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The CO-H_2 Reaction over ZrO_2 to Form Isobutene Selectively

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The CO-H_2 reaction over ZrO_2 was studied in detail. Methanol and isobutene were selectively formed at 473—523 and 623—673 K, respectively. The activation energies for C_2, C_3, and linear C_4 hydrocarbon formation are 79, 84, and 96 kJ mol^{-1} (523—723 K), while that for branched-chain C_4 hydrocarbons is about 210 kJ mol^{-1} (523—623 K). At 673 K the rate of C_4 hydrocarbon formation is as follows: $r=kP_{H_2}\cdot P_{CO}^2$, while those of C_1, C_2, and C_3 are written by the functions having the maximum values regarding CO pressure. C_4 hydrocarbons consist mostly of isobutene at the temperature. From these results it was concluded that isobutene is formed via different path from those of C_1, C_2, C_3, and linear C_4 hydrocarbons. The addition of high electronegative oxides such as SiO_2 and Nb_2O_5 resulted in the decrease of isobutene and the increase of methane. The selective formation of isobutene proceeds over pure ZrO_2 and ZrO_2 modified with 3a Group and basic metal oxides. The nature of active site for isobutene formation was discussed.

There have been vast researches on the hydrogenation of CO over transition metal catalysts and the products obtained are mostly comprised of hundreds of hydrocarbons and oxgenated products. In those cases the carbon chains of the products are usually linear and the distributions of hydrocarbons are described by the Schulz-Flory rule. Therefore, there have been only few studies on the selective formation of special hydrocarbons,[1-5] and even in the cases with high selectivity the catalysts are not so stable for the long time reaction and the high temperature treatment, because of the delicate method of catalyst preparation.[2,4,5]

On the other hand, difficultly reducible metal oxides have been used as catalyst supports and only few have been studied as catalysts. One of the features of metal oxide catalysts is to form branched-chain hydrocarbon products directly from CO and H_2. Thus, ThO_2,[6] La_2O_3,[7] and Dy_2O_3[7] produce branched-chain, saturated, and aliphatic hydrocarbons such as isobutane under very severe conditions, and ZrO_2 selectively forms isobutene under mild conditions such as at 69 kPa and 623 K.[8] These catalysts are stable for the reaction at 723 K[6,8] and the pretreatment at 973 K.[8] The selective formation of isobutene is found out also in the other oxide catalysts such as CeO_2 and La_2O_3 under the mild conditions.[9] In this paper we describe in detail the CO-H_2 reaction over ZrO_2 to form isobutene selectively.

Experimental

Materials. Zirconium hydroxide was precipitated by hydrolysis of $ZrO(NO_3)_2$ with about 5% aqueous ammonia solution, washed with deionized water until no ammonia was detected with Nesler's test, dried overnight at 393 K, and calcined at 773 K for 3 h. Mixed oxides of ZrO_2 with oxides of Ca, Sc, Y, Nd, and Sm were prepared from the mixed solution of $ZrO(NO_3)_2$ and each of the nitrates in similar manners to the ZrO_2 case. The impregnated ZrO_2 catalysts with Al_2O_3 and SiO_2 were prepared using the nitrate and the ethoxide solution, respectively, and were calcined around 673 K for several hours in order to remove the nitrate and the ethoxide ions and then at 773 K for 3 h. A mixed hydroxide of ZrO_2 and Nb_2O_5 was precipitated from aqueous HCl solutions of $NbCl_5$ and $ZrOCl_2$ with aqueous ammonia solution, and treated similarly to the ZrO_2 case. Zirconium sponge was purchased from Mitsuwa Pure Chemicals.

Procedure. Reactions were carried out in a glass vacuum reaction system with a gas-circulating pump and also a flow system under the atmospheric pressure. In the reaction with the vacuum system a mixture of CO and H_2 (1:3) was purified by gas circulation through a trap at liquid nitrogen temperature for 1 h before contacting with the catalyst (1.5 g), which was preevacuated at 973 K for 3 h. The initial pressure was 69 kPa and the gas flow rate was about 35 ml(STP) min^{-1}.

The reaction was also carried out in the flow system with a quartz reactor of 12 mm of outside diameter, to investigate the pressure dependence of the reaction rate. The reaction temperature was measured by a thermocouple inserted in the catalyst bed (5.0 g). The catalyst was heated at 873 K for 3 h under a nitrogen stream at about 100 ml(STP) min^{-1}, and then H_2 and CO were introduced after cooling the catalyst to a given reaction temperature. The total flow rate was kept constant by changing that of nitrogen.

Analyses. Products except for methane were collected at the liquid nitrogen temperature. GC, IR, and MS were used for analyses of products and CO. Quantitative analyses were conducted by GC equipped with a Porapak Q column for CO_2, H_2O, methanol, dimethyl ether, and hydrocarbons including CH_4, VZ-7 and VZ-10 columns (Gasukuro Kogyo Inc.) for isomer of C_4 and C_5 hydrocarbons, and a molecular sieve 5A column (Nishio Industry Co.) for CO.

Results and Discussion

Temperature Dependence of Hydrocarbon Formation. Table 1 shows the yield of products formed from the CO-H_2 reaction over ZrO_2 using the gas-circulating glass reaction system at the temperature from 473 to 723 K for the initial 25 h. Yields of methanol and dimethyl ether reaches the maximum values around 523 and 573 K, respectively, and that of

Table 1. Product Yield from CO–H_2 Reaction over ZrO_2[a)]

T/K	Yield/C-base μmol				
	Hydrocarbon	MeOH	Me_2O	CO_2	H_2
473	0.17	11	3.6	0.6	4.5
523	0.86	43	22	11	37
573	8.8	16	84	60	38
623	145	2.7	9.2	240	47
673	282	0.0	0.28	350	160
723	308	0.0	0.0	430	200

a) ZrO_2 (1.5 g) was evacuated at 973 K for 3 h before reaction. Initial pressure (H_2/CO=3) was 69 kPa. Products were collected for the initial 25 h.

Table 2. Product Distributions in C_4 Hydrocarbons

T/K	Selectivity/mol%						$C_4/\sum C_i$
	n-C_4H_{10}	i-C_4H_{10}	1-C_4H_8	t-2-C_4H_8	c-2-C_4H_8	i-C_4H_8	C-base %
523	3.0	0.4	63	3.3	1.3	29	27
573	0.3	0.0	0.5	7.7	0.5	91	60
623	0.0	1.1	0.2	1.0	0.7	97	89
673	0.3	4.2	1.7	3.4	2.4	88	78
723	10	11	3.0	8.0	11	57	49

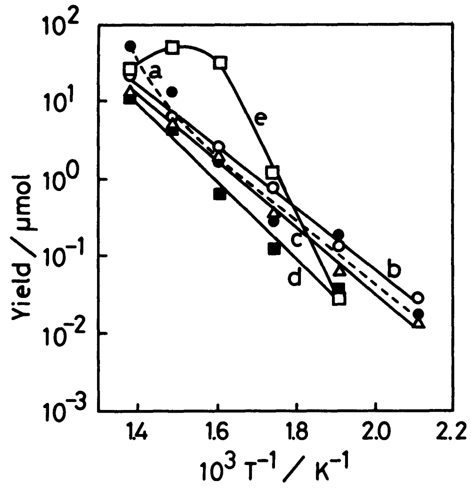

Fig. 1. Arrhenius plots of hydrocarbon yields formed from CO–H_2 reaction over ZrO_2 at 60 kPa (H_2/CO=3). a(●): C_1, b(○): C_2, c(△): C_3, d(■): linear C_4, and e(□): branched-chain C_4.

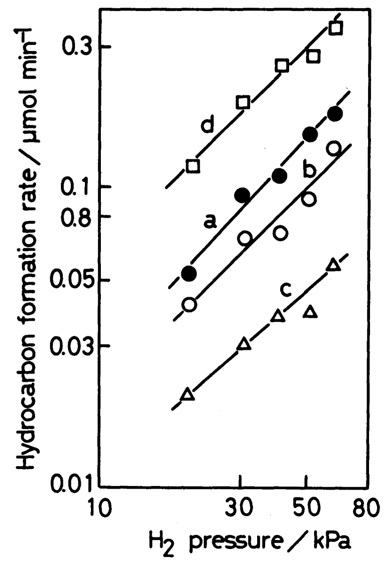

Fig. 2. H_2 pressure dependence of hydrocarbon formation rate at 673 K and 40 kPa of CO pressure. a: C_1, b: C_2, c: C_3, and d: C_4.

hydrocarbons increases rapidly with an increase in the reaction temperature. The temperature dependences of the yields of C_1 to C_4 hydrocarbons are shown in Fig. 1. The plots for C_2 and C_3 hydrocarbons are almost linear in the wide temperature range between 523 and 723 K and their apparent activation energies are 79 and 84 kJ mol^{-1}, respectively. Methane yields are close to those of C_2 and C_3 hydrocarbons, although they are rather scattered. The yields of linear C_4 hydrocarbons evaluated from the isomer distribution shown in Table 2 are plotted rather linearly in the temperature range and the activation energy is about 96 kJ mol^{-1}. On the other hand, the yield of branched-chain C_4 hydrocarbons has maximum value around 673 K. The activation energy evaluated in the narrow range between 523 and 623 K is about 210 kJ mol^{-1}. The isomer distributions in Table 2 show that at 523 K 1-butene is mainly formed but above 573 K the main product is isobutene and no or little skeletal isomerization takes place at 623 K. These results indicate that the branched-chain hydrocarbons are probably formed by the different path from the linear ones.

Pressure Dependence of Hydrocarbon Formation. Figure 2 shows the H_2 pressure dependences of the formation rates of hydrocarbons from C_1 to C_4. The rates are proportional to the pressure. For the rate of

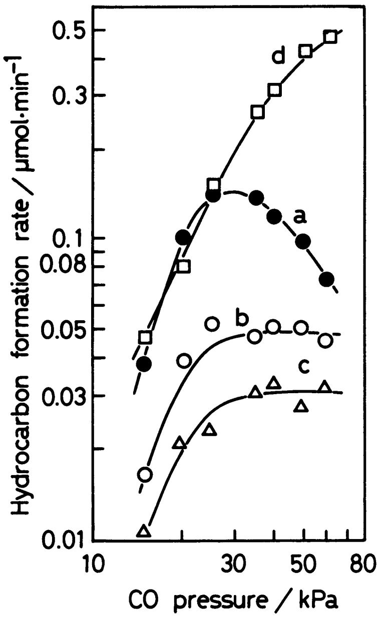

Fig. 3. CO pressure dependence of hydrocarbon formation rate at 673 K and 40 kPa of H_2.

methanation over metal catalysts it is reported that the exponents of the H_2 pressure vary between 0.7 and 1.6.[10,11] For the Fischer–Tropsch reaction various values between 0 and 2 are reported, although the exponent value under usual conditions is reported to be about 1.[12,13] Thus, oxide catalysts such as ZrO_2 show the same dependence on the H_2 pressure as the metal catalysts.

Figure 3 shows the CO pressure dependence of the rates. Differing from the H_2 pressure dependence, the plots are not linear for all hydrocarbons. The rates of C_1, C_2, and C_3 hydrocarbon formation increase with an increase in the pressure range of about 30 kPa. The rate of C_1 hydrocarbon formation reaches the maximum value around 30 kPa, while those of C_2 and C_3 become nearly constant above that value. On the other hand, the rate of C_4 hydrocarbon formation is almost proportional to the square of the pressure. Since C_4 hydrocarbons consist mostly of isobutene at the temperature shown in Table 2, the difference of the CO pressure dependence means that the mechanism of isobutene formation is probably different from those of linear hydrocarbons.

The formation of branched-chain, aliphatic, and saturated hydrocarbons in the isosynthesis reaction has been explained by the mechanism of the conversion of methanol which is produced as a primary product.[6,7] Since ZrO_2 is one of the isosynthesis catalysts[6] and methoxide species is observed on the ZrO_2 surface under the reaction conditions,[14] the surface methoxide species is one of the possible precursor for the hydrocarbon formations. The formation of linear hydrocarbons such as C_{1-3} and linear C_4 hydrocarbons might take place in a similar mechanism to isosynthesis reactions, because the Arrhenius plots are almost linear from the low temperature, at which methanol is selectively formed, to the high temperature and methoxide species are observed in the temperature range under the reaction conditions.[14] On the other hand, the formation of isobutene begins to take place above 623 K, at which the amounts of methanol and dimethyl ether decrease and the rate of the formation depends on the CO pressure in the second order. These results suggest that the formation of isobutene proceeds probably via some species in addition to the methoxide. That is, the formation path of isobutene from the CO–H_2 reaction over ZrO_2 may be different from the methanol conversion suggested in the isosynthesis. Recently, the mechanisms of aldol condensation type have been proposed for the formation of branched-chain olefins over ZrO_2[15] and CeO[16] catalysts. However, the lack of experimental evidence in the former case and the low selectivity of C_4 hydrocarbons in the latter case make obscure the agreement with the highly selective CO–H_2 reaction over ZrO_2 in the present study. Reaction mechanisms for the isobutene formation are under investigation.

Effect of Metal Oxide Additives over ZrO_2. It has been shown that the preparation methods of the ZrO_2 catalyst affect the product selectivity, i.e., ZrO_2 prepared from zirconium oxynitrate with aqueous ammonia solution produces isobutene selectively from CO and H_2, while ZrO_2 from the alkoxide with water produces methane.[17] Therefore, the modification of ZrO_2 by the addition of the second oxide component may lead to the change of product selectivity and the hydrocarbon formation activity. Table 3 shows the hydrocarbon yields and selectivities with some modified ZrO_2 catalysts. When the CO–H_2 reaction over Zr sponges proceeds, a large amount of H_2 was absorbed and small amounts of widely dispersed hydrocarbons were formed. Zirconium sponges pretreated with H_2 gives methane as a main product. Therefore, isobutene formation over the ZrO_2 catalyst hardly participates in low valent zirconium.

Among the mixed oxide catalysts, SiO_2- and Nb_2O_5-added catalysts are not C_4-selective but rather methane-selective. In the reaction using these catalysts the large amounts of hydrocarbons are produced than those of CO_2. On the other hand, in the case of the other mixed oxide catalysts the amounts of hydrocarbons formed are less than that of CO_2, indicating the presence of unrecovered carbon species. Since methoxide species and formate ions are formed on the ZrO_2 surface under the reaction conditions,[14] the time course of the reaction showed the large amount of CO–H_2 gas absorption in the initial few hours of the reaction, and no coke formation was

Table 3. Effect of Metal Oxide Addition to ZrO_2 on Hydrocarbon Formation Activity and Selectivity[a]

No.	Catal.[b]	Area	Yield (C-base µmol)			Selectivity (C-base%)					
		$m^2 \cdot g^{-1}$	H.C.	MeOH & Me_2O	CO_2	C_1	C_2	C_3	C_4	C_5	C_6
1	Zr[c]	ca. 3	7	+	3	18	29	24	9	4	16
2	Zr(H)[d]	ca. 3	20	0	11	64	19	8	7	1	1
3	ZrO_2	59	364	6	370	4	6	7	77	5	1
4	NaOH(13)[e]	33	93	6	106	3	1	3	85	6	2
5	CaO(10)	25	257	5	320	15	11	9	59	6	1
6	Al_2O_3(10)	—[f]	31	13	72	33	27	2	28	5	5
7	SiO_2(10)	—[f]	67	0	6	90	5	2	3	1	+
8	Sc_2O_3(1)	75	227	3	260	15	8	6	66	4	1
9	Y_2O_3(1)	61	356	6	426	4	5	6	77	7	1
10	CeO_2(10)	69	381	3	434	5	4	5	73	12	2
11	Nd_2O_3(1)	67	366	3	371	4	6	6	77	7	+
12	Nd_2O_3(5)	55	246	4	386	5	5	4	77	8	1
13	Sm_2O_3(1)	54	356	7	497	6	6	6	74	7	1
14	Nb_2O_5(10)[g]	67	287	+	84	65	4	3	13	12	2

a) Catalyst: 1.5 g, initial pressure: 67(Nos. 6, 7), 71(Nos. 1, 2, 4), and 84 kPa(the others), reaction temperature: 623(Nos. 6, 7) and 673 K(the others), reaction time: initial 24(Nos. 1, 2, 4) and 25 h(Nos. 6, 7), and 5—24 h(the others). b) ZrO_2 used as the catalyst (No. 3) and mixed oxide catalysts (Nos. 4—13) were prepared from $ZrO(NO_3)_2$ and numbers in parentheses mean the atomic ratio of added metal to 100 of Zr. c) Preevacuation temperature: 673 K. d) Pretreatment with H_2: 873 K, 91 kPa, and 3 h. e) The catalyst was prepared by the addition of aqueous NaOH solution to $ZrO(NO_3)_2$ solution and XPS spectra showed that the ratio of Na to Zr on the surface was about 0.13. f) Not determined. g) The catalyst was prepared from hydrochloric solution of $NbCl_5$ and $ZrOCl_2$ (1:10) by the coprecipitation method using aqueous ammonia solution.

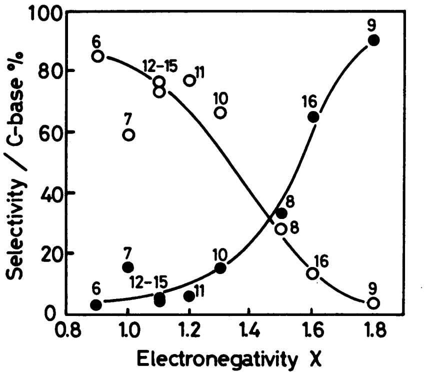

Fig. 4. Relation of C_1 (—●—) and C_4 (—○—) hydrocarbon selectivity to electronegativity. Numbers correspond to the Run No. in Table 3.

observed for 24 h reaction, most of the unrecovered carbon could be the surface-adsorbed species and a part of the carbon might be unrecovered higher hydrocarbons.

The presence of NaOH on ZrO_2 causes a little increase in the isobutene selectivity (85%) compared with that (77%) over the unmodified ZrO_2 catalyst, although the activity is lowered to about one forth. The addition of Al_2O_3 results in the lower selectivity for C_4 hydrocarbons. The SiO_2-added catalyst is rather methane-selective. These results indicate that there are two types of active sites on ZrO_2, one of which is effective for C_4 hydrocarbon formation and the other is for methane formation. Then, oxides of Sc, Y, some La Group elements, and Nb were used as difficulty reducible transition metal oxides. The addition of elements of lanthanum group, Sc, and Y oxides causes the selectivity and the activity to change only little, while that of Nb_2O_5 leads to the decrease of C_4 hydrocarbon and the increase of methane. Since the mixed oxide of SiO_2 or Al_2O_3 with ZrO_2 exhibits the solid acidity, which is not found on both oxides,[18] this selectivity change may relate to the electronegativity[19] of the additives. Figure 4 shows the relation of the electronegativity to the selectivity of C_1 and C_4 hydrocarbons. The addition of higher electronegative oxide results in the lower selectivity for C_4 hydrocarbons and the higher selectivity for methane. This may indicate that the increase in the acidity on ZrO_2 promotes the formation of methane and retards the formation of C_4 hydrocarbons. In the presence of NaOH with the much lower electronegativity than ZrO_2, the selectivity of C_4 hydrocarbons has the highest value. Thus, the pure ZrO_2 catalyst, ZrO_2 with 3a group and also basic metal oxides such as NaOH are the effective catalysts for selective formation of C_4 hydrocarbons, especially isobutene. This suggests the importance of basic character of active site for isobutene formation.

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