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Effect of Additives on Selective Formation of Isobutene from the CO-H_2 Reaction over ZrO_2

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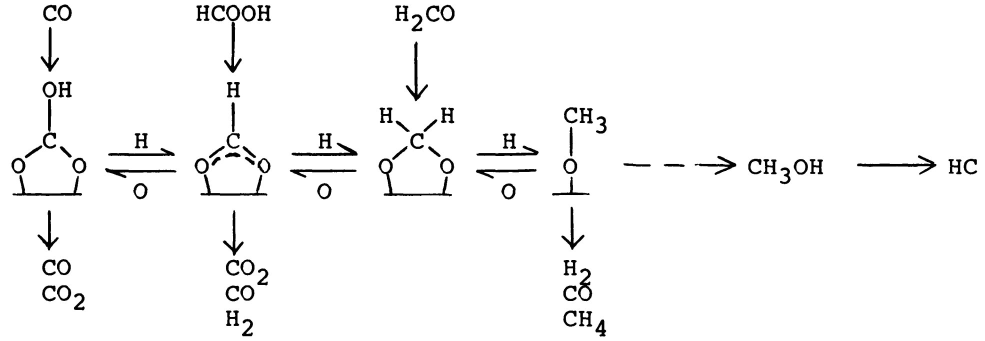
The CO-H_2 reaction over ZrO_2 was carried out in the presence of various organic additives. The addition of dimethyl ether, methylal, acetaldehyde, and dimethyl acetal showed the marked enhancement effects on the hydrocarbon formation keeping the high selectivity for isobutene. Ethylene was little effective. The addition of acetone, propanal, and propylene resulted in the decrease in the formation of isobutene and the increase in that of *n*-butenes. The presence of CO and H_2 was essential to the selective formation of isobutene. The formation pathways of isobutene and the other hydrocarbons are discussed.

The CO–H_2 reaction has been mostly performed using transition metal catalysts to produce a broad spectrum of compounds with linear carbon chains. Selective formation of saturated, branched-chain, aliphatic hydrocarbons has been carried out using the difficultly reducible oxide catalysts such as ThO_2[1] and Dy_2O_3[2] under very severe conditions and CdO catalysts combined with acid supports under mild conditions.[3] Recently, we found that the CO–H_2 reaction over ZrO_2 under mild conditions such as 673 K and atmospheric pressure produces isobutene selectively.[4,5]

The isosynthesis reaction[6] has been suggested to proceed via methanol which is formed as a primary product from CO and H_2.[1,2] He and Ekerdt[7,8] observed the appearance of methoxide species along with formate ion after the treatment of ZrO_2 with a mixture of CO and H_2 at reduced pressure and at reaction temperatures from 673 to 773 K followed by evacuation at 298 K, and proposed the following pathway for the formations of methanol and hydrocarbons from CO and H_2 over ZrO_2. This methanism is similar to that in the isosynthesis reaction, in that methanol is a precursor to hydrocarbons.

We have reported that the CO–H_2 reaction over ZrO_2 at 673 K forms the hydrocarbons consisting mainly of isobutene and that adsorbed species on the ZrO_2 surface during the reactions are both methoxide and formate species.[9] Therefore, the first question is how the methoxide species participates in the formation of hydrocarbons. We also reported that the formation path of isobutene is different from that of the other hydrocarbons such as C_2, C_3, and linear C_4 hydrocarbons on the basis of their different dependences on the reaction temperature and CO pressure,[5] i.e., the yields of C_2, C_3, and linear C_4 hydrocarbons are linearly plotted by the Arrhenius equation in the wide temperature range from 473 to 723 K, while that of isobutene increases rapidly above 573 K and the activation energy for the formation of isobutene is much higher than those of the other hydrocarbons. Furthermore, the formation rate of isobutene depends on the CO pressure nearly in the second order, while those of the other hydrocarbons do not. Therefore, the second question is how the formation of isobutene is correlated with that of the other hydrocarbons. Here we describe the relation of surface methoxide species to the formation of hydrocarbons and the effect of addition of various organic compounds having the carbon chain from C_1 to C_3 to the CO–H_2 reaction on the formations of isobutene and the other hydrocarbons.



Experimental

Materials. ZrO_2 was prepared as described previously.[5] H_2 was purchased from Showa Denko Co. CO, ethylene, and propylene were purchased from Takachiho Kagaku Kogyo K. K. Iron carbonyl in CO gas was removed by active carbon cooled at Dry Ice or liquid nitrogen temperature. Oxygenates were purchased from Kanto Chemical Co. and used without further purification.

Procedures. Reactions were carried out in a conventional flow system with a quartz reactor of 12 mm in diameter and a glass vacuum system with a gas-circulating pump. The flow reactions with organic additives were carried out at 1 atm total pressure and at the total flow rate of 100 ml·min^{-1}. Feed of dimethyl ether was controlled finely by two needle valves and its concentration was determined by G.C. The other organic compounds were added using syringe. The glass vacuum system was used for the investigation of time course of the CO–H_2 reaction. Products were analyzed by GC as described previously.[5]

Results

1) Reaction of Methanol. The reaction of methanol over isosynthesis catalysts at 723 K and 300 atm has been reported to form the products of the same hydrocarbon distribution as the CO–H_2 reaction.[1,2] On the other hand, the reaction of methanol over ZrO_2 under mild conditions such as 643 K and 0.23 kPa of the methanol partial pressure produced only dimethyl ether in the steady state. Since the CO–H_2 reaction in the presence of 0.25 kPa of water produced only CO_2 of 0.15 kPa, no formation of hydrocarbons in the methanol reaction over the ZrO_2 catalyst will be due to the inhibition of the further reaction of dimethyl ether for the hydrocarbon formation by water.

2) Reaction of Dimethyl Ether. Since dimethyl ether is an anhydride of methanol, the reaction of dimethyl ether is expected to occur without the inhibition by water. Table 1 shows the conversion of dimethyl ether and the distribution of hydrocarbons formed. Increasing the feed of dimethyl ether from 0.012 to 2.5 ml·min^{-1} decreases the conversion from 99 to 28% and the total yield of C_1 to C_6 hydrocarbons based on the dimethyl ether consumed from 72 to 6%. At the highest feed, 50% of dimethyl ether consumed decomposes into CO and H_2. One of the reasons why the increase in the feed of dimethyl ether results in the low yield of hydrocarbons is likely that the decomposition of dimethyl ether increases with an increase in the feed. The product distribution in Table 1 shows that the reaction of dimethyl ether alone yields a broad spectrum of hydrocarbons. Although the highest yield in the hydrocarbons is achieved in C_2 hydrocarbons, the yield is low.

The addition of H_2 to the dimethyl ether reaction leads to the higher yield of hydrocarbons, which

Table 1. Effect of Additives to CO–H_2 Reaction on Hydrocarbon Yields[a]

Run	Feed rate/ml min^{-1}				DME conv.
	N_2	H_2	CO	DME	%
1	91	0	0	0.012	99
2	91	0	0	0.04	99
3	91	0	0	0.48	80
4	91	0	0	2.5	28
5	54	36	0	0.12	100
6	18	36	36	0	–
7	18	36	36	0.05	100
8	18	36	36	0.12	100
9	18	36	36	0.39	100
10	18	36	36	2.2	95
11	18	36	36	0.14[c]	100

Run	Hydrocarbon yield/carbon base µmol min^{-1}								$\sum C_i$[b] / 2(DME consumed) %
	CO	CO_2	C_1	C_2	C_3	C_4	C_5	C_6	
1	–	0	0.11	0.25	0.27	0.08	0.06	+	72
2	–	0	0.19	0.23	0.22	0.14	0.29	+	30
3	–	0	1.3	2.8	0.64	1.1	0.60	+	15
4	63	0	1.8	6.9	1.5	2.3	0.48	0.28	6
5	–	–	0.89	1.7	0.85	0.78	0.26	0.02	41
6	–	3.2	0.03	0.14	0.17	2.3	0.25	+	–
7	–	6.1	0.38	0.57	0.41	3.5	0.53	–	121
8	–	9.2	0.34	0.61	0.65	5.2	0.43	0.01	68
9	–	5.7	1.4	2.7	2.1	8.3	0.48	0.01	43
10	64	7.5	17	27	12	29	6.6	1.2	50
11	–	–	1.3	0.9	0.45	4.2	0.65	0.06	41[d]

a) ZrO_2: 4.0 g, reaction temperature: 643 K. b) Sum of carbon base yield of C_1 to C_6 hydrocarbons. c) Methylal was used instead of dimethyl ether. d) $\sum C_i/3$ (methylal consumed).

consist mainly of alkanes as shown in Table 1. The addition of CO instead of H_2 resulted in the rapid deactivation giving methane selectively.

3) Reaction of Dimethyl Ether in the Presence of CO and H_2. The conversion of dimethyl ether and the distribution of hydrocarbons formed in the presence of CO and H_2 are presented in Table 1. It is clear from the higher conversion of dimethyl ether and the higher yields of hydrocarbons that the presence of either CO or H_2 improves the reactivity of dimethyl ether. The main products are C_2 and C_4 hydrocarbons. The effect of CO and H_2 is particularly remarkable for the formation of C_4, because it is rather minor products in the absence of both CO and H_2. The yield of C_4 hydrocarbons in the absence of CO and H_2 is so low that it does not overcome the amount in the CO–H_2 reaction without dimethyl ether. The three reactant system of dimethyl ether, CO, and H_2 forms C_4 with much higher yield. The maximum yield is obtained at 2.2 ml·min^{-1} of the feed, above which the yield decreases with an increase in the feed.

Table 2 shows the isomer distribution in the C_4 hydrocarbons. In the absence of CO and H_2 the selectivity of isobutene increases, as the feed of dimethyl ether increases. In the presence of CO and H_2 the selectivity to isobutene is more than 90%.

At the dimethyl ether feed of 2.2 ml·min^{-1} in the three reactant system, the concentration of CO in the outlet of catalyst bed was higher by 4% than that in the inlet. This means that a large amount of dimethyl ether decomposes into CO and H_2 despite of the presence of CO and H_2. The carbon balance from CO formed and the hydrocarbons recovered shows that 16% of dimethyl ether consumed is still unrecovered, even though the decomposition into CO and H_2 is taken into account.

4) Relation between Formations of Methanol and Hydrocarbons. The enhancement effect of dimethyl ether on the isobutene formation mentioned above stimulated us to investigate the relation between the formation of methanol and hydrocarbons at low temperatures, where methanol is main in the products, the selectivity of isobutene in hydrocarbons is low,[5] and methoxide is one of the main adsorbed species on the catalyst surface.[9]

The time courses of the formation of methanol and dimethyl ether in the CO–H_2 reaction over ZrO_2 at 473 and 523 K are shown in Fig. 1. There are induction

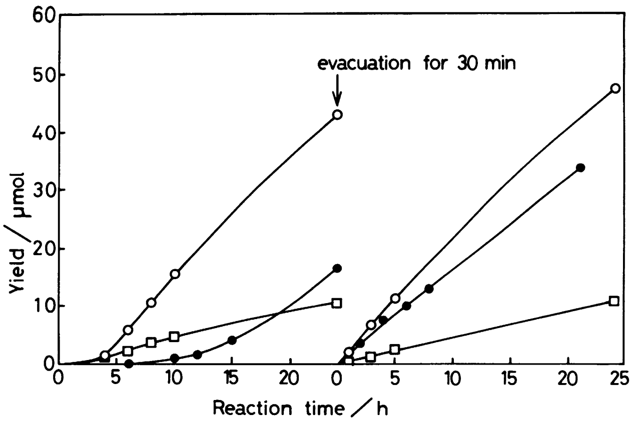


Fig. 1. Time course of methanol and dimethyl ether yields from CO and H_2 (CO/H_2=1/3) at 69 kPa over ZrO_2.
-●-; methanol at 473 K, -○-; methanol at 523 K, and -□-; dimethyl ether.

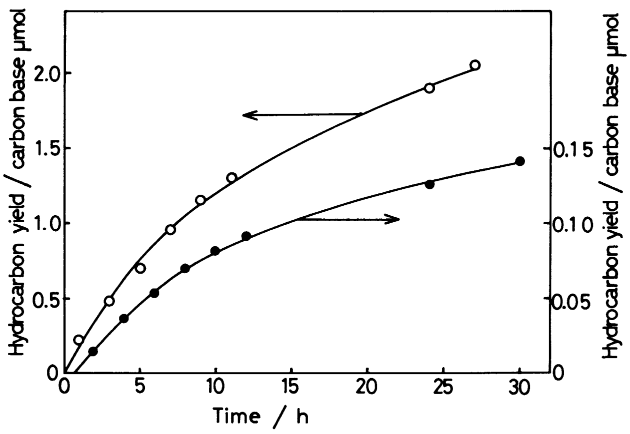


Fig. 2. Time course of hydrocarbon yields from CO and H_2 (CO/H_2=1/3) at 69 kPa over ZrO_2.
-●-; 473 K (hydrocarbon distribution after 24 h reaction is C_1: 18, C_2: 26, C_3: 12, C_4: 10 μmol, and C_5^+: trace), -○-; 523 K (hydrocarbon distribution after 24 h reaction is C_1: 56, C_2: 42, C_3: 12, C_4: 20 μmol, and C_5^+: trace).

Table 2. Isomer Distribution in C_4 Hydrocarbons

Run	Feed rate/ml·min^{-1}				Selectivity/%				
	N_2	CO	H_2	DME	C_4H_{10}	1-C_4H_8	*t*-2-C_4H_8	*c*-2-C_4H_8	*i*-C_4H_8
1	91	0	0	0.01	4	+	20	23	53
2	91	0	0	0.43	5	+	11	15	69
3	91	0	0	0.7	+	+	11	12	77
4	91	0	0	6.2	+	+	5	3	92
5	18	36	36	0	+	1	1	1	97
6	18	36	36	0.23	+	+	5	3	92
7	18	36	36	0.7	2	+	2	3	93
8	18	36	36	4.4	+	+	2	1	97
9	18	36	36	6.1[a]	+	+	2	1	97

a) Methylal was used instead of dimethyl ether.

Table 3. Effect of Olefin Addition to CO–H_2 Reaction on Hydrocarbon Distribution[a)]

Run	Olefin[b)]	Temp	Product/C-base μmol·min^{-1}				
		K	C_1	C_2	C_3	C_4	C_5
1	—	643	0.02	0.14	0.20	2.7	0.18
2	Ethylene	643	0.25	c)	1.2	6.0	0.20
3	—	633	0.08	0.26		2.1	0.10
4	Propylene	633	0.18	0.24	c)	2.4	0.10

Run	Selectivity in C_4 hydrocarbons/%				
	C_4H_{10}	1-C_4H_8	*t*-2-C_4H_8	*c*-2-C_4H_8	*i*-C_4H_8
1	+	+	1.5	1.5	97
2	1	+	2	2	84
3	+	+	1.5	1.5	97
4	1	14	26	24	35

a) Catalyst: 5.0 g, feed rate: 100 ml·min^{-1} (CO/H_2/N_2=40/40/20). b) Feed rate of olefin: 1.0 ml·min^{-1}. c) Conversions of olefins were less than few %.

Table 4. Effect of Oxygenate Addition to CO–H_2 Reaction on Hydrocarbon Distribution[a)]

Run	Oxygenate μmol·min^{-1}	Product/carbon base μmol·min^{-1}					Selectivity in C_4 hydrocarbons/%				
		C_1	C_2	C_3	C_4	C_5	C_4H_{10}	1-C_4H_8	*t*-2-C_4H_8	*c*-2-C_4H_8	*i*-C_4H_8
1	$C_2H_5OC_2H_5$ (96)	0.20	29	0.90	0.08	1.9	—	—	—	—	—
2	CH_3CHO[b)] (1.2)	0.17	1.2	1.0	9.2	0.7	+	+	1	2	97
3	$CH_3CH(OCH_3)_2$ (2.2)	0.2	0.4	0.18	4.4	0.2	1	+	1	1	97
4	CH_3CH_2CHO (0.3)	0.2	0.4	2.7	0.40	5.0	18	17	29	29	24
5	CH_3COCH_3 (2.8)	0.34	0.30	2.2	0.44	0.15	—	—	—	—	—

a) Catalyst: 5.0 g, feed rate: 100 ml·min^{-1} (CO/H_2/N_2=40/40/20), temperature: 643 K. b) Acetaldehyde was used as a solution of methylal (12 μmol·min^{-1}).

times of 12 and 3 h for the formation of two oxygen-containing products at the temperatures, respectively. However, the induction times disappear in the repeated reaction after the reaction for 24 h followed by the evacuation for 30 min at the same temperatures.

At 523 K the CO–H_2 reaction was carried out for 1 h, during which no product was detected except for hydrocarbons by G.C. However, when the products trapped at liquid nitrogen temperature was dissolved into water and analyzed using GC-MS, a small amount of formaldehyde was detected. Almost the same amount of formaldehyde was found in the products collected from initial 1 to 2 h. Thus, within the induction time for methanol formation, hydrocarbons and formaldehyde were already formed.

On the other hand, the formation of hydrocarbons at 473 and 523 K is accompanied by no or a short induction time as shown in Fig. 2. The hydrocarbon distributions are rather similar to that in the reaction of dimethyl ether alone.

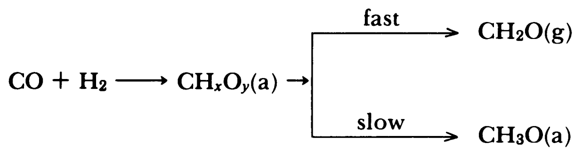
5) Effect of Organic Additives on the Formation of Isobutene. Table 3 shows the effect of the addition of ethylene and propylene to the CO–H_2 reaction. The addition of them seems to affect little the yield of hydrocarbons. However, in the addition of propylene, the main isomer in C_4 hydrocarbons changes into 1- and 2-butenes, although in the case of ethylene it is still isobutene.

Table 4 shows the effect of the addition of C_2 and C_3 oxygenates. The addition of diethyl ether only leads to produce mainly ethylene and C_4 hydrocarbons are minor. Acetaldehyde markedly enhanced the yield of hydrocarbons keeping the high selectivity for isobutene for initial few hours, after which the activity and selectivity were rapidly lowered to form yellow oily products. As it was very hard to control the amount of acetaldehyde added, dimethy acetal was used instead of C_2 aldehyde. The reaction was stable to form the higher yield of hydrocarbons with the high selectivity for C_4 hydrocarbons as shown in Table 4.

The addition of propanal leads to the decrease of C_4 hydrocarbons and the increase of the other hydrocarbons, especially C_5. The main isomer in C_4 hydrocarbons is changed from isobutene with the selectivity of 97% in the absence of propanal to 1- and 2-butenes with that of 75% in the presence of propanal. The addition of acetone also leads to the decrease of C_4 hydrocarbons. The most of acetone is converted to propylene.

Discussion

1) The Formation of C_2, C_3, and Linear C_4 Hydrocarbons. The treatment of ZrO_2 evacuated at 993 K with a mixture of CO and H_2 at room temperature results in the formation of some paraformaldehyde type adsorbed species.[5] The CO–H_2 reaction over ZrO_2 at 523 K produced formaldehyde in the initial stage of the reaction during the induction time for the formation of methanol and dimethyl ether. On the other hand, disappearance of induction time in repeated reaction shown in Fig. 1 may indicate that the induction time means the time taken to accumulate a surface intermediate which is not easily removed by evacuation at 523 K. Since formate and oxymethylene species on oxide surfaces are adsorbed forms of formyl and formaldehyde, respectively,[9–11] the formation of formaldehyde and methanol with and without induction time, respectively, may indicate the following relation of relative rates at the low temperatures,

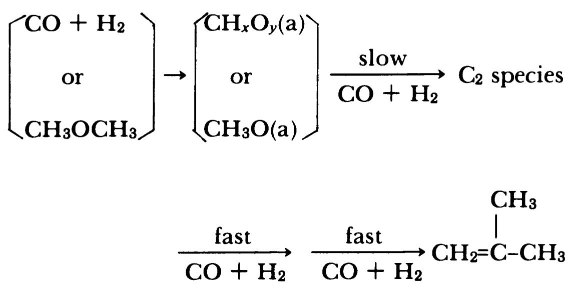


where $CH_xO_y(a)$ means adsorbed species such as formate, formyl, or formaldehyde.

On the other hand, the time course of hydrocarbon formations at 523 and 473 K shows no or a short induction time as shown in Fig. 2. Therefore, the hydrocarbons are not formed via methanol or methoxide species. Although dissociation of CO is possible for the common Fischer–Tropsch catalyst metals and polymerization of CH_2 formed from the carbon atoms and hydrogen is proposed as the mechanism of hydrocarbon formation,[12] there has been no report on the cleavage of C–O bond over oxide catalysts which requires a multiple catalyst site. We have no evidence for the cleavage also in the case of the reaction over ZrO_2. Since formaldehyde is formed without induction time, $CH_xO_y(a)$ is a possible candidate of the intermediate in the hydrocarbon formation. The formose reaction to form various carbohydrates having carbon–carbon bonds from formaldehyde in the presence of base catalysts[13] and the cleavage of carbon–oxygen bond of formaldehyde coordinated on zirconium complex[14] may suggest the possible pathway of direct hydrocarbon formation from the intermediate. Since the formation of C_2, C_3, and linear C_4 hydrocarbons are plotted by Arrhenius equation in the temperature range between 473 and 723 K, the formation path must be the same in the wide temperature range between 473 and 723 K.

2) The Formation of Isobutene. The formation of branched-chain hydrocarbons from CO and H_2 has been described by the pathway via the reaction of carbonyl of formaldehyde, acetaldehyde, and acetone coordinated on ZrO_2 with CO or methoxide species.[15,16] However, the present results that the addition of acetone or propanal to a mixture of CO and H_2 results in the decrease of C_4 hydrocarbons eliminate the formation of isobutene by either the carbonylation of acetone or propanal or the aldol condensation-type reaction of propanal.

The second order dependence of the isobutene formation on CO pressure[5] suggests that the formation of C_2 species from C_1 species is a slow process. The marked enhancement effect of C_2 oxygenate such as acetaldehyde or acetal on the isobutene formation may support the suggestion. On the other hand, the enhancement effect of dimethyl ether and the indispensability of CO and H_2 shown in Table 1 may suggest that methoxide or CH_xO_y species formed from dimethyl ether reacts with CO and H_2 to form the C_2 species. In the temperature range where isobutene is selectively formed, methanol and dimethyl ether are formed so fast as to be in equilibrium with a gas of CO and H_2. Thus, the following pathway is written. Further detailed mechanism is under investigation.



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