M/BCS (M = Ni, Co; BCS = 30 mol% $BaCl_2/Sm_2O_3$): effective catalysts for the partial oxidation of ethane to a feedstock gas suitable for ethene hydroformylation

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The M (M = Ni, Co)-loaded $BaCl_2$-promoted Sm_2O_3 (BCS) catalysts have been investigated for the partial oxidation of ethane to a feedstock gas suitable for ethene hydroformylation. It is found that at a temperature of 700 °C and a C_2H_6/O_2 molar ratio of 2/1, the product mixtures over 5 wt% Ni/BCS and 7 wt% Co/BCS were with $C_2H_4/CO/H_2$ and $C_2H_4/CO_x/H_2$ ($CO_x = CO + CO_2$) molar ratios close to 1/1/1 at a contact time of 1.19×10^{-4} h g ml^{-1} and close to 1/1/2 at a contact time of 2.78×10^{-4} h g ml^{-1}. It is suggested that, besides reaction conditions, defect structures, M loading, and M dispersion of the catalysts are governing factors for the generation of the required feedstock gas.

KEY WORDS: Ni or Co catalysts; $BaCl_2$-modified Sm_2O_3; ethane partial oxidation; generation of feedstock gas suitable for ethene hydroformylation.

1. Introduction

The conversion of light paraffin, such as ethane, to value-added products has attracted much attention in the past decades. The partial oxidation of ethane has been the subject of intensive and extensive researches (*e.g.* 1–7]). Most efforts have been placed into the development of active and selective catalysts for ethene production. As a matter of fact, not much attention has been paid to the syngas (CO + H_2) formed in the oxidation reaction. In the hydroformylation of C_2H_4, CO, and H_2, important chemicals such as propanal and propanol can be generated:

$$C_2H_4 + CO + H_2 \rightarrow CH_3CH_2CHO \qquad (1)$$

$$C_2H_4 + CO + 2H_2 \rightarrow CH_3CH_2CH_2OH. \qquad (2)$$

We believe that it is possible to produce, catalytically, a mixture of $C_2H_4 + CO + H_2$ with a $C_2H_4/CO/H_2$ molar ratio suitable for the hydroformylation reaction (to propanal, $C_2H_4/CO/H_2$ molar ratio = 1/1/1; to propanol, $C_2H_4/CO/H_2$ molar ratio = 1/1/2) [8–10]. So far, we have not come across any reports on such an attempt in the literature. In our previous studies on ethane oxidative dehydrogenation [7,11–13], we observed that the doping of alkaline earth halides MX_2 (M = Ba, Sr; X = F, Cl, Br) to rare earth oxides Ln_2O_3 (Ln = Ho, Y, Nd, Sm, Er) could reduce C_2H_4 and C_2H_6 deep oxidation, resulting in a decrease in CO_2 selectivity but an increase in C_2H_4 and CO selectivity as well as C_2H_6 conversion. It is well known that supported nickel and cobalt are active catalysts for syngas formation in the oxidation of methane or ethane [14–17]. We envisage that by regulating the loading of Ni or Co and optimizing the reaction conditions such as temperature, C_2H_6/O_2 molar ratio, and contact time, one can generate a catalyst over which a feedstock gas suitable for ethene hydroformylation could be produced. In this paper, we present the result of such an attempt over M/BCS (M = Ni, Co; BCS = 30 mol% $BaCl_2/Sm_2O_3$).

2. Experimental

The BCS was prepared by adopting the wet-impregnation method [7]. The calcination temperature was 950 °C (for 12 h) which is beneficial for ionic exchanges between the $BaCl_2$ and Sm_2O_3 phases [7]. The MO_x (M = Ni, Co)/BCS precursors were prepared by impregnating BCS with a desired amount of $M(NO_3)_2$, respectively, in aqueous solution. The paste formed after evaporation at 80 °C was dried overnight and then calcined at 500 °C for 4 h. The M/BCS catalysts were obtained by reducing the MO_x/BCS precursors at 500 °C in a flow of 10% H_2–90% He (30 ml min^{-1}) for 1 h. The catalyst particle size adopted was 80–100 mesh.

The crystal phases of the catalysts were determined by an X-ray diffractometer (D-MAX, Rigaku) operating at 40 kV and 200 mA using Cu K_α radiation. The patterns recorded were referred to the powder diffraction files—

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1998 ICDD PDF Database for identification. The surface areas of the catalysts were measured on a Nova 1200 apparatus.

The H_2–O_2 titration experiments were performed in a quartz micro-reactor (i.d. = 4 mm). The sample (10 mg) was first treated in 10% H_2–90% He (20 ml min^{-1}) at 500 °C for 1 h, followed by cooling in the same atmosphere to room temperature before He purging for 0.5 h. For titration, O_2 (He as a carrier gas, 20 ml min^{-1}) pulses were introduced to the catalyst until there was no observable increase in O_2 signal intensity which was monitored by a mass spectrometer (HP G-1800A). The pulse size was 50.0 μl. The total uptake of O_2 was then used for the calculation of M dispersion, assuming that each surface M atom chemisorbs one H atom.

The procedures for catalytic evaluation have been described elsewhere [7]. The catalyst mass was 0.5 g. The flow rate of C_2H_6, O_2, and He was regulated by a mass flow controller. The C_2H_6/O_2 molar ratio was set to 1/1, 1.2/1, 2/1, 3/1, and 4/1. At a total flow rate of 20, 30, 50, 70, 100, and 120 ml min^{-1}, contact time was (0.69, 0.83, 1.19, 1.67, 2.78, and 4.17) × 10^{-4} h g ml^{-1}, respectively. A product mixture was analyzed on-line by a Shimadzu 8A TCD gas chromatography (GC) with Porapak Q and 5 Å molecular sieve columns. The distribution of a component in the product mixture was calculated by supposing that there were only C_2H_4, CH_4, CO, CO_2, and H_2 in the outlet (H_2O was removed before GC analysis). The balances of carbon, oxygen, and hydrogen were estimated to be 100 ± 5, 100 ± 3, and 100 ± 5%, respectively, for every run over the catalysts.

3. Results

3.1. Physical properties of catalysts

The crystal phase compositions, Ni and Co dispersion, and surface areas of the M/BCS catalysts are listed in table 1. Below an M loading of 5 wt%, we detected only cubic Sm_2O_3 and monoclinic $BaCl_2$. At an M loading of 5 or 7 wt%, we detected very weak XRD signals of metallic Ni (or Co). One can observe that Ni and Co dispersion on BCS reached a maximum at 5 and 7 wt%, respectively. A similar situation appeared for the surface area of the two series of catalysts.

3.2. Effect of Ni and Co loading

The catalytic performances of BCS and M/BCS under the reaction condition of temperature = 700 °C, contact time = 1.19 × 10^{-4} h g ml^{-1}, and C_2H_6/O_2 molar ratio = 2/1 are summarized in table 2. Under such a condition, quartz sand (5.0 g) showed 8.6% C_2H_6 conversion with product distribution of 78.2% C_2H_4, 6.4% CO, 8.2% CO_2, 4.0% CH_4, and 3.2% H_2. For 30 mol% $BaCl_2/Sm_2O_3$ (*i.e.* BCS), C_2H_4 content in product mixture was much higher than that over M/BCS. With the rise in Ni or Co loading, C_2H_6 conversion as well as CO and H_2 content in product mixture increased, whereas C_2H_4, CO_2 and CH_4 content decreased. It should be noted that O_2 conversion over BCS and M/BCS was almost 100%. From table 2, one can observe that $C_2H_4/CO/H_2$ and $C_2H_4/CO_x/H_2$ molar ratios were 1.00/0.98/1.04 and 1.00/1.12/1.04, respectively, over the 5 wt% Ni/BCS catalyst; they were 1.00/1.04/1.11 and 1.00/1.18/1.11, respectively, over the 7 wt% Co/BCS catalyst. Product mixtures with these molar ratios are suitable for ethene hydroformylation to propanal as they are close to 1/1/1.

3.3. Effect of reaction temperature

The catalytic performances of 5 wt% Ni/BCS and 7 wt% Co/BCS as related to reaction temperature at a contact time of 1.19 10 h g ml^{-1} and a C_2H_6/O_2 molar ratio of 2/1 are shown in table 3. With a rise in temperature, conversion of C_2H_6 and concentration of CO and

Table 1
Physical properties of the M (M = Ni, Co)/BCS catalysts

Catalyst	Crystal phase [a]	Ni (or Co) dispersion [b] (mol%)	Surface area ($m^2 g^{-1}$)
BCS	Sm_2O_3 (s), $BaCl_2$ (m)	–	3.9
1 wt% Ni/BCS	Sm_2O_3 (s), $BaCl_2$ (m)	9.1	4.3
1 wt% Co/BCS	Sm_2O_3 (s), $BaCl_2$ (m)	9.2	4.2
3 wt% Ni/BCS	Sm_2O_3 (s), $BaCl_2$ (m)	9.3	4.8
3 wt% Co/BCS	Sm_2O_3 (s), $BaCl_2$ (m)	9.3	4.4
5 wt% Ni/BCS	Sm_2O_3 (s), $BaCl_2$ (m)	9.6	5.2
5 wt% Co/BCS	Sm_2O_3 (s), $BaCl_2$ (m)	9.2	4.8
7 wt% Ni/BCS	Ni (vw), Sm_2O_3 (s), $BaCl_2$ (m)	9.2	4.7
7 wt% Co/BCS	Co (vw), Sm_2O_3 (s), $BaCl_2$ (m)	9.5	5.1
9 wt% Ni/BCS	Ni (vw), Sm_2O_3 (s), $BaCl_2$ (m)	8.8	4.1
9 wt% Co/BCS	Co (vw), Sm_2O_3 (s), $BaCl_2$ (m)	8.9	4.4

[a] XRD line intensity: s, strong; m, medium; vw, very weak; w, weak.

[b] Estimated according to the results of H_2–O_2 experiments.

Table 2
Catalytic performance of *M* (*M* = Ni, Co)/BCS as related to *M* loading at 700 °C, 1.19×10^{-4} h g ml^{-1}, and C_2H_6/O_2 molar ratio = 2/1

Ni (or Co) loading (wt%)	Conversion (%)	Product distribution (%)					Molar ratio	
	C_2H_6	C_2H_4	CO	CO_2	CH_4	H_2	$C_2H_4/CO/H_2$	$C_2H_4/CO_x/H_2$ [a]
0	63.4	65.6	9.6	19.2	4.4	1.2	1.00/0.15/0.02	1.00/0.44/0.02
1	65.6	53.7	18.1	16.2	3.6	8.4	1.00/0.34/0.16	1.00/0.64/0.16
	(66.8) [b]	(60.2)	(14.3)	(11.4)	(3.2)	(10.9)	(1.00/0.24/0.18)	(1.00/0.43/0.18)
3	68.8	41.8	25.0	8.4	2.0	22.8	1.00/0.60/0.55	1.00/0.80/0.55
	(69.9)	(46.5)	(20.1)	(6.3)	(1.7)	(27.4)	(1.00/0.43/0.59)	(1.00/0.57/0.59)
5	72.4	31.4	30.6	4.6	0.8	32.6	1.00/0.98/1.04	1.00/1.12/1.04
	(74.2)	(38.6)	(25.5)	(5.2)	(0.4)	(30.3)	(1.00/0.66/0.79)	(1.00/0.80/0.79)
7	74.6	28.3	33.4	3.0	0.5	34.8	1.00/1.18/1.23	1.00/1.29/1.23
	(75.4)	(30.3)	(31.5)	(4.3)	(0.2)	(33.7)	(1.00/1.04/1.11)	(1.00/1.18/1.11)
9	76.7	21.6	38.7	2.2	0.3	37.2	1.00/1.79/1.72	1.00/1.89/1.72
	(77.9)	(25.2)	(32.5)	(3.1)	(0.1)	(39.1)	(1.00/1.29/1.55)	(1.00/1.41/1.55)

[a] $CO_x = CO + CO_2$.
[b] The data in parentheses were obtained over Co/BCS.

H_2 in product mixture increased while concentration of C_2H_4, CO_2, and CH_4 decreased. The mixtures with $C_2H_4/CO/H_2$ and $C_2H_4/CO_x/H_2$ molar ratios suitable for ethene hydroformylation to propanal were obtained at 700 °C.

3.4. *Effect of C_2H_6/O_2 molar ratio*

Summarized in table 4 are the catalytic performances of 5 wt% Ni/BCS and 7 wt% Co/BCS *versus* C_2H_6/O_2 molar ratio at a temperature of 700 °C and a contact time of 1.19×10^{-4} h g ml^{-1}. When the C_2H_6/O_2 molar ratio was increased from 1/1 to 4/1, conversion of C_2H_6 and content of CO and CO_2 in product mixture dropped whereas the content of C_2H_4 and H_2 augmented; there was little change in CH_4 concentration. At a C_2H_6/O_2 molar ratio of 2/1, the $C_2H_4/CO/H_2$ and $C_2H_4/CO_x/H_2$ mixtures were the most suitable for ethene hydroformylation to propanal.

3.5. *Effect of contact time*

Listed in table 5 are the catalytic performances of 5 wt% Ni/BCS and 7 wt% Co/BCS as a function of contact time at 700 °C and C_2H_6/O_2 molar ratio = 2/1. With the prolongation of contact time, C_2H_6 conversion and H_2 concentration increased while concentration of C_2H_4, CO, CO_2, and CH_4 decreased. $C_2H_4/CO/H_2$ and $C_2H_4/CO_x/H_2$ mixtures with molar ratios close to 1/1/1 were obtained at contact time = 1.19×10^{-4} h g ml^{-1}. At 2.78×10^{-4} h g ml^{-1}, $C_2H_4/CO/H_2$ and $C_2H_4/CO_x/H_2$ mixtures with molar ratios equal to 1.00/1.06/1.80 and 1.00/1.13/1.80 were obtained over 5 wt% Ni/BCS; over 7 wt% Co/BCS, they were

Table 3
Catalytic performance of 5 wt% Ni/BCS and 7 wt% Co/BCS as related to reaction temperature at 1.19×10^{-4} h g ml^{-1} and C_2H_6/O_2 molar ratio = 2/1

Reaction temperature (°C)	Conversion (%)	Product distribution (%)					Molar ratio	
	C_2H_6	C_2H_4	CO	CO_2	CH_4	H_2	$C_2H_4/CO/H_2$	$C_2H_4/CO_x/H_2$ [a]
660	65.3	53.2	21.4	9.2	1.5	14.7	1.00/0.40/0.28	1.00/0.58/0.28
	(68.1) [b]	(57.3)	(17.4)	(7.8)	(1.3)	(16.2)	(1.00/0.30/0.28)	(1.00/0.44/0.28)
680	68.6	40.6	26.3	65	1.2	25.4	1.00/0.65/0.63	1.00/0.81/0.63
	(71.2)	(41.1)	(25.8)	(5.9)	(0.5)	(26.7)	(1.00/0.63/0.65)	(1.00/0.77/0.65)
700	72.4	31.4	30.6	4.6	0.8	32.6	1.00/0.98/1.04	1.00/1.12/1.04
	(75.4)	(30.3)	(31.5)	(4.3)	(0.2)	(33.7)	(1.00/1.04/1.11)	(1.00/1.18/1.11)
720	77.5	25.6	33.7	3.2	0.6	37.9	1.00/1.32/1.48	1.00/1.44/1.48
	(79.7)	(22.8)	(34.7)	(2.9)	(0.2)	(39.4)	(1.00/1.52/1.73)	(1.00/1.65/1.73)
740	82.6	20.8	35.5	1.9	0.3	41.5	1.00/1.71/2.00	1.00/1.80/2.00
	(84.1)	(15.9)	(38.7)	(2.0)	(0.2)	(43.2)	(1.00/2.43/2.72)	(1.00/2.56/2.72)

[a] $CO_x = CO + CO_2$.
[b] The data in parentheses were obtained over Co/BCS.

Table 4
Catalytic performance of 5 wt% Ni/BCS and 7 wt% Co/BCS as related to C_2H_6/O_2 molar ratio at 700 °C and 1.19×10^{-4} h g ml^{-1}

Molar ratio C_2H_6/O_2	Conversion (%) C_2H_6	Product distribution (%)					Molar ratio	
		C_2H_4	CO	CO_2	CH_4	H_2	$C_2H_4/CO/H_2$	$C_2H_4/CO_x/H_2$ [a]
1/1	84.8	27.1	28.7	25.6	0.3	18.3	1.00/1.06/0.68	1.00/2.00/0.68
	(86.2) [b]	(27.4)	(27.7)	(24.5)	(0.3)	(20.1)	(1.00/1.01/0.73)	(1.00/1.91/0.73)
1.2/1	78.6	29.9	30.0	15.4	0.5	24.2	1.00/1.00/0.81	1.00/1.52/0.81
	(81.3)	(30.2)	(29.2)	(12.8)	(0.2)	(27.6)	(1.00/0.97/0.91)	(1.00/1.39/0.91)
2/1	72.4	31.4	30.6	4.6	0.8	32.6	1.00/0.98/1.04	1.00/1.12/1.04
	(75.4)	(30.3)	(31.5)	(4.3)	(0.2)	(33.7)	(1.00/1.04/1.11)	(1.00/1.18/1.11)
3/1	54.4	36.6	23.6	3.8	0.6	35.4	1.00/0.65/0.97	1.00/0.75/0.97
	(56.7)	(38.8)	(20.2)	(3.6)	(0.3)	(37.1)	(1.00/0.52/0.96)	(1.00/0.61/0.96)
4/1	45.2	43.2	15.2	2.6	0.4	38.6	1.00/0.35/0.89	1.00/0.41/0.89
	(48.6)	(45.6)	(11.7)	(2.7)	(0.2)	(40.8)	(1.00/0.26/0.90)	(1.00/0.32/0.90)

[a] $CO_x = CO + CO_2$.
[b] The data in parentheses were obtained over Co/BCS.

Table 5
Catalytic performance of 5 wt% Ni/BCS and 7 wt% Co/BCS as related to contact time at 700 °C and C_2H_6/O_2 molar ratio = 2/1

Contact time ($\times 10^{-4}$ h g ml^{-1})	Conversion (%) C_2H_6	Product distribution (%)					Molar ratio	
		C_2H_4	CO	CO_2	CH_4	H_2	$C_2H_4/CO/H_2$	$C_2H_4/CO_x/H_2$ [a]
0.69	48.8	36.6	34.5	8.5	2.2	18.2	1.00/0.94/0.50	1.00/1.18/0.50
	(52.6) [b]	(35.9)	(34.9)	(8.8)	(1.1)	(19.3)	(1.00/0.97/0.54)	(1.00/1.22/0.54)
0.83	63.5	33.8	32.2	5.7	1.5	26.8	1.00/0.95/0.79	1.00/1.12/0.79
	(66.7)	(32.9)	(32.9)	(5.4)	(0.6)	(28.2)	(1.00/1.00/0.86)	(1.00/1.16/0.86)
1.19	72.4	31.4	30.6	4.6	0.8	32.6	1.00/0.98/1.04	1.00/1.12/1.04
	(75.4)	(30.3)	(31.5)	(4.3)	(0.2)	(33.7)	(1.00/1.04/1.11)	(1.00/1.18/1.11)
1.67	79.6	28.4	28.7	3.1	0.6	37.0	1.00/1.01/1.30	1.00/1.12/1.30
	(80.1)	(26.6)	(28.4)	(3.3)	(0.3)	(41.4)	(1.00/1.07/1.56)	(1.00/1.19/1.56)
2.78	84.2	25.3	26.8	1.9	0.4	45.6	1.00/1.06/1.80	1.00/1.13/1.80
	(85.9)	(24.6)	(26.3)	(2.2)	(0.2)	(46.7)	(1.00/1.07/1.90)	(1.00/1.16/1.90)
4.17	88.6	14.4	34.9	1.7	0.2	48.8	1.00/2.42/3.39	1.00/2.54/3.39
	(91.2)	(15.2)	(33.9)	(1.8)	(0.1)	(49.0)	(1.00/2.23/3.22)	(1.00/2.35/3.22)

[a] $CO_x = CO + CO_2$.
[a] The data in parentheses were obtained over Co/BCS.

1.00/1.07/1.90 and 1.00/1.16/1.90, respectively. With molar ratios close to 1/1/2, the mixtures are suitable for ethene hydroformylation to propanol. Further rise in contact time would result in an increase in H_2 and CO_x concentration and a decrease in C_2H_4 concentration.

4. Discussion

In the past several years, we have reported the promotion of rare earth oxide (Ln_2O_3) by alkaline earth halides (MX_2) for the oxidative dehydrogenation of ethane [7,11–13]. The promotional effects of MX_2 can be closely associated with the activation of gaseous O_2 by the defects formed in ionic exchanges between the MX_2 and Ln_2O_3 phases. In view of the fact that the 30 mol% $BaCl_2$-modified Sm_2O_3 catalyst shows good selectivities of CO and H_2 in ethane oxidation, we chose it for the present investigation. The purpose of loading BCS with Ni or Co is to enhance the amount of syngas in product mixture. From table 1, one can see that the metal was well dispersed and the addition of Ni or Co showed the effect of enhancing the surface area of the catalyst. It is apparent that, in the absence of Ni or Co, the amounts of CO and H_2 generated over BCS were low (table 2). With the rise in Ni or Co loading, there was a rapid increase in CO and H_2 concentration but a considerable decrease in C_2H_4 concentration.

The oxidation of ethane over M/BCS is complex. It includes quite a number of chemical reactions:

(i) direct oxidation of ethane

$$6C_2H_6 + 5O_2 \rightarrow 4C_2H_4 + 4CO + 4H_2 + 6H_2O \quad (3)$$

$$6C_2H_6 + 3O_2 \rightarrow 4C_2H_4 + 4CO + 8H_2 + 2H_2O \quad (4)$$

$$2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O \quad (5)$$

$$2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O \quad (6)$$

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O \quad (7)$$

$$C_2H_6 + O_2 \rightarrow CO + CH_4 + H_2O \quad (8)$$

(ii) carbon dioxide and steam reforming of methane

$$2CH_4 + CO_2 + H_2O \rightarrow 3CO + 5H_2 \quad (9)$$

(iii) carbon dioxide and steam reforming of ethane

$$C_2H_6 + CO_2 + H_2O \rightarrow 3CO + 4H_2. \quad (10)$$

Furthermore, the CO and H_2 formed in the above reactions would react with O_2 to produce CO_2 and H_2O, respectively. In order to obtain a suitable $C_2H_4/CO/H_2$ ratio, one has to control the amount of defects in BCS (critical for C_2H_4 generation) as well as the loading and dispersion of Ni or Co (critical for syngas generation). One can see from table 2 that too small a Ni or Co loading would result in low syngas productivity but too much would cause ethene concentration to decrease. From table 3, one can observe that above 700 °C, C_2H_4 concentration decreased and syngas concentration increased whereas there was little change in CO_2 and CH_4 concentration, indicating that above 700 °C, C_2H_6 oxidation proceeded mainly according to reactions (6)–(10). A significant drawback of most Ni-based catalysts used for syngas production from methane at or above 700 °C is sintering and coking induced by the agglomeration of Ni particles. In the present study, however, we observed no coking and metal sintering on the catalysts. The good dispersion of Ni (at a 5 wt% loading) or Co (at a 7 wt% loading) as well as the decoration of Ni crystallites with Sm_2O_3 (similar to the case of Ni/La_2O_3 [16]) would give rise to an appropriate amount of ethene as well as syngas in product mixture (tables 2–5). In the past years, Al_2O_3- or La_2O_3-supported Ni or Co catalysts have been reported to be active for the production of syngas from the partial oxidation as well as the steam and carbon dioxide reforming of methane [16,18–20]. Recently, we found that M/Ln_2O_3 (M = Ni, Co; Ln = La, Nd, Sm) derived from $LnMO_3$ and Ln_2MO_4 precursors were catalytically active for the steam and carbon dioxide reforming of ethane [17]. Therefore, the low concentration of CO_2 and CH_4 in product mixtures (tables 2–5) are a result of reactions (9) and (10). From table 5, one can observe that a change in contact time would influence the distribution of the products. At 1.19×10^{-4} h g ml^{-1}, the C_2H_4/CO(or CO_x)/H_2 molar ratio was close to 1/1/1, indicating that ethane was oxidized mainly via reaction (3); whereas at 2.78×10^{-4} h g ml^{-1}, the $C_2H_4/CO/H_2$ and $C_2H_4/CO_x/H_2$ molar ratios were close to 1/1/2, indicating that ethane was oxidized mainly via reaction (4). Too long a contact time would result in syngas enrichment (table 5).

Very recently, Tominaga and Sasaki [21] found that the ruthenium complexes derived from $H_4Ru_4(CO)_{12}$ and LiCl could catalyze the hydroformylation of alkenes, carbon dioxide, and hydrogen. Such catalysts should also be effective for the generation of propanal and propanol from C_2H_4, CO_2, and H_2:

$$C_2H_4 + CO_2 + 2H_2 \rightarrow CH_3CH_2CHO + H_2O \quad (11)$$

$$C_2H_4 + CO_2 + 3H_2 \rightarrow CH_3CH_2CH_2OH + H_2O. \quad (12)$$

In other words, a $C_2H_4/CO_2/H_2$ mixture with molar ratio of 1/1/2 and 1/1/3 would be suitable for the generation of CH_3CH_2CHO and $CH_3CH_2CH_2OH$, respectively. Stoichiometrically speaking, a $C_2H_4/CO/H_2$ mixture with molar ratio close to 1/1/1 is suitable for propanal production whereas that with one close to 1/1/2 is suitable for propanol production. According to reactions (3) and (4), a C_2H_6/O_2 molar ratio of 1.2/1 is expected for the generation of a 1/1/1 mixture, and a C_2H_6/O_2 molar ratio of 2/1 is expected for the generation of a 1/1/2 mixture; however, we did not observe such trends in our results (table 4). It is obvious that there are other secondary reactions to be considered. In the blank experiment, quartz sand showed poor activity under similar conditions, indicating that the homogeneous reaction was not significant. In other words, the good performance is a result of the catalytic action of 5 wt% Ni/BCS and 7 wt% Co/BCS. We suggest that the generation of a mixture with an appropriate C_2H_4/CO (or CO_x)/H_2 molar ratio in ethane oxidation is closely associated with the defects and metal dispersion of the 5 wt% Ni/BCS and 7 wt% Co/BCS catalysts.

5. Conclusion

In the oxidation of ethane to a feedstock gas suitable for ethene hydroformylation, 5 wt% Ni/BCS and 7 wt% Co/BCS performed the best among the M/BCS (M = Ni, Co) catalysts. At 700 °C and C_2H_6/O_2 molar ratio = 2/1, the two catalysts showed a $C_2H_4/CO/H_2$ or $C_2H_4/CO_x/H_2$ molar ratio close to 1/1/1 at contact time = 1.19×10^{-4} h g ml^{-1} and close to 1/1/2 at contact time = 2.78×10^{-4} h g ml^{-1}; the former case is suitable for ethene hydroformylation to propanal, the latter case is suitable for ethene hydroformylation to propanol. We have demonstrated that it is possible to generate catalytically a feedstock gas suitable for ethene hydroformylation from ethane and oxygen directly. In order to achieve that, one has to control the reaction condition as well as regulate the defect structure, metal loading and metal dispersion of the M/BCS catalysts.

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