

The CO-H₂ Reaction over ZrO₂ to Form Isobutene Selectively

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The CO-H₂ reaction over ZrO₂ was studied in detail. Methanol and isobutene were selectively formed at 473–523 and 623–673 K, respectively. The activation energies for C₂, C₃, and linear C₄ hydrocarbon formation are 79, 84, and 96 kJ mol⁻¹ (523–723 K), while that for branched-chain C₄ hydrocarbons is about 210 kJ mol⁻¹ (523–623 K). At 673 K the rate of C₄ hydrocarbon formation is as follows: $r = kP_{H_2} \cdot P_{CO}^2$, while those of C₁, C₂, and C₃ are written by the functions having the maximum values regarding CO pressure. C₄ hydrocarbons consist mostly of isobutene at the temperature. From these results it was concluded that isobutene is formed via different path from those of C₁, C₂, C₃, and linear C₄ hydrocarbons. The addition of high electronegative oxides such as SiO₂ and Nb₂O₅ resulted in the decrease of isobutene and the increase of methane. The selective formation of isobutene proceeds over pure ZrO₂ and ZrO₂ 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 oxygenated 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 H₂. Thus, ThO₂,⁶⁾ La₂O₃,⁷⁾ and Dy₂O₃⁷⁾ produce branched-chain, saturated, and aliphatic hydrocarbons such as isobutane under very severe conditions, and ZrO₂ 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 CeO₂ and La₂O₃ under the mild conditions.⁹⁾ In this paper we describe in detail the CO-H₂ reaction over ZrO₂ to form isobutene selectively.

Experimental

Materials. Zirconium hydroxide was precipitated by hydrolysis of ZrO(NO₃)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 ZrO₂ with oxides of Ca, Sc, Y, Nd, and Sm were prepared from the mixed solution of ZrO(NO₃)₂ and each of the nitrates in similar manners to the ZrO₂ case. The impregnated ZrO₂ catalysts with Al₂O₃ and SiO₂ 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 ZrO₂ and Nb₂O₅ was precipitated from aqueous HCl solutions of NbCl₅ and ZrOCl₂ with aqueous ammonia solution, and treated similarly to the ZrO₂ 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 H₂ (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 H₂ 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 CO₂, H₂O, methanol, dimethyl ether, and hydrocarbons including CH₄, VZ-7 and VZ-10 columns (Gasukuro Kogyo Inc.) for isomer of C₄ and C₅ 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-H₂ reaction over ZrO₂ 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-H₂ Reaction over ZrO₂^{a)}

T/K	Yield/C-base μmol				
	Hydrocarbon	MeOH	Me ₂ O	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) ZrO₂ (1.5 g) was evacuated at 973 K for 3 h before reaction. Initial pressure (H₂/CO=3) was 69 kPa. Products were collected for the initial 25 h.

Table 2. Product Distributions in C₄ Hydrocarbons

T/K	Selectivity/mol%						C ₄ / $\sum C_i$ C-base %
	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₄ H ₁₀	1-C ₄ H ₈	<i>t</i> -2-C ₄ H ₈	<i>c</i> -2-C ₄ H ₈	<i>i</i> -C ₄ H ₈	
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

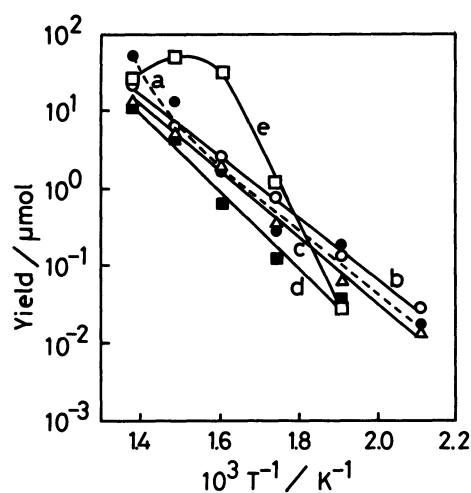


Fig. 1. Arrhenius plots of hydrocarbon yields formed from CO-H₂ reaction over ZrO₂ at 60 kPa (H₂/CO=3). a(●): C₁, b(O): C₂, c(Δ): C₃, d(■): linear C₄, and e(□): branched-chain C₄.

hydrocarbons increases rapidly with an increase in the reaction temperature. The temperature dependences of the yields of C₁ to C₄ hydrocarbons are shown in Fig. 1. The plots for C₂ and C₃ 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 C₂ and C₃ hydrocarbons, although they are rather scattered. The yields of linear C₄ 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 C₄ hydrocarbons has maximum value

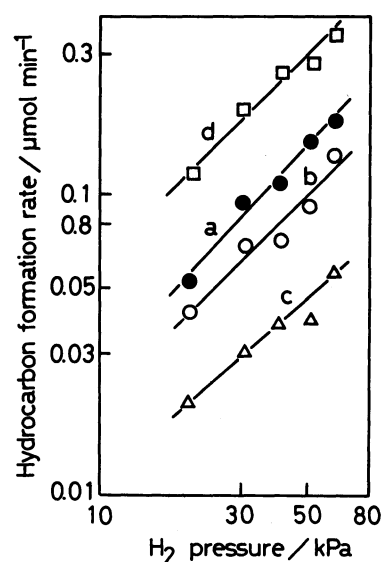


Fig. 2. H₂ pressure dependence of hydrocarbon formation rate at 673 K and 40 kPa of CO pressure. a: C₁, b: C₂, c: C₃, and d: C₄.

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 H₂ pressure dependences of the formation rates of hydrocarbons from C₁ to C₄. The rates are proportional to the pressure. For the rate of

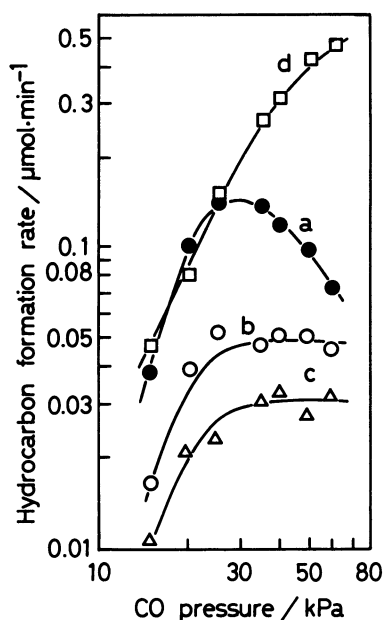


Fig. 3. CO pressure dependence of hydrocarbon formation rate at 673 K and 40 kPa of H₂.

methanation over metal catalysts it is reported that the exponents of the H₂ 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 ZrO₂ show the same dependence on the H₂ pressure as the metal catalysts.

Figure 3 shows the CO pressure dependence of the rates. Differing from the H₂ pressure dependence, the plots are not linear for all hydrocarbons. The rates of C₁, C₂, and C₃ hydrocarbon formation increase with an increase in the pressure range of about 30 kPa. The rate of C₁ hydrocarbon formation reaches the maximum value around 30 kPa, while those of C₂ and C₃ become nearly constant above that value. On the other hand, the rate of C₄ hydrocarbon formation is almost proportional to the square of the pressure. Since C₄ 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 ZrO₂ is one of the isosynthesis catalysts⁶ and methoxide species is observed on the ZrO₂ 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

C₁₋₃ and linear C₄ 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-H₂ reaction over ZrO₂ 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 ZrO₂¹⁵ and CeO₂¹⁶ catalysts. However, the lack of experimental evidence in the former case and the low selectivity of C₄ hydrocarbons in the latter case make obscure the agreement with the highly selective CO-H₂ reaction over ZrO₂ in the present study. Reaction mechanisms for the isobutene formation are under investigation.

Effect of Metal Oxide Additives over ZrO₂. It has been shown that the preparation methods of the ZrO₂ catalyst affect the product selectivity, i.e., ZrO₂ prepared from zirconium oxynitrate with aqueous ammonia solution produces isobutene selectively from CO and H₂, while ZrO₂ from the alkoxide with water produces methane.¹⁷ Therefore, the modification of ZrO₂ 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 ZrO₂ catalysts. When the CO-H₂ reaction over Zr sponges proceeds, a large amount of H₂ was absorbed and small amounts of widely dispersed hydrocarbons were formed. Zirconium sponges pretreated with H₂ gives methane as a main product. Therefore, isobutene formation over the ZrO₂ catalyst hardly participates in low valent zirconium.

Among the mixed oxide catalysts, SiO₂- and Nb₂O₅-added catalysts are not C₄-selective but rather methane-selective. In the reaction using these catalysts the large amounts of hydrocarbons are produced than those of CO₂. On the other hand, in the case of the other mixed oxide catalysts the amounts of hydrocarbons formed are less than that of CO₂, indicating the presence of unrecovered carbon species. Since methoxide species and formate ions are formed on the ZrO₂ surface under the reaction conditions,¹⁴ the time course of the reaction showed the large amount of CO-H₂ gas absorption in the initial few hours of the reaction, and no coke formation was

Table 3. Effect of Metal Oxide Addition to ZrO₂ on Hydrocarbon Formation Activity and Selectivity^{a)}

No.	Catal. ^{b)}	Area m ² ·g ⁻¹	Yield (C-base μmol)			Selectivity (C-base%)					
			H.C.	MeOH & Me ₂ O	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 ₂ O 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 ₂ O ₃ (1)	75	227	3	260	15	8	6	66	4	1
9	Y ₂ O 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 ₂ O ₃ (1)	67	366	3	371	4	6	6	77	7	+
12	Nd ₂ O ₃ (5)	55	246	4	386	5	5	4	77	8	1
13	Sm ₂ O ₃ (1)	54	356	7	497	6	6	6	74	7	1
14	Nb ₂ O 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) ZrO₂ used as the catalyst (No. 3) and mixed oxide catalysts (Nos. 4—13) were prepared from ZrO(NO₃)₂ and numbers in parentheses mean the atomic ratio of added metal to 100 of Zr. c) Preevacuation temperature: 673 K. d) Pretreatment with H₂: 873 K, 91 kPa, and 3 h. e) The catalyst was prepared by the addition of aqueous NaOH solution to ZrO(NO₃)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 NbCl₅ and ZrOCl₂ (1:10) by the coprecipitation method using aqueous ammonia solution.

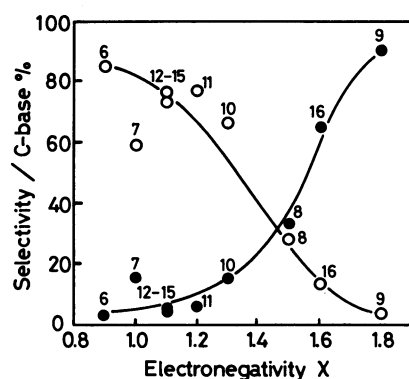


Fig. 4. Relation of C₁ (—●—) and C₄ (—○—) hydrocarbon selectivity to electronegativity. Numbers correspond to the Run No. in Table 3.

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 ZrO₂ causes a little increase in the isobutene selectivity (85%) compared with that (77%) over the unmodified ZrO₂ catalyst, although the activity is lowered to about one fourth. The addition of Al₂O₃ results in the lower selectivity for C₄ hydrocarbons. The SiO₂-added catalyst is rather methane-selective. These results indicate that there are two types of active sites on ZrO₂, one of which is effective for C₄ 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 Nb₂O₅ leads to the decrease of C₄ hydrocarbon and the increase of methane. Since the mixed oxide of SiO₂ or Al₂O₃ with ZrO₂ exhibits the solid acidity, which is not found on both oxides,¹⁸⁾ this selectivity change may relate to the electronegativity¹⁹⁾ of the additives. Figure 4 shows the relation of the electronegativity to the selectivity of C₁ and C₄ hydrocarbons. The addition of higher electronegative oxide results in the lower selectivity for C₄ hydrocarbons and the higher selectivity for methane. This may indicate that the increase in the acidity on ZrO₂ promotes the formation of methane and retards the formation of C₄ hydrocarbons. In the presence of NaOH with the much lower electronegativity than ZrO₂, the selectivity of C₄ hydrocarbons has the highest value. Thus, the pure ZrO₂ catalyst, ZrO₂ with 3a group and also basic metal oxides such as NaOH are the effective catalysts for selective formation of C₄ hydrocarbons, especially isobutene. This suggests the importance of basic character of active site for isobutene formation.

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