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Partial oxidation of ethane to synthesis gas over Co-loaded catalysts

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Abstract

Attention has been increasingly paid to the partial oxidation of lower alkanes to synthesis gas, due to its intrinsic energy saving process. We studied the partial oxidation of ethane (POE) on Co loaded on various supports. The POE performance varied as follows: Y_2O_3, CeO_2, ZrO_2, $La_2O_3 \gg SiO_2$, Al_2O_3, $TiO_2 > MgO$. Comparing Y_2O_3 and CeO_2, the carbon deposition during the POE was negligible on CeO_2 and therefore CeO_2 was the most preferable support. By changing space velocity and O_2 partial pressure, reaction mechanism of POE was studied and it was revealed that two-step mechanism was prevailing; combustion of ethane to H_2O and CO_2 and subsequent reforming of ethane with H_2O and CO_2 to synthesis gas. Co/CeO_2 catalyst exhibited high and stable catalytic activity for 10 h; high ethane conversion of 18% (maximum ethane conversion 20% at $O_2/C_2H_6 = 0.2$) with H_2 and CO selectivities of 93 and 84%, respectively.

Keywords: Partial oxidation; Ethane; Catalyst; Cobalt

1. Introduction

Hydrogen production from natural gas has been conducted by the steam reforming (SR) (reaction (1)) [1]:

$$CH_4 + H_2O \rightarrow 3H_2 + CO \quad \Delta H^0_{298} = +206\,\mathrm{kJ/mol} \tag{1}$$

The reaction (1) is highly endothermic and is run at a high temperature, nearly 1073 K. This energy consuming reaction is, as a result, exhausting a large amount of CO_2 into the atmosphere.

On the other hand, the catalytic partial oxidation of methane (POM) (reaction (2)) is an exothermic reaction and has the advantage that it proceeds at lower temperatures than the reaction (1). Since Ashcroft et al. [2] recalled attention to this reaction in 1990, this field of chemistry has attracted much interest of many researchers [2–7]:

$$CH_4 + 1/2O_2 \rightarrow 2H_2 + CO \quad \Delta H^0_{298} = -36\,\mathrm{kJ/mol} \tag{2}$$

We have found that Ir-loaded TiO_2 catalyst exhibited high methane conversion at a low temperature of 873 K without carbon deposition that is one of the problems in this reaction (2) [8]. However, iridium is a precious metal with limited reserves, and it might be of slight difficulty to apply to an industrial process. Therefore, it is desired to exploit a new catalyst for industrial use. Though Ni-loaded catalysts have been used for the steam reforming, when they are used for the catalytic partial oxidation, they suffer from sintering and carbon deposition [9,10].

To overcome this, Takehira et al. [11] applied solid-phase crystallization method to Ni-loaded $MgO–Al_2O_3$ catalyst, which had highly dispersed Ni metal and high durability against coke deposition.

Ethane and propane have smaller H/C ratios than methane, and for the partial oxidation of such alkanes, superior characteristics to carbon deposition are required:

$$C_2H_6 + O_2 \rightarrow 3H_2 + 2CO \quad \Delta H^0_{298} = -136\,\mathrm{kJ/mol} \tag{3}$$

The final objective of carrying out the partial oxidation of ethane (POE) (reaction (3)) is in a direct use of natural gas, typically ca. 90% of methane and ca. 6% of ethane [12], at the

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on-site gas field without separating respective components. A few studies have been reported using Ni-loaded catalysts [13] and noble metal-loaded catalysts [14] in the POE. For example, Liu et al. [12] carried out the partial oxidation of natural gas to synthesis gas over LiLaNiO/γ-Al_2O_3 catalyst and reported that the catalyst maintained high activity for 500 h. Dai et al. [15] reported that M/BCS (M = Ni, Co; BCS = 30 mol% $BaCl_2$/Sm_2O_3) catalyst afforded a high activity for synthesis gas and ethylene production on the POE.

Although many studies with the Co-loaded catalysts are reported in the POM [5–7,16–20], there remain rooms for POE with Co-loaded catalysts. Recently, we have found that Co-loaded oxidized diamond catalysts afforded high activity for the POM and POE at 923 K without carbon deposition for prolonged run [20,21].

This paper deals with the POE on Co-loaded catalysts, and reports that CeO_2 was a promising support for this reaction.

2. Experimental

2.1. Catalyst preparation

The catalyst supports used in this study were CeO_2, Y_2O_3, SiO_2 (Wako Pure Chemical Industries Ltd.), Al_2O_3 (Sumitomo Chemical Co.), MgO (1000A; Ube Industries Ltd.), TiO_2 (P25; Japan Aerosil Co.), La_2O_3 and ZrO_2 (Nacalai Tesque Inc.). CeO_2 and Y_2O_3 were prepared by thermal decomposition of $Ce(NO_3)_3\cdot 6H_2O$ and $(CH_3COO)_3Y\cdot 4H_2O$ (Wako Pure Chemical Industries Ltd.) at 873 K under air for 5 h, respectively.

The supported cobalt catalysts containing 0.5–3 wt.% of Co as metal were prepared by impregnating the suspended supports with an aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ (Wako Pure Chemicals Ltd.), followed by evaporation-to-dryness under vacuum. Supported catalyst precursors were calcined at 873 K for 5 h in air prior to the reaction. After the calcination, the catalysts were crashed and sieved to pass 100 mesh. The surface areas of the supports and catalysts are shown in Table 1.

2.2. Catalytic reaction

The partial oxidation of ethane was carried out with a fixed-bed flow-type quartz reactor (8 mm i.d. × 350 mm length and 4 mm i.d. × 200 mm length) at a temperature range of 823–1023 K under an atmospheric pressure. After placing a 60 mg (20, 30 or 120 mg) of the catalyst in the reactor, it was reduced at 873 K for 1 h before the reaction in 10 mL/min of H_2 and 20 mL/min of Ar. Then O_2 and C_2H_6 were introduced with a molar ratio from 1:5 to 1:1. Total gas flow rate was fixed at 30 mL/min. Products (H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6 and O_2) were analyzed with an online high speed gas chromatograph equipped with TCD detectors (PC-Chrom, M200 Chromato Analyzer) using Molecular Sieve 5A and Poraplot Q columns. Selectivities to CO, CO_2, CH_4 and C_2H_4 were calculated from the absolute amounts of produced CO, CO_2, CH_4 and C_2H_4 against C_2H_6 conversion. H_2 selectivity was calculated similarly provided that reactions (3) and (4) were only proceeded. Amounts of H_2O and carbon deposited were obtained by the weights of H_2O in a water trap and the catalyst bed.

Table 1
Surface areas of various supports and Co (2.0 wt.%)-loaded catalysts

Catalyst	SA (m^2/g) [support]	SA (m^2/g)
Co/Y_2O_3	3	10
Co/CeO_2	62	51
Co/ZrO_2	46	40
Co/La_2O_3	1	8
Co/SiO_2	197	171
Co/Al_2O_3	152	140
Co/TiO_2	46	29
Co/MgO	16	30

These samples were calcined for 5 h at 873 K. SA: surface area.

2.3. Catalyst characterization

Surface area of the support and catalyst was measured by the BET method using N_2 at 77 K with an automatic Micromeritics Gemini 2375.

A JEOL JEM2010 was used to obtain high-resolution transmission electron microscope (HR-TEM) images at 200 kV and a JEOL field emission scanning electron microscope (FE-SEM) JSM6700 was employed to evaluate the catalyst surface.

3. Results and discussion

3.1. Activities of Co-loaded catalysts in the partial oxidation of ethane

Influence of various support materials on ethane conversion and composition of effluent gas was examined (Fig. 1). In order to evaluate resistance to carbon deposition, non-stoichiometric

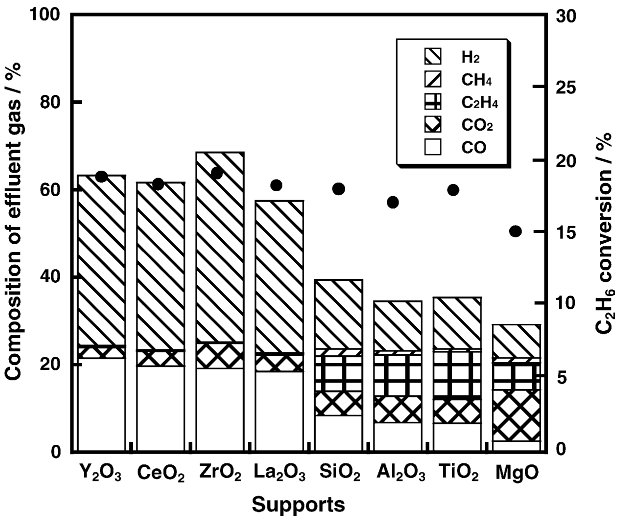

Fig. 1. Performance of Co (2 wt.%)-loaded catalysts on the C_2H_6 conversion and product composition in the partial oxidation of ethane. Catalyst: 60 mg, flow rate: 30 mL/min (O_2/C_2H_6 = 0.2), space velocity: 30,000 (mL h^{-1} g-cat^{-1}), reaction temperature: 923 K. Catalysts were reduced with H_2 for 1 h at 873 K before the reaction.

Table 2
Effect of Co-loading level on CeO_2 on the partial oxidation of ethane

Loading level	Conv. (%) C_2H_6	Eff. conv. C_2H_6	Conv. (%) O_2	Selectivity (%)					H_2/CO (ratio)	H_2O (mmol)	Carbon (mmol)
				H_2	CO	CO_2	C_2H_4	CH_4			
No catalyst	28.9	4.6	98.2	3.8	14.6	0.6	74.9	9.4	0.4	40.4	0.39
0.0	11.7	5.7	100.0	14.4	4.2	44.8	49.4	1.6	5.2	24.3	0.01
0.5	15.6	15.2	100.0	86.3	74.3	23.2	1.5	0.9	1.7	7.5	0.07
1.0	18.0	17.5	100.0	90.5	82.3	15.0	1.0	1.4	1.7	5.1	0.13
2.0	17.7	17.3	100.0	92.6	83.7	14.0	1.3	0.9	1.7	3.8	0.02
3.0	18.2	17.5	100.0	92.7	86.3	7.3	1.1	2.4	1.6	2.8	1.48

Catalyst: 60 mg, flow rate: $C_2H_6/O_2 = 25$ mL/min/5 mL/min, space velocity: 30,000 mL h^{-1} g-cat^{-1}. Reaction time: 2 h, reaction temperature: 923 K. Effective C_2H_6 conversion indicates the C_2H_6 conversion to synthesis gas and CO_2. Catalysts were reduced with H_2 for 1 h at 873 K.

O_2/C_2H_6 (0.2) feed ratio was employed intentionally. The maximum ethane conversion is limited to 20%, if only reaction (3) proceeds. On the other hand, if the complete oxidation (reaction (4)) occurs, ethane conversion is calculated as 5.7%:

$$C_2H_6 + 7/2O_2 \rightarrow 3H_2O + 2CO_2 \quad \Delta H^0_{298} = -1428\,\text{kJ/mol} \tag{4}$$

As shown in Fig. 1, ethane conversions were in the range from 15 to 20% in all the support materials. The order of the catalytic activity for synthesis gas production was Y_2O_3, CeO_2, ZrO_2, $La_2O_3 \gg SiO_2$, Al_2O_3, $TiO_2 > MgO$. POE on catalysts supported on Y_2O_3, CeO_2, ZrO_2 and La_2O_3 give predominantly H_2 and CO. With SiO_2, Al_2O_3, TiO_2 and MgO as support materials; however, oxidative dehydrogenation of ethane (reaction (5)) occurred to give large amounts of ethene and H_2O, in addition to the deep oxidation of ethane to H_2O and CO_2:

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \quad \Delta H^0_{298} = -105\,\text{kJ/mol} \tag{5}$$

Over Co/Y_2O_3, the highest yield of synthesis gas was obtained with H_2 and CO selectivities of 92 and 87%, respectively. However, carbon deposition by the decomposition of ethane (reaction (6)) was observed with this catalyst after the reaction for 2 h. Although Co/CeO_2 catalyst exhibited slightly lower ethane conversion and selectivity for CO compared to Co/Y_2O_3, no significant carbon deposition was observed. Therefore, CeO_2 was selected as the best support material for Co in the POE and used in the following study:

$$C_2H_6 \rightarrow H_2 + CH_4 + C \quad \Delta H^0_{298} = +10\,\text{kJ/mol} \tag{6}$$

3.2. Effect of Co-loading level over CeO_2 on the POE

Table 2 illustrates the effect of Co-loading level on the effective ethane conversion to synthesis gas and CO_2, product selectivities, H_2/CO ratio, the amount of H_2O and the amount of carbon deposited on the catalyst. Here, the effective conversion was calculated by subtracting the amount of ethane converted to ethene and methane from the total ethane conversion. Without Co-loading, CeO_2 alone afforded ethane (reaction (7)), H_2O and CO_2 and the selectivity to synthesis gas was very low, indicating that Co on CeO_2 is essential for the POE. Otsuka et al. [22] reported that CeO_2 reacted with CH_4 to produce H_2 and CO with a ratio of 2 and the reduced cerium oxide (CeO_{2-x}) could be oxidized to CeO_2 by the reaction with H_2O and CO_2. However, in the presence of oxygen, ethane and CeO_2 did not give H_2 and CO:

$$C_2H_6 \rightarrow H_2 + C_2H_4 \quad \Delta H^0_{298} = +137\,\text{kJ/mol} \tag{7}$$

With an increase in the Co-loading level, the selectivity to synthesis gas increased and the highest selectivities to H_2 and CO were obtained with 3 wt.% Co/CeO_2. Increased carbon deposition, however, was observed with this catalyst. Since only a small amount of carbon deposition was observed on 2 wt.% Co, Co (2 wt.%)/CeO_2 was the best one in the POE.

3.3. Effect of reaction temperature on the POE

Table 3 illustrates the effect of the reaction temperature on the POE over Co/CeO_2 catalyst. Synthesis gas was predominantly produced above 873 K, and at 923 K, the ethane conversion of 18% with H_2 and CO selectivities of 93 and 84% were respectively obtained. Molar ratio of H_2/CO was about 2,

Table 3
Effect of reaction temperature on the partial oxidation of ethane

Reac. temp. (K)	Conv. (%) C_2H_6	Eff. conv. C_2H_6	Conv. (%) O_2	Selectivity (%)					H_2/CO (ratio)	H_2O (mmol)	Carbon (mmol)
				H_2	CO	CO_2	C_2H_4	CH_4			
823	9.8	9.8	100.0	67.7	38.8	60.4	0.2	0.5	2.6	12.9	0.04
873	13.4	13.3	100.0	13.4	64.8	34.1	0.4	0.6	1.9	8.6	0.04
923	17.7	17.3	100.0	92.6	83.7	14.0	1.3	0.9	1.7	3.8	0.02
973	37.4	20.7	100.0	62.0	51.3	3.9	35.9	8.6	1.8	3.9	0.33
1023	47.6	18.7	100.0	51.1	36.8	2.5	51.3	9.1	2.1	3.9	0.28

Catalyst: Co(2 wt.%)/CeO_2, 60 mg, flow rate: $C_2H_6/O_2 = 25$ mL/min/5 mL/min, space velocity: 30,000 mL h^{-1} g-cat^{-1}, reaction time: 2 h. Effective C_2H_6 conversion indicates the C_2H_6 conversion to synthesis gas and CO_2. Catalysts were reduced with H_2 for 1 h at 873 K.

Table 4
Effect of space velocity on the partial oxidation of ethane

Space velocity (mL h^{-1} g-cat^{-1})	Conv. (%) C_2H_6	Eff. conv. C_2H_6	Conv. (%) O_2	Selectivity (%)					H_2/CO (ratio)	H_2O (mmol)	Carbon (mmol)
				H_2	CO	CO_2	C_2H_4	CH_4			
15000	22.4	21.5	100.0	91.9	87.9	5.9	1.0	3.1	1.5	3.0	1.28
30000	17.7	17.3	100.0	92.6	83.7	14.0	1.3	0.9	1.7	3.9	0.02
60000	15.8	15.4	100.0	87.4	76.5	21.0	1.6	0.9	1.7	6.6	0.05
90000	13.9	13.5	100.0	76.6	65.6	31.2	2.2	0.8	1.8	12.2	0.09

Catalyst: Co(2 wt.%)/CeO_2, flow rate: C_2H_6/O_2 = 25 mL/min/5 ml/min, reaction time: 2 h. Effective C_2H_6 conversion indicates the C_2H_6 conversion to synthesis gas and CO_2. Catalysts were reduced with H_2 for 1 h at 873 K.

and this is higher than the stoichiometric value of 1.5. At a lower temperature of 823 K, complete oxidation (reaction (4)) occurred to give H_2O and CO_2. These observations suggest that firstly complete oxidation of ethane (reaction (4)) proceeds to give H_2O and CO_2, and then H_2O and CO_2 reforming of ethane (reactions (8) and (9)) proceeds. In the reforming reactions, CO_2 reforming proceeded at a lower reaction rate than that with H_2O:

$$C_2H_6 + 2H_2O \rightarrow 5H_2 + 2CO \quad \Delta H^0_{298} = +347\,\text{kJ/mol} \qquad (8)$$

$$C_2H_6 + 2CO_2 \rightarrow 3H_2 + 4CO \quad \Delta H^0_{298} = +430\,\text{kJ/mol} \qquad (9)$$

At 973 K, ethane conversion reached 37% exceeding limiting conversion of POE and large amounts of ethene and methane were produced, where thermal and catalytic oxidative dehydrogenation of ethane (reactions (5) and (7)) did proceed. Thus, synthesis gas selectivity decreased and in addition to reactions (5) and (7) the decomposition of ethane (reaction (6)) might also have occurred.

3.4. Effect of space velocity on the POE

Table 4 illustrates the effect of space velocity on the POE over Co/CeO_2 catalyst. In order to understand the reaction pathway of synthesis gas production and carbon formation over the catalyst, the space velocity was varied by changing the amount of the catalyst at 923 K. When the space velocity was higher than 30,000, methane selectivity and the amount of deposited carbon decreased dramatically. Ethane conversion and synthesis gas selectivity decreased, and CO_2 selectivity increased with increasing the space velocity from 30,000 to 90,000. Irrespective of the space velocities, O_2 conversion was nearly 100%, indicating that POE on Co/CeO_2 catalyst would proceed via two-step mechanism; complete oxidation of the ethane (reaction (4)) and subsequent H_2O and CO_2 reforming (reactions (8) and (9)). Such a two-step mechanism is widely accepted in the POM over various supported metal catalysts [23–25].

3.5. Effect of O_2 partial pressure and thickness of catalyst bed

Fig. 2a shows the effect of O_2 partial pressure in the POE over Co/CeO_2 catalyst at 923 K, keeping the total flow rate at 30 mL/min. For the O_2/C_2H_6 feed ratio of 0.2, 0.5 and 1.0, the maximum ethane conversion is limited to 20, 50 and 100%, respectively, if only partial oxidation of ethane (reaction (3)) occurs. On the other hand, if the complete oxidation (reaction (4)) proceeds, the maximum ethane conversion is limited to 5.7, 14.3 and 28.6%, respectively.

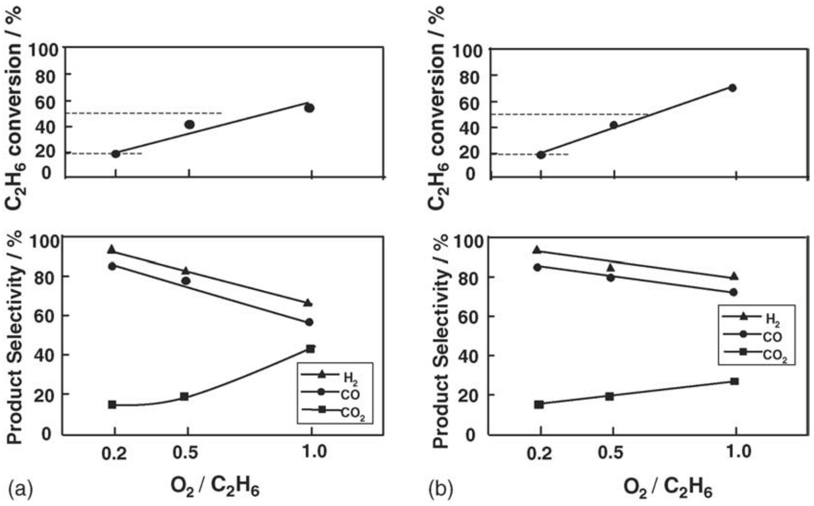

Fig. 2. Effect of O_2 partial pressure and reactor's diameter on the C_2H_6 conversion and product selectivity over Co(2 wt.%)/CeO_2 in the partial oxidation of ethane. (a) Reactor's inner diameter was 8 mm; (b) reactor's inner diameter was 4 mm. Gas flow rate: 30 mL/min (O_2/C_2H_6 = 0.2–1.0). Other conditions are the same as caption to Fig. 1.

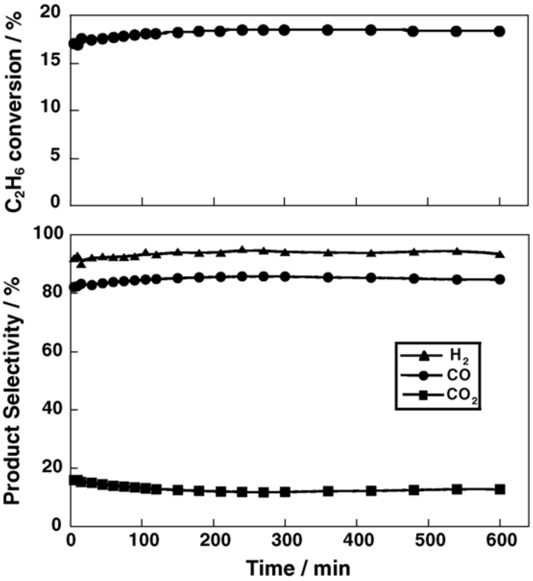

Fig. 3. Life test of Co(2 wt.%)/CeO_2 catalyst in the partial oxidation of ethane. Other conditions are the same as caption to Fig. 1.

With decreasing the O_2 partial pressure, H_2 and CO selectivities increased, and CO_2 selectivity decreased. Ethene and methane selectivities were low and below 4%. O_2 conversion was 100% in every case.

From these findings, it is suggested that H_2O and CO_2 reforming (reactions (8) and (9)) proceeded easily with a decrease in the O_2 partial pressure. In addition, at high O_2/C_2H_6 feed ratio of 1.0, the synthesis gas selectivity decreased notably with an increase in CO_2 selectivity. The reactor used throughout the experiment was a differential type reactor, where the reactor diameter (8 mm i.d.) was large enough compared to the catalyst bed length of 1.5 mm. When the POE was conducted under stoichiometric $O_2/C_2H_6 = 1$, complete oxidation of ethane (reaction (4)) proceeded and resulted in high ethane conversion. Thus, decreasing the ethane concentration for the following reforming reactions deprived sufficient contact time with H_2O and CO_2, and consequently low selectivities for H_2 and CO were observed. Considering this in mind, the reactor having a smaller diameter (4 mm i.d.) was employed with the same amount of the catalyst. Here, the catalyst bed length increased to 6.0 mm. Fig. 2b shows the effect of O_2 partial pressure on the POE using the narrow bore reactor under the same reaction conditions as those shown in Fig. 2a. In the O_2/C_2H_6 feed ratio of 0.2 and 0.5, the results were similar to those in the large bore reactor (Fig. 2a). In the O_2/C_2H_6 feed ratio of 1.0, however, the synthesis gas selectivity markedly increased and CO_2 selectivity decreased, as compared to those values with the large bore reactor. These results clearly support that POE over Co/CeO_2 proceeded via two-step mechanism.

3.6. Stability of Co/CeO_2 catalyst in the POE

Catalytic performance of Co/CeO_2 catalyst was tested for a prolonged period of 10 h at 923 K. Fig. 3 shows the conversion of ethane and H_2 and CO selectivities as a function of reaction time. Production of very small amounts of ethene and methane is not shown here. Co/CeO_2 catalyst exhibited a high and stable catalytic activity; a high ethane conversion of 18% with H_2 and CO selectivities of 93 and 84%, respectively. In addition, significant carbon deposition was not observed after 10 h.

3.7. Stability of Co/CeO_2 catalyst at different O_2 partial pressures

Using the narrow 4 mm diameter reactor, catalytic performance of Co/CeO_2 catalyst was tested for a prolonged period at 923 K. Fig. 4 shows the conversion of ethane and selectivities of H_2 and CO as a function of reaction time. At $O_2/C_2H_6 = 0.5$, the ethane conversion of 42% was kept constant for 5 h with H_2 and CO selectivities of 86 and 80%, respectively

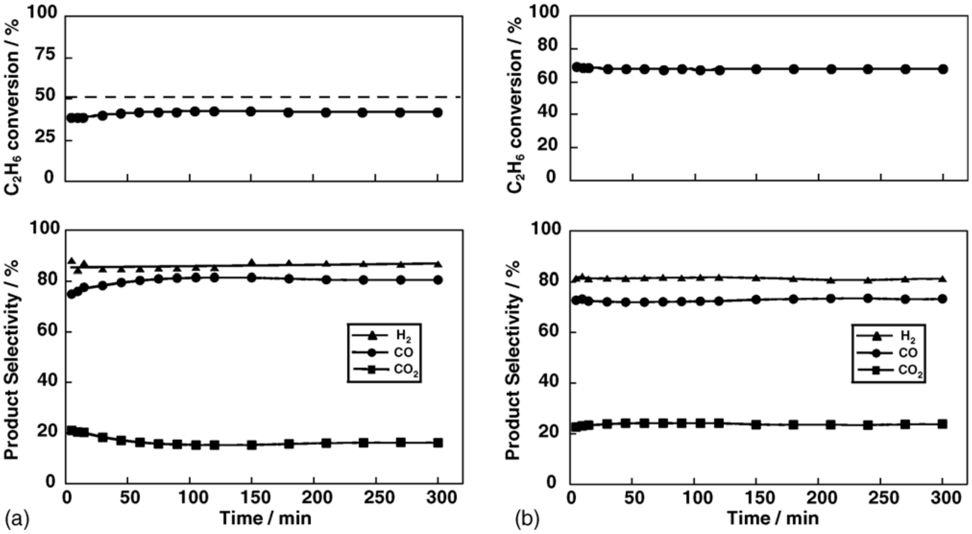

Fig. 4. Life test of Co(2 wt.%)/CeO_2 catalyst in the partial oxidation of ethane with a narrow diameter reactor: (a) $O_2/C_2H_6 = 0.5$; (b) $O_2/C_2H_6 = 1$. Other conditions are the same as caption to Fig. 1.

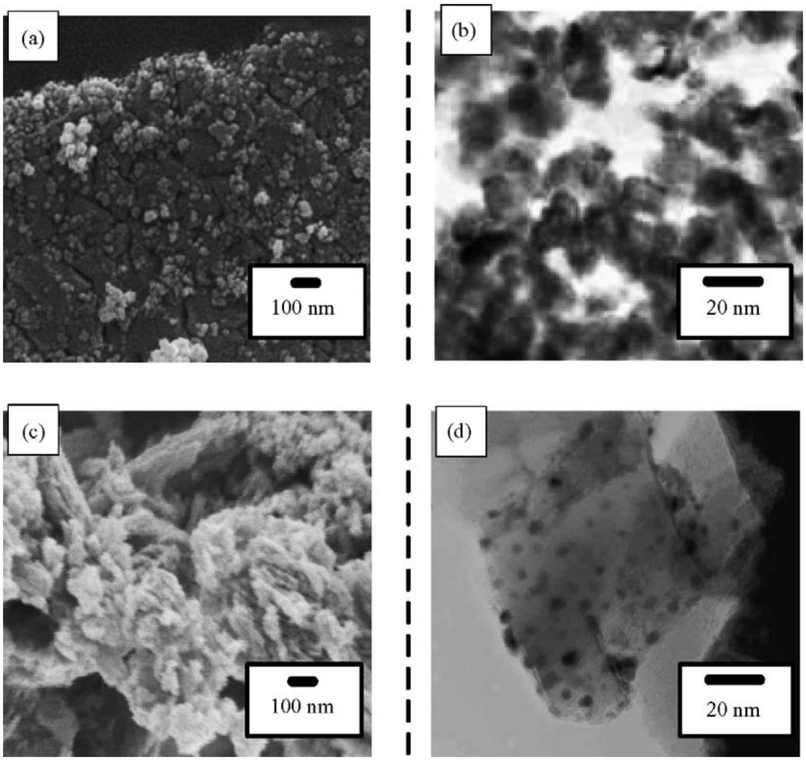

Fig. 5. FE-SEM (a and c) and HR-TEM (b and d) images of Co(2 wt.%)/CeO_2 catalysts. (a) and (b) Catalyst after H_2 reduction at 873 K for 1 h; (c) and (d) Catalyst after the reaction with $O_2/C_2H_6 = 1$ at 923 K for 5 h.

(Fig. 4a). At $O_2/C_2H_6 = 1$, an initial ethane conversion of 67% was again kept constant for 5 h with H_2 and CO selectivities of 80 and 73%, respectively (Fig. 4b). In addition, carbon deposition on these catalysts was small, and amounted to 4.3×10^{-2} g/g-catalyst after 5 h. The reason for such a small amount of carbon deposition seems to be ascribed to the finely dispersed Co species on CeO_2 as described below, as a result the lattice oxygen of CeO_2 would react with carbon on Co to give CO if it was formed by the decomposition of hydrocarbon on Co. Thus, Co (2 wt.%)/CeO_2 catalyst kept the initial activity for prolong period irrespective of O_2/C_2H_6 ratios, indicating that the catalyst was attractive for the partial oxidation of ethane.

3.8. FE-SEM and HR-TEM images of Co/CeO_2 catalysts

Fig. 5 shows FE-SEM and HR-TEM images of Co/CeO_2 catalysts; reduced (a, b) and after the POE (c, d). In the SEM the image of the reduced catalyst (Fig. 5a), small particles were observed on the large flat part. TEM image of the same sample (Fig. 5b) afforded particles of 20–40 nm. Such a morphological structure observed in reduced Co/CeO_2 catalysts seems to indicate that a part of CeO_2 was dissolved during impregnation of acidic cobalt nitrate solution and deposited on Co species. Pino et al. [26] reported that the similar morphological structure was observed over Pt/CeO_2 catalysts prepared by co-precipitation. Then, leached out CeO_2 forms a thin film that covers most of Co surface. Furthermore, the reduction can induce an additional migration of reduced ceria species onto the Co surface, making the identification more difficult. Generally, TEM image contrast is proportional to atomic weight of each element. However, in our samples, CeO_2 is so light compared to Co particles, showing that this part of CeO_2 is very thin in comparison with Co particles.

We attempted the XPS analysis of these reduced catalysts, but the no distinct peak of Co species was observed. This may be closely related to the SEM and TEM observations that Co species seemed encapusulated in CeO_2.

After the POE reaction for 5 h at 923 K, the morphology of the catalyst surface drastically changed. In SEM observation, small particles disappeared and larger non-flat wrinkles appeared. In SEM and TEM observations, no filamentous or flat face carbon deposition was seen after 5 h. On the TEM image, however, very clear fine metallic Co particles of 2–10 nm were observed. (Fig. 5d).

Such a highly dispersed Co species seems to be the reason for the high catalytic performance to POE.

4. Conclusions

In the partial oxidation of ethane (POE) with Co-loaded catalyst, the activity order related to the supports was as follows: Y_2O_3, CeO_2, ZrO_2, $La_2O_3 \gg SiO_2$, Al_2O_3, $TiO_2 > MgO$. Co on Y_2O_3 and CeO_2 exhibited the best performance. However, the Y_2O_3 supported catalyst gave a significant amount of carbon deposition after the reaction for 2 h, whereas the Co-loaded on CeO_2(Co/CeO_2) catalysts afforded a high activity without significant carbon deposition at 923 K. The reaction appeared to proceed in two-step mechanism; (1) complete oxidation of ethane and (2) H_2O and CO_2 reforming reactions. FE-SEM and HR-TEM images showed Co particle size was very small from 2 to 10 nm after the reaction. Thus, Co/CeO_2 was suggested to be a suitable catalyst for the POE.

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