Catalysis Letters 24 (1994) 349–354

Synergic enhancement effect of zirconium oxide, cerium oxide and iron or cobalt oxide on the formation of isobutene from CO and H_2

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Received 19 June 1993; accepted 9 November 1993

Fe_2O_3 or CoO modified CeO_2–ZrO_2 catalysts lead to four times higher yield of hydrocarbons than ZrO_2 with C_4 hydrocarbons selectivity of more than 50% and isobutene selectivity of more than 80%. XRD and XPS measurements suggested that the interaction of Fe or Co oxide with CeO_2 causes the higher Ce^{3+} concentration with their higher oxidation state. Their combination with ZrO_2 synergistically causes the active and selective formation of isobutene.

Keywords: Mixed oxide catalysts; Fe_2O_3– or CoO–CeO_2–ZrO_2; CO hydrogenation; isobutene

1. Introduction

We have reported that isobutene is selectively formed from CO and H_2 over oxide catalysts and that the formation of a branched carbon chain is a characteristic of oxide catalysts [1]. As isobutene is a raw material for synthesizing MTBE in addition to methacrylic acid, the fact that CO hydrogenation over oxide catalysts is able to form isobutene has attracted attention. However, oxide catalysts are much less active than metal catalysts, as it is typically shown by the fact that "isosynthesis reaction" over oxide catalysts such as ThO_2 was carried out under very severe reaction conditions such as 723 K and 600 atm [2]. On the other hand, ZrO_2 oxide is so active as to hydrogenate ethylene at 223 K [3] and CO to surface formate and methoxide species at 273 K [4]. This indicates that the oxide catalysts can easily activate H_2 and CO even at 273 K. Different from metal catalysts on which CO strongly adsorbs to retard the adsorption of H_2, the CO hydrogenation over oxide catalysts under higher CO pressure would be favorable [5]. The low efficiency of oxide catalysts for the CO hydrogenation would be attributed to the strong adsorption of water [3] and CO_2 [6] which are formed in the CO hydrogenation reaction. Therefore, active oxide catalysts for the CO hydrogenation to form branched chain hydrocarbons may be obtainable if the retardation by water and CO_2 can be overcome. This paper describes the mixed oxide catalysts effective for the CO hydrogenation to form branched chain hydrocarbons and a brief discussion of the enhancement effect of the mixed oxide catalysts on the formation of isobutene.

2. Experimental

Catalysts were prepared by precipitation of hydroxide with ca. 3% aqueous ammonia solution from mixed nitrate solution and drying at 425°C overnight, except for the rhodium-containing mixed oxide catalyst which was prepared from trichlororhodium hexahydrate and nitrates of cerium and zirconium. Reaction was carried out with a conventional flow system equipped with a quartz reactor and a gas doser of 5 ml for GC under 1 atm pressure. Product yields were passed at about 10 h after startup of the reaction and reached the state of very slow deactivation after 20 h. Therefore, all data were obtained between 20–25 h. The products were determined by GC. XPS spectra were recorded on a Shimadzu ESCA 750 spectrometer. XRD spectra were recorded on a Rigaku Geigerflex RAD-1VB spectrometer. Samples for XRD measurement were heated at 773 K for 3 h under N_2.

3. Results and discussion

In the investigation of the mixed oxide catalysts containing ZrO_2 as a main component lanthanide oxides have been reported to be relatively good second components [5]. Table 1 shows the hydrocarbon yield from the CO hydrogenation and the selectivities for C_4 hydrocarbons and isobutene with ZrO_2, CeO_2, ZrO_2–CeO_2 or ZrO_2–Pr_2O_3, and CeO_2–Y_2O_3 or CeO_2–La_2O_3 catalysts. The Ce-containing catalysts are more active for the hydrocarbon formation than the other lanthanide-containing catalysts. CeO_2 can activate CO and H_2 in the presence of water to form ketones and secondary alcohols, while ZrO_2 catalyzes only the water–gas shift reaction in the presence of water [7]. Therefore the higher activity of CeO_2-containing catalysts may come from the ability characteristic of CeO_2 that CeO_2 can perform the CO hydrogenation reaction along with the water–gas shift reaction even in the presence of water. The selectivities for C_4 hydrocarbons in total amount of hydrocarbons and for isobutene in C_4 hydrocarbons with ZrO_2 are the highest among various oxides [1]. The addition of lanthanide oxide other than CeO_2 to ZrO_2 results in a decrease in the hydrocarbon yield and the C_4 hydrocarbon selectivity, although the selectivity is still higher than those with catalysts that do not contain ZrO_2, as shown in table 1. Therefore, ZrO_2–CeO_2 catalyst seems to be the best combination for both hydrocarbon formation and C_4 selectivity.

Table 2 shows the effect of transition metal addition to ZrO_2–CeO_2 catalyst. The addition of oxides of Cr, Ni, and Cu causes a decrease in the C_4 hydrocarbon

Table 1
Hydrocarbon yield, selectivity of C_4 hydrocarbons, and selectivity of isobutene in C_4 hydrocarbons in the CO hydrogenation over ZrO_2- or CeO_2-containing oxide catalysts[a]

Run	Catalyst[b]	Conv. to HC (%)	Selectivity (%)						i-$C_4/\sum C_4$ (%)
			C_1	C_2	C_3	C_4	C_5	C_{6+}	
1	ZrO_2 (100)	0.029	9	8	6	70	7	+	86
2	CeO_2–ZrO_2 (1–1)	0.062	23	10	8	49	10	+	82
3	Pr_2O_3–ZrO_2 (1–10)	0.026	25	8	6	53	8	+	87
3	CeO_2 (100)	0.090	14	24	13	31	15	3	66
4	Y_2O_3–CeO_2 (1–10)	0.12	15	31	15	24	13	2	nd
5	La_2O_3–CeO_2 (1–10)	0.10	14	26	14	28	15	3	61

[a] The reaction was carried out at 673 K at 1 atm pressure of $CO/H_2/N_2 = 2/2/1$. Runs 1–3: total flow rate = 100 ml min^{-1} and catalyst = 2.0 g. Runs 4 and 5: total flow rate = 50 ml min^{-1} and catalyst = 1.0 g. HC: hydrocarbons. nd: not determined. +: trace. i-$C_4/\sum C_4$: isobutene selectivity in C_4 hydrocarbons.

[b] Values in parentheses are the atomic ratios of metal ions. Surface areas are 53, 69, 67, 27, 63, and 79 $m^2\ g^{-1}$ in the order of run number.

selectivity and no increase in the hydrocarbon yield. The addition of ZnO leads to a marked decrease in the selectivities of C_4 hydrocarbons and of isobutene, although the hydrocarbon yield is much higher. Thus, the addition of oxides of Cr, Ni, Cu, and Zn causes no positive effect on the formation of C_4 hydrocarbons. Since isobutene selectivity in C_4 hydrocarbons is more than 70%, this indicates that the addition of those four oxides is not useful to the formation of branched hydrocarbons. Only the addition of oxides of Fe and Co leads to the increase in the hydrocarbon yield, keeping the selectivities of C_4 hydrocarbons and of isobutene at the relatively high levels. The use of lanthanides other than Ce results in low hydrocarbon yield and low selectivity for C_4 hydrocarbons. The use of rhodium instead of Fe or Co leads to a very high conversion of CO, but no formation of isobutene. The hydrocarbons produced over the Rh-containing catalyst have the typical Schulz–Flory distribution, as shown also by the absence of isobutene in C_4 hydrocarbons. Thus, only the mixing of oxides of Fe or Co with CeO_2–ZrO_2 showed the enhancement effect on the higher hydrocarbon yield with the higher selectivities for C_4 hydrocarbons and isobutene. The addition of alkali or alkaline earth oxide seemed to be effective for isobutene formation [5]. However, the addition of these oxides caused a rapid deactivation by formation of a large amount of coke, although the initial formation rate of hydrocarbons was very high with the high selectivities of C_4 hydrocarbons and of isobutene.

Table 2
Hydrocarbon yield, C_4 hydrocarbon selectivity, and isobutene selectivity in C_4 hydrocarbons in the CO hydrogenation over ZrO_2–lanthanum oxide–transition metal oxide catalysts [a]

Run	Catalyst [b]	Conv. to HC (%)	Selectivity (%)						i-$C_4/\sum C_4$ (%)
			C_1	C_2	C_3	C_4	C_5	C_{6+}	
1	Cr_2O_3–CeO_2–ZrO_2 (10–100–100)	0.065	14	13	13	44	10	6	83
2	ZnO–CeO_2–ZrO_2 (10–100–100)	0.16	22	28	13	23	9	5	72
3	Fe_2O_3–CeO_2–ZrO_2 (10–100–100)	0.11	14	14	13	42	9	8	88
4	CoO–CeO_2–ZrO_2 (10–100–100)	0.14	11	12	11	55	7	4	93
5	NiO–CeO_2–ZrO_2 (10–100–100)	0.072	30	10	15	23	11	11	83
6	CuO–CeO_2–ZrO_2 (10–100–100)	0.051	16	11	12	42	13	6	81
7	Fe_2O_3–Sm_2O_3–ZrO_2 (2–20–100)	0.038	60	11	1	26	2	+	nd
8	Fe_2O_3–Pr_2O_3–ZrO_2 (2–20–100)	0.011	51	14	3	29	3	+	nd
9	CoO–La_2O_3–CeO_2 (10–100–100)	0.035	27	17	16	23	11	6	62
10	CoO–Sm_2O_3–CeO_2 (10–100–100)	0.043	18	17	19	27	11	8	71
11	Rh_2O_3–CeO_2–ZrO_2 (1–100–100)	1.1	29	12	23	14	10	12	+

[a] The reaction was carried out at 673 K at 1 atm pressure over 2.0 g of catalyst. Total flow rate was 100 ml min^{-1} and $CO/H_2/N_2 = 2/2/1$. HC, C_{6+}, nd, +, and i-$C_4/\sum C_4$ are as in table 1.

[b] Surface areas of catalysts are 53, 86, nd, 57, 76, nd, nd, 91, 68, 69, and 69 m^2 g^{-1} in the order of run number.

Table 3 shows the results with ZrO_2 and CeO_2 catalysts modified with Fe_2O_3 or CoO. The addition of Fe_2O_3 of $Fe/Zr = 1/100$ causes a decrease in C_4 hydrocarbons and an increase in C_1 hydrocarbon (run 2). When the ratio is increased to 5/100, the effect is much clearer (run 1). On the other hand, with the Fe_2O_3– or CoO–CeO_2 catalyst the effect on the increase in C_1 hydrocarbon and the decrease in C_4 hydrocarbons is not so clear, even though the atomic ratio is increased to 10/100 (runs 3 and 4). These results indicate that Fe_2O_3 and CoO mixed with CeO_2 do not show the characteristic of each oxide alone but stress the property of CeO_2 as shown in the comparison of runs 3 and 4 in table 3 with run 3 in table 1, while Fe_2O_3 mixed with ZrO_2 tends to show the property of Fe_2O_3 alone (runs 1 and 2). A single component oxide of Fe_2O_3 or CoO without modification with CeO_2 was reduced to metallic Fe or Co at 673 K under CO and H_2 to form hydrocarbons with Schulz–Flory distribution. The use of Sm or Pr instead of Ce leads to a

Table 3
Hydrocarbon yield, C_4 hydrocarbon selectivity, and isobutene selectivity in C_4 hydrocarbons in the CO hydrogenation over ZrO_2–Fe_2O_3 or ZrO_2–CoO and CeO_2–Fe_2O_3 or CoO catalysts [a]

Run	Catalyst [b]	Conv. to HC (%)	Selectivity (%)						i-$C_4/\sum C_4$ (%)
			C_1	C_2	C_3	C_4	C_5	C_{6+}	
1	Fe_2O_3–ZrO_2 (5–100)	0.078	65	4	3	26	2	+	nd
2	Fe_2O_3–ZrO_2 (1–100)	0.049	44	8	5	38	5	+	86
3	Fe_2O_3–CeO_2 (10–100)	0.22	27	14	10	32	12	5	69
4	CoO–CeO_2 (10–100)	0.13	20	26	12	22	13	7	58

[a] The reaction was carried out at 673 K at 1 atm pressure over 2.0 g of catalyst. Total flow rate was 100 ml min^{-1} and $CO/H_2/N_2 = 2/2/1$. HC, C_{6+}, nd, +, and i-$C_4/\sum C_4$ are as in table 1.

[b] Parentheses show the atomic ratios of metal ions. Surface areas are 110, 99, nd, and 67 $m^2\ g^{-1}$ in the order of run number.

decrease in C_4 hydrocarbons and increase in C_1 hydrocarbon. Therefore, the effect of the mixing of CeO_2 with Fe_2O_3 of CoO may be to keep the higher valency of iron and cobalt such as 2 or 3. The effect of the retention of the higher oxidation state by the combination with CeO_2 is shown also in the case of the other metal ions than Fe or Co, as shown in runs 1 to 6 in table 2. Thus, Ce ion is essential for the retention of the higher oxidation state by the complexation with Fe or Co ion, while Zr ion is needed to keep higher C_4 hydrocarbons and higher isobutene selectivities.

The XRD diffraction pattern of CeO_2–ZrO_2 showed the broad peaks due to $Ce_{1-x}Zr_xO_2$ or its mixture with CeO_2 as main peaks and the broad peaks and shoulders due to ZrO_2. The diffraction patterns of Fe_2O_3–CeO_2–ZrO_2, and CoO–CeO_2–ZrO_2 are consistent with that of CeO_2–ZrO_2. On the other hand, the diffraction patterns of CeO_2–ZrO_2 modified with the oxide of Cr, Zn, Ni, or Cu showed only the broad peaks due to $Ce_{1-x}Zr_xO_2$ shifted to higher angles than those due to CeO_2–ZrO_2 and no presence of ZrO_2. These results may indicate the interaction of Fe and Co ions with CeO_2–ZrO_2 is different from that of Cr, Zn, Ni and Cu ions. No further clear clarification on the difference could be obtained, since the peaks of XRD were broad and no pattern due to added transition metals could be detected. XPS spectra of Fe_2O_3– and CoO–CeO_2–ZrO_2 after the CO hydrogenation reaction showed the peak at 885.9 eV [8] due to Ce^{3+} even after exposure to air, while no peak due to Ce^{3+} was observed on CeO_2 and CeO_2–ZrO_2 after exposure to air. Ce^{3+} ion is shown to be the active site on CeO_2 catalyst [9]. Therefore, if a part of the role of the added Fe and Co ions is the retention of Ce^{3+} in the mixed oxides, it may be a possible speculation that the higher activity of CeO_2–ZrO_2 modified with Fe or Co ions may come from the ability of Ce^{3+}-stabilization. This may also be supported by the result that hydrocarbon distributions with the three component catalysts are almost the same as that with CeO_2–ZrO_2. Thus, the synergy of Fe or Co, Ce, and Zr is essential for the isobutene formation with high yield and high selectivity.

The results of the CO–H_2 reaction were obtained after the reaction for 20–25 h and most of the results were continued for 40–45 h. The products were detected by C_7 oxygenates and C_{11} hydrocarbons. However, as Hindermann et al. stated on the basis of the Fischer–Tropsch synthesis with metal catalysts, it is possible that a short non-steady-state experiment gives high C_2–C_4 selectivity and the longer-term behavior of the catalyst should be observed [10]. The reaction for a long time period and the higher pressure experiment are under investigation.

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