasing temperature up to 1,073 K. $Ce_{0.1}Ni_{2.5}Ca_{10}$ showed the highest CH_4 selectivity at 923 K, but yielded the lowest CH_4 selectivity at and above 1,023 K.

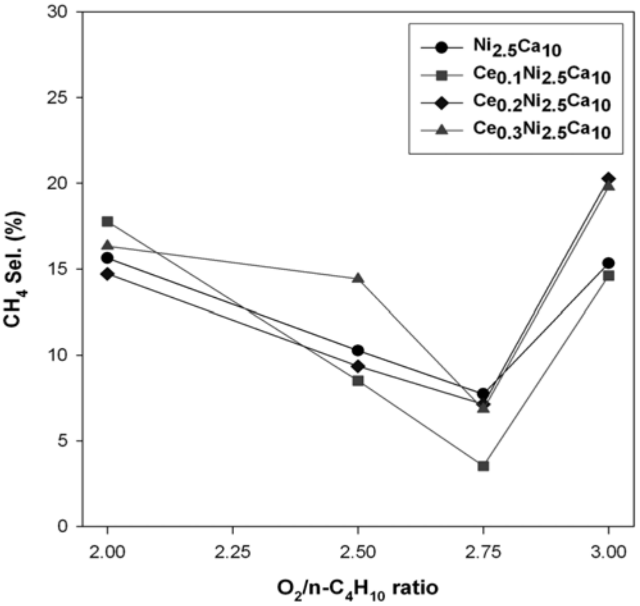

Fig. 5. CH_4 selectivity vs. O_2/n-C_4H_{10} ratio over the catalysts with different ceria contents at 1,023 K (catalyst charge=0.05 g, VHSV=120,000 cm^3/g-cat·h).

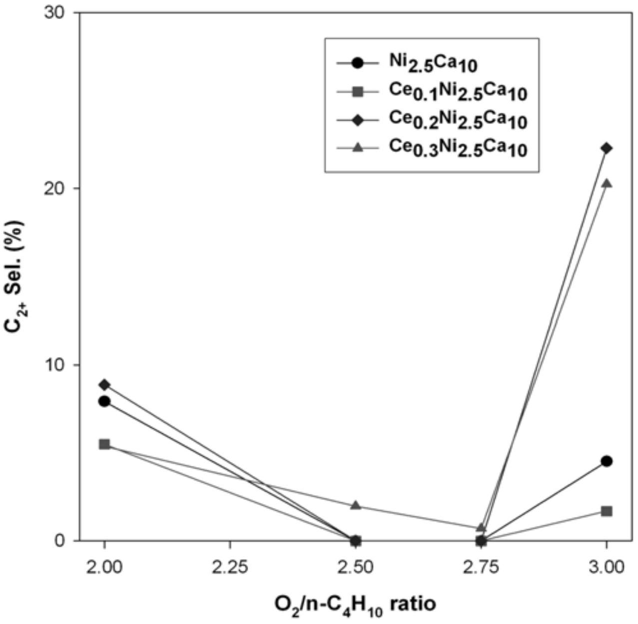

Fig. 6. C_{2+} selectivity vs. O_2/n-C_4H_{10} ratio over the catalysts with different ceria contents at 1,023 K (catalyst charge=0.05 g, VHSV=120,000 cm^3/g-cat·h).

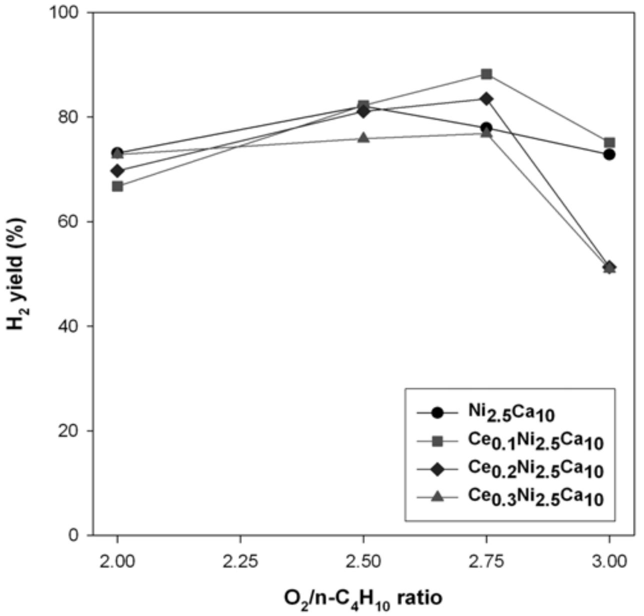

Fig. 7. H_2 yield vs. O_2/n-C_4H_{10} ratio over the catalysts with different ceria contents at 1,023 K (catalyst charge=0.05 g, VHSV=120,000 cm^3/g-cat·h).

Fig. 3 and Tables 3 and 4 show a marked effect of excess oxygen on the C_{2+} selectivity. Compared with the case of the O_2/n-C_4H_{10} ratio of 2.0, the C_{2+} selectivity with the O_2/n-C_4H_{10} ratio of 2.75 decreased drastically, and at 1,023 K it became practically zero. These results clearly show that hydrocarbon products were more readily converted to CO and H_2 when excess oxygen was fed, and hence the H_2 yield improved significantly in the whole temperature range, as shown in Fig. 4. $Ce_{0.1}Ni_{2.5}Ca_{10}$ exhibited the lowest C_{2+} selectivity and the highest H_2 yield in the whole temperature. On the whole the unpromoted catalyst $Ni_{2.5}Ca_{10}$ yielded higher C_{2+} selectivity. This indicates that some excess oxygen is required in utilizing the oxygen storage capacity of ceria [11-13], which promotes the partial oxidation of hydrocarbons.

The effects of the O_2/n-C_4H_{10} feed ratio and the ceria content are summarized in Figs. 5-7 by comparing the data obtained at 1,023 K. The CH_4 selectivity (Fig. 5) decreased gradually as the O_2/n-C_4H_{10} ratio increased from 2.0 to 2.75 but increased sharply at the O_2/n-C_4H_{10} ratio of 3.0. The C_{2+} selectivity showed similar trend. Particularly in the cases of O_2/n-C_4H_{10}=2.5 and 2.75, the C_{2+} selectivity became practically zero over $Ce_{0.1}Ni_{2.5}Ca_{10}$. Accordingly, H_2 yield (Fig. 7) over all the catalysts was the highest with the O_2/n-C_4H_{10} ratio of 2.75, and $Ce_{0.1}Ni_{2.5}Ca_{10}$ showed the highest yield (~90%) with this O_2/n-C_4H_{10} ratio. In case of O_2/n-C_4H_{10}=3.0, the H_2 yield decreased sharply for all the catalysts. This is considered because too much oxygen may inhibit the reduction of Ni or induce the oxidation of Ni, which results in poorer catalytic activity.

2. Durability Test

The stability of the catalyst is an important concern in partial oxidation over the nickel catalyst which is prone to induce coke formation. Durability tests were carried out with a fixed O_2/n-C_4H_{10} ratio (2.5 or 2.75) at 1,023 K and the results are shown in Figs. 8-10.

With the O_2/n-C_4H_{10} ratio of 2.5, the experiment over $Ni_{2.5}Ca_{10}$ was stopped at 21 hours due to severe carbon deposition, which resulted in pressure build-up in the reactor. Over $Ce_{0.2}Ni_{2.5}Ca_{10}$ it

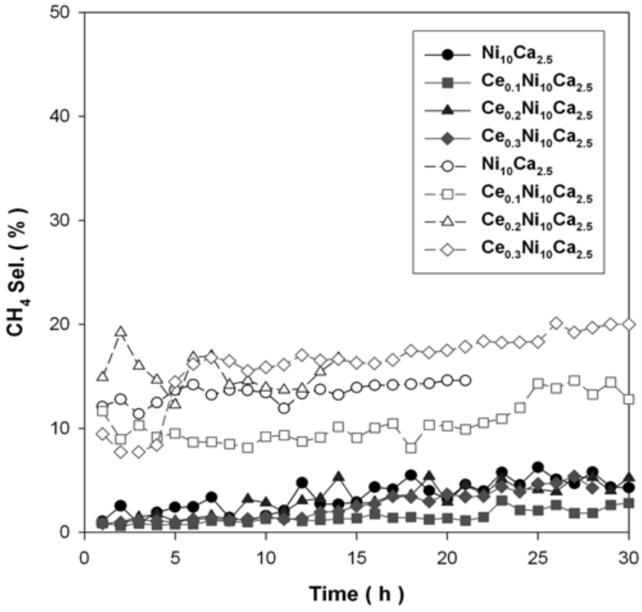

Fig. 8. **CH_4 selectivity during durability test over the catalysts with different ceria contents at 1,023 K (catalyst charge=0.05 g, VHSV=120,000 cm^3/g-cat·h, open symbols: O_2/n-C_4H_{10}=2.5, closed symbols: O_2/n-C_4H_{10}=2.75).**

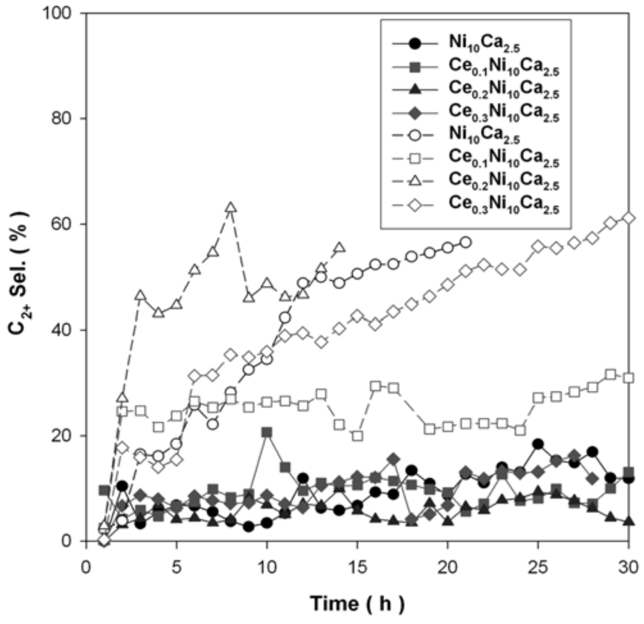

Fig. 9. **C_{2+} selectivity during durability test over the catalysts with different ceria contents at 1,023 K (catalyst charge=0.05 g, VHSV=120,000 cm^3/g-cat·h, open symbols: O_2/n-C_4H_{10}=2.5, closed symbols: O_2/n-C_4H_{10}=2.75).**

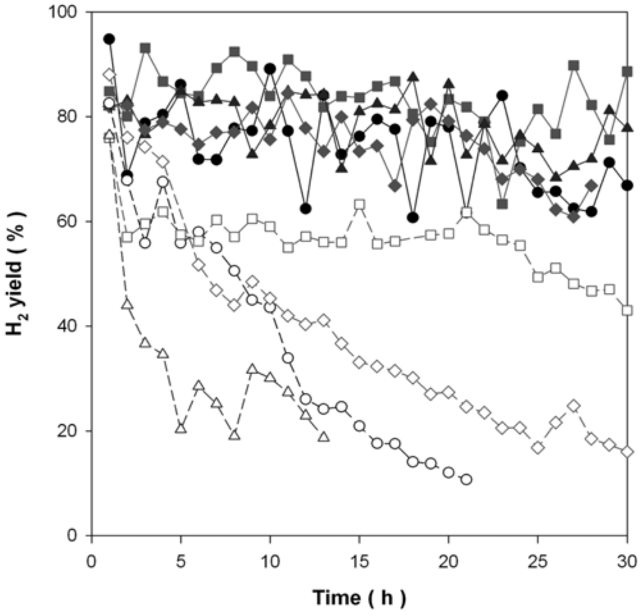

Fig. 10. **H_2 yield during durability test over the catalysts with different ceria contents at 1,023 K (catalyst charge=0.05 g, VHSV=120,000 cm^3/g-cat·h, open symbols: O_2/n-C_4H_{10}=2.5, closed symbols: O_2/n-C_4H_{10}=2.75; ○, ●: $Ni_{2.5}Ca_{10}$, □, ■: $Ce_{0.1}Ni_{2.5}Ca_{10}$, △, ▲: $Ce_{0.2}Ni_{2.5}Ca_{10}$, ◇, ◆: $Ce_{0.3}Ni_{2.5}Ca_{10}$).**

lasted only 14 hours because the H_2 yield was so low. The CH_4 selectivity (Fig. 8) gradually increased with time over all the catalysts. $Ce_{0.1}Ni_{2.5}Ca_{10}$ showed the lowest CH_4 selectivity. The C_{2+} selectivity (Fig. 9) increased quite rapidly over all the catalysts. Among them, $Ce_{0.1}Ni_{2.5}Ca_{10}$ showed the slowest increase, reaching 30% at 30 hours. In Fig. 10, $Ce_{0.1}Ni_{2.5}Ca_{10}$ showed the highest H_2 yield during the entire period of the test.

In the case of the O_2/n-C_4H_{10} ratio of 2.75, all the catalysts showed very low CH_4 selectivity (<5%) and C_{2+} selectivity (<10%) compared with the case of the O_2/n-C_4H_{10} ratio of 2.5 (Fig. 8, 9), and thus the H_2 yield became much higher (Fig. 10). Among the catalysts tested, $Ce_{0.1}Ni_{2.5}Ca_{10}$ showed constant and the lowest hydrocarbon selectivity and the highest H_2 yield for 30 hours. In summary, $Ce_{0.1}Ni_{2.5}Ca_{10}$ has the best stability in regard of activity and carbon deposition and the higher hydrogen yield and better catalyst stability were obtained with the O_2/n-C_4H_{10} ratio of 2.75 than with the ratio of 2.5. In other words, the O_2/n-C_4H_{10} ratio of 2.75 is the optimum which best utilizes the oxygen storage capacity of ceria but does not induce the deterioration of Ni by too excessive oxidation.

CONCLUSIONS

For partial oxidation of n-butane with ideal stoichiometric O_2/n-C_4H_{10} ratio of 2.0, all the catalysts showed similar activity and the promotion effect of ceria was not pronounced. When more oxygen was fed, the n-C_4H_{10} conversion increased and the hydrocarbon selectivity decreased, and thus the H_2 yield was improved. Especially, the improvement by the ceria promoter was remarkable owing to the oxygen storage capacity of ceria. The durability of the catalyst was also improved by ceria. The optimal O_2/n-C_4H_{10} ratio and ceria content (x) were determined to be 2.75 and 0.1, respectively. With the higher O_2/n-C_4H_{10} 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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REFERENCES

1. N. Laosiripojana and S. Assabumrungrat, *J. Power Source*, **158**, 1348 (2006).
2. N. Katsutoshi, S. Katsutoshi, N. Hiroyasu and T. Yasaku, *Appl. Catal. A*, **327**, 139 (2007).
3. D. G. Loffler, K. Taylor and D. Manson, *J. Power Source*, **117** 84 (2003).
4. S. Y. Lee, J. H. Kwak, M. S. Kim, S. W. Nam, T. H. Lim, S. A. Hong and K. J. Yoon, *Korean J. Chem. Eng.*, **24**, 226 (2007).
5. J. H. Jun, S. J. Lee, S. H. Lee, T. J. Lee, S. J. Kong, T. H. Lim, S. W. Nam, S. A. Hong and K. J. Yoon, *Korean J. Chem. Eng.*, **20**, 829 (2003).
6. K. H. Kim, S. Y. Lee and K. J. Yoon, *Korean J. Chem. Eng.*, **23**, 356 (2006).
7. K. H. Kim, S. Y. Lee, S. W. Nam, T. H. Lim, S. A. Hong and K. J. Yoon, *Korean J. Chem. Eng.*, **23**, 17 (2006).
8. A. K. Avci, D. L. Trimm, A. E. Aksoylu and Z. I. Nsan, *Appl. Catal. A*, **258**, 235 (2004).
9. D. J. Moon, J. W. Ryu, S. D. Lee and B. S. Ahn, *Korean J. Chem. Eng.*, **19**, 921 (2002).
10. J. H. Jun, K. S. Jeong, T. J. Lee, S. J. Kong, T. H. Lim, S. W. Nam, S. A. Hong and K. J. Yoon, *Korean J. Chem. Eng.*, **21**, 140 (2004).
11. B. S. Shin, J. H. Bae, J. P. Yoo, S. J. Choung, Y. I. Song and G. K. Yeo, *Korean J. Chem. Eng.*, **15**, 474 (1998).
12. L. V. Mattos, E. R. de Oliveira, P. D. Resende, F. B. Noronha and F. B. Passos, *Catal. Today*, **77**, 245 (2002).
13. L. V. Mattos and F. B. Noronha, *J. Catal*., **233**, 453 (2005).
14. J. H Jun, T. J. Lee, T. H. Lim, S. W. Nam, S. A. Hong and K. J. Yoon, *J. Catal*., **221**, 178 (2004).