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SELECTIVE FORMATION OF ISO-BUTENE FROM CARBON MONOXIDE AND HYDROGEN OVER ZIRCONIUM OXIDE CATALYST

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Iso-butene was selectively produced from CO-H_2 reaction over ZrO_2 catalyst under moderate conditions (0.5-21 atm, 300-450 °C).

The selective formation of iso-butane from CO-H_2 using metal oxide catalysts such as ThO_2, ZrO_2 and CeO_2 has been reported by Ziesecke et al.[1)] Recently Nazar et al. reported the selective formation of butenes (70 mol% among the total hydrocarbons produced; 1-butene: 33 mol%, iso-butene: 3.0%, t-2-butene: 18.5%, and c-2-butene: 15.5%) over $Co(0)_n$/NaY-zeolite catalysts at 247 °C and under 1 atm.[2)] Kieffer et al. have reported the formation of C_4 hydrocarbons (30.9% among the total hydrocarbons) produced from CO-H_2 on rare earth metal oxides such as La_2O_3 and Dy_2O_3 under severe conditions at 400 to 475 °C and under 400 atm.[3)] We report here a highly selective formation of iso-butene (nearly 80 mol% among all hydrocarbons produced) from CO-H_2 over ZrO_2 at 350 °C.

The catalysts were prepared by precipitation from solution of zirconium oxy-nitrate with NH_4OH and by calcination of the hydroxides at 500 °C for 3 h. The CO-H_2 (1:3) reactions over catalysts (ca. 1.5 g) were carried out in a conventional gas-circulating glass vacuum system and also in a flow system with a Hastelloy A reaction vessel for high pressure conditions (10 and 21 atm). The products were collected at liquid nitrogen temperature for initial 25 h with circulating system and for 10 min with a flow system except for methane which was collected with gas sampler, and analyzed by GC, MS, and IR techniques.

Results are summarized in Tables 1 and 2. The reaction of CO-H_2 over ZrO_2 around 250 °C proceeds to form mainly methanol, where the induction period of the reaction was observed for 5 h. At 300 °C dimethyl ether (DME) was mainly obtained. When the reaction temperature was raised to 350 °C large amounts of hydrocarbons were produced in stead of methanol and DME, and above 350 °C we could observe no induction period of the reactions. At 350 °C the selectivity of C_4 hydrocarbons in total hydrocarbons was to be 81.7 mol%. The C_4 hydrocarbons were analyzed in detail. The results are shown in Table 3. The marked selective formations of iso-butene among C_4 hydrocarbons are shown. The reaction rate of forming iso-butene was nearly proportional to the pressures of CO and H_2 respectively. The activity and selectivity to produce iso-butene after 240 h did not change.

High-pressure experiments (10 and 21 atm) were also carried out with a flow reactor at a space velocity of 2300 h^{-1} and at 400 °C as shown in Tables 1 and 2. Iso-butene selectivity in hydrocarbons in high-pressure experiments was similar to that in the low-pressure ones. The formation of methanol and DME may be due to a thermodynamic reason. The effects of the additives to the catalysts such as alkali metal and other oxides, and the reaction mechanism of the formation of iso-butene are under investigation.

Table 1. Product distribution (mol%) from the reaction of CO-H_2 on ZrO_2[a)]

T/°C	P/atm	CO %conv.	CO_2	MeOH	MeOMe	Hydrocarbons
200[b)]	0.68	0.4	4.3	81.8	13.4	0.5
250[b)]	0.68	1.9	17.4	65.2	16.7	0.6
300[b)]	0.68	4.8	49.7	13.3	34.8	2.2
350[b)]	0.68	10	83.8	0.9	1.6	13.6
400[b)]	0.68	18	80.8	0.0	0.0	19.2
450[b)]	0.68	21	76.6	0.0	0.0	23.4
400[c)]	10	5.3	83.6	2.4	1.6	12.3
400[c)]	21	33.8	81.6	3.4	5.5	9.6

a) ZrO_2: 1.5 g, H_2/CO=3. b) The catalyst was evacuated at 700 °C for 3 h before CO-H_2 reaction with gas-circulation system (470 ml). The products were collected at liquid nitrogen temperature for initial 25 h. The surface area of the catalyst was ca. 50 m^2/g. c) The reactor was washed with N_2 flow at 400 °C for 2 h before CO-H_2 reaction.

Table 2. Selectivity in hydrocarbons (mol%)

T/°C	P/atm	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5^+
200	0.68	24.2	37.6	2.0	18.8	-	17.4	-	-
250	0.68	42.7	31.3	1.1	10.4	-	14.6	-	-
300	0.68	10.1	29.0	0.3	13.0	-	47.5	-	-
350	0.68	4.1	6.7	0.2	5.1	-	81.7	0.9	1.3
400	0.68	14.9	5.3	2.1	5.1	1.1	63.7	2.9	4.9
450	0.68	41.3	9.7	6.7	8.2	2.1	23.0	6.0	2.9
400	10	11.9	16.2	1.3	4.3	0.5	60.3	0.8	4.8
400	21	10.2	15.4	0.8	3.3	0.4	62.3	0.7	6.9

Table 3. The product distribution in C_4 hydrocarbons (mol%)

T/°C	P/atm	n-C_4H_{10}	i-C_4H_{10}	1-C_4H_8	c-2-C_4H_8	t-2-C_4H_8	i-C_4H_8
350	0.68	0.0	1.1	0.2	0.7	1.0	97.1
400	0.68	0.3	4.1	1.7	2.3	3.3	88.4
400	21	0.1	0.6	1.7	0.8	1.0	96.4
450	0.68	10.8	11.0	2.9	7.9	10.7	56.8

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