Catalysis Letters 14 (1992) 123–126

Isoprene formation from CO and H_2 over CeO_2 catalysts

Ken-ichi Maruya *, Kazumi Ito, Kazuhito Kushihashi, Yoshiho Kishida,
Kazunari Domen and Takaharu Onishi

Research Laboratory of Resources Utilization, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Received 1 February 1992; accepted 31 March 1992

The CO–H_2 reaction over CeO_2 catalysts at around 623 K and 67 kPa forms isoprene with about 20% and 70% selectivities in total and C_5 hydrocarbons, respectively. The formation of dienes may be due to the low and high activity of CeO_2 for alkene and CO hydrogenation, respectively.

Keywords: Isoprene; CO; H_2; CeO_2 catalysts

1. Introduction

The CO–H_2 reaction is usually carried out on metal catalysts to produce a wide variety of linear carbon chain products. On the other hand, difficult-to-reduce metal oxides such as ThO_2 [1], Dy_2O_3 [2], and ZrO_2 [3,4] which have usually been used as supports or additives of the catalysts, selectively form branched chain hydrocarbons. The hydrocarbons produced over these catalysts are alkenes and alkanes and the formation of highly unsaturated compounds such as acetylenes and dienes has only rarely been reported [5].

While CeO_2 also forms isobutene as one of the main products like the other difficult-to-reduce oxide catalysts, CeO_2 catalysts, especially In_2O_3-added CeO_2, can produce C_2 hydrocarbons with more than 40% selectivity for all hydrocarbons and with less than 0.5% ethane [6]. This seemed unusual, because C_2 hydrocarbons produced by other oxide catalysts contain much higher amounts of ethane, and alkane contents in C_3 and C_4 hydrocarbons are much higher [7]. The detailed analysis of hydrocarbons produced over CeO_2 catalysts showed the formation of isoprene and butadiene. The formation of diene compounds from the CO–H_2 reaction appears new. Thus, we describe here the formation of isoprene from CO and H_2 over CeO_2 catalysts under mild conditions.

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2. Experimental

CeO_2 was prepared by the precipitation from the aqueous nitrate solution with NH_4OH, dried at 303 K overnight, and then calcined at 773 K for 3 h. Mixed oxides (ratio of Ce to added metal = 10) were prepared from the mixed nitrates in the same manner as that of CeO_2. Catalysts were evacuated at 973 K for 3 h before reaction. The CO–H_2 reaction was carried out at 67 kPa of a mixed gas ($CO/H_2 = 1$) in a glass vacuum system with a gas circulation pump.

3. Results and discussion

Table 1 shows the product formation rates from CO and H_2 over CeO_2 catalysts at 623 K. The formation rates of CO_2 are much higher than those of hydrocarbons. The rates of hydrocarbons reached the steady states within the initial few hours, while it took more than 2 days to reach the steady states and the stable material balance between the hydrocarbons and the sum of CO_2 and H_2. The excess of CO_2 over hydrocarbons may come from the water gas shift reaction with H_2O or OH species in or on catalysts or the further reduction of the catalysts, though the pretreatment of catalysts was carried out. The addition of rare earth oxides leads to the decrease in the selectivity of higher hydrocar-

Table 1

Product formation rate and hydrocarbon selectivity from CO and H_2 over CeO_2 catalysts at 623 K[a]

Catalyst	Rate[b] (C-base μmol h^{-1})			Selectivity[c] (%)						Area ($g\ m^{-1}$)
	HC[e]	CO_2	H_2O	C_1	C_2	C_3	C_4	C_5	C_6^+	
CeO_2	12	34	[d]	8	7	3	27	21	34	21
Dy_2O_3-CeO_2	7	18	[d]	8	23	10	24	21	14	48
Tb_2O_3-CeO_2	18	32	[d]	15	20	8	26	25	6	53
Nd_2O_3-CeO_2	18	36	1.3	12	26	8	16	19	19	14
Pr_2O_3-CeO_2	27	137	7.0	8	26	9	19	22	16	34
Pr_2O_3-CeO_2[f]	8.7	[d]	[d]	4	22	6	29	26	13	22
Pr_2O_3-CeO_2[g]	30	39	[d]	11	31	9	24	18	7	32
SrO-CeO_2[h]	30	62	[d]	11	12	6	20	18	33	34

[a] Reaction temperature: 623 K, initial pressure: 600–700 Torr, catalyst: 1.0 g. Catalyst was evacuated at 973 K for 3 h and then treated with H_2 at 773 K for 16 h before reaction.

[b] Average values from initial 3 to 25 h.

[c] Selectivity in hydrocarbons. Oxygenates were less than 1% of hydrocarbons.

[d] Not determined.

[e] Hydrocarbons.

[f] Pr/Ce = 1/1.

[g] Pr/Ce = 5/100, reaction temperature: 643 K.

[h] Catalyst was prepared from the reaction of cerium nitrate with strontium hydroxide.

bons than C_6 and to the increase in that of C_2 hydrocarbons, maintaining the relatively high selectivity of C_5 hydrocarbons. The addition of rare earth oxides is most effective at In/Ce = 0.5–1/10, as shown by the substantial decrease in activity at the ratio = 1. The hydrocarbon formation rate with Pr_2O_3 alone was less than 1.0 μmol g^{-1} h^{-1}. Thus, the active site could be on the surface of CeO_2. The XRD analysis of Pr_2O_3-added CeO_2 showed little shifts of the *d*-value of the fluorite structure, suggesting the incorporation of Pr^{3+} ion into CeO_2 to promote the formation of oxygen defect [8]. The role of rare earth oxides could be the acceleration of the formation of Ce^{3+}, which may be the active site for the hydrocarbon formation [7]. Raising the reaction temperature leads to decreasing selectivity of C_5 hydrocarbons, though it raises the total hydrocarbon yield. The reaction at 523 K over Pr_2O_3-CeO_2 (Pr/Ce = 1/10) formed hydrocarbons, methanol, 2-methylpropanal, and ketones with the formation rates of 4.7, 1.6, 1.9, and 4.5 C-base 10^{-8} mol h^{-1}, respectively. The hydrocarbon distribution was essentially the same as that at 623 K, though C_5 and C_6^+ hydrocarbons increased and C_2 hydrocarbons decreased. The ketones mostly consisted of diisopropyl ketone. Thus, lowering reaction temperature results in the increase of oxygenates and the decrease of hydrocarbons.

The addition of SrO leads to the increase in the total hydrocarbon formation rate and the yield of C_6^+. The addition of Al_2O_3 or SiO_2 resulted in the formation of methane as a main product. The XRD spectra of these catalysts showed only fluorite structure due to CeO_2. These results suggest that catalyst basicity participates in the formation of higher hydrocarbons. The feature of the hydrocarbon distribution with the rare earth oxide-added catalysts is the relatively high selectivity of C_5 hydrocarbons. The isomer distribution of C_5 hydrocarbons is shown in table 2. It is clear that the main isomer is 2-methyl-1,3-butadiene. The isomer distribution of C_4 hydrocarbons is shown in table 3. Butadiene from 10 to 30%, which was previously thought to be one of the isomers of C_5 hydrocarbons [4,6,7], is formed. Raising the reaction temperature to 673 K resulted in the low selectivities of 1,3-C_4H_6 in C_4 hydrocarbons of 20% and of 2-CH_3-1,3-C_4H_5 in C_5 of 57%.

Table 2
Isomer distribution in C_5 hydrocarbons

Catalyst	Selectivity [a] (%)				
	1-C_5	1,3-C_5H_8	2-CH_3-1-C_4H_7	2-CH_3-2-C_4H_7	2-CH_3-1,3-C_4H_5
CeO_2	+	12	5	12	71
Dy_2O_3-CeO_2	1	3	12	5	83
Tb_2O_3-CeO_2	+	2	3	9	86
Nd_2O_3-CeO_2	1	5	5	11	78
Pr_2O_3-CeO_2	1	2	4	8	81

[a] iso-C_5H_{10}, 3-CH_3-1-C_4H_7, and trans- and cis-2-C_5H_{10} were less than 0.5%; *n*-C_5H_{12} was not detected.

Table 3
Isomer distribution in C_4 hydrocarbons

Catalyst	Selectivity [a] (%)				
	n-C_4H_{10}	iso-C_4H_{10}	iso-C_4H_8	cis-2-C_4H_8	1,3-C_4H_6
CeO_2	–	1	66	+	33
Dy_2O_3-CeO_2‘	1	2	61	+	34
Tb_2O_3-CeO_2	1	1	86	+	11
Nd_2O_3-CeO_2	3	4	74	1	18
Pr_2O_3-CeO_2	3	5	75	+	17

[a] Very small amounts of 1-C_4H_8 and trans-2-C_4H_8 were detected.

The formation of diene compounds on the cerium-containing catalysts may come from the low ability of CeO_2 to hydrogenate olefin [7]. Isoprene is the smallest branched diene compound and this may be a reason of the high selectivity in C_5 hydrocarbons, as in the case of isobutene in alkenes [3,4]. The hydrocarbons from CO and H_2 over CeO_2 contain both a series of branched alkenes and diene compounds, and this is the reason why the selectivity of C_5 hydrocarbons does not become larger.

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