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Reaction path of methoxy species to isobutene and its dependence on oxide catalysts in CO hydrogenation

Ken-ichi Maruya [*], Miyuki Kawamura, Makiko Aikawa, Michikazu Hara, Toru Arai

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226, Japan

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Abstract

CO hydrogenation in the presence of dimethyl ether (DME) was carried out on some selective catalysts for the formation of isobutene. ZrO_2, ZrO_2–CeO_2, ZrO_2–CeO_2–CoO showed a high enhancement effect on hydrocarbon formation, CeO_2 almost no effect, and ZrO_2–CeO_2–Fe_2O_3 formed methane selectively. CO hydrogenation on DME-preadsorbed CeO_2 resulted in an increase in methane production and the retardation of the other hydrocarbons. The preadsorption of dimethoxymethane was most effective for the formation of ethene. The reaction path of methoxy species to methyl and methylene was discussed. © 1998 Elsevier Science S.A.

Keywords: CO hydrogenation; Isobutene; Methoxy species; Oxide catalysts

1. Introduction

Methoxy species on metal oxide surfaces are very important as intermediates in catalytic CO hydrogenation. Oxide catalysts for CO hydrogenation characteristically form branched chain compounds [1–4]. We have reported that ZrO_2 catalyst selectively forms isobutene from CO and H_2, although the activity is very low [3]. The observation of surface intermediates on the ZrO_2 catalyst by IR, solid state NMR, and chemical trapping experiments showed the presence of only formate and methoxy species [5]. The tracer studies using ^{13}CO showed that carbon of methoxy species is incorporated into the central position of isobutene formed in the CO hydrogenation [6]. This indicates that methoxy species are key intermediates for the formation of isobutene from CO and H_2. CeO_2 is also selective catalyst for the formation of branched chain compounds, i.e., isobutene in C_4 and isoprene in C_5 hydrocarbons from CO and H_2 [7]. However, the surface species on CeO_2 during CO hydrogenation proved difficult to analyze by IR measurements [8]. On the other hand, chain growth for C_2 to C_3 species and the subsequent chain branching to iso-C_4 compounds are thought to occur by aldol condensation-type reactions in ‘isosynthesis’ [9] and isobutanol synthesis from CO and H_2 [10]. Therefore, the formation of C_2 oxygenates for the starting material of aldol condensation-type reactions would be the key reaction in branched C_4 compound formation. The reaction of methoxy species with CO and H_2 on the metal oxides is essential for the catalytic ability of these catalysts. Here we describe the reaction of dimethyl ether with CO and H_2 over oxide catalysts and discuss the reaction path of methoxy species to C_2 oxygenates.

2. Results and discussion

2.1. Effect of addition of DME on CO hydrogenation over oxide catalysts

The effects of DME addition to CO and H_2 over some single component and mixed oxide catalysts are listed in Table 1. The addition of DME leads to an increase of hydrocarbon production and the decrease of CO_2. The increase is most noticeable for C_1 and C_2 hydrocarbons, resulting in the lower selectivity of total C_4 hydrocarbons. This product distribution pattern seems to approach to that of reaction of DME alone (C_1: 13.6, C_2: 52.0, C_3: 11.3, C_4: 17.4, C_5: 3.6, and C_{6+}: 2.1%). However, the isobutene selectivity in C_4 hydrocarbons is higher in the presence of DME than

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[*] Corresponding author.

Table 1
Formation rate of hydrocarbons and CO_2 and distribution of hydrocarbons in the presence of DME at 643 K[a]

Catalyst (atomic ratio)	DME feed rate (ml min^{-1})	Formation rate (μmol h^{-1} g^{-1})							Isobutene/ΣC4 (%)
		CO_2	C_1	C_2	C_3	C_4	C_5	C_{6+}	
ZrO_2	0	49	+	0.4	0.2	3.3	0.1	+	86
	0.5	4	1.5	5.0	2.3	8.0	2.1	2.1	
	1.0	3	1.5	5.0	2.3	7.8	2.1	2.1	92
CeO_2	0	93	2.7	1.7	1.2	5.6	3.2	2.6	66
	0.5	96	3.6	1.8	1.3	6.1	3.6	1.6	
	1.0	100	3.2	2.0	1.4	6.3	3.8	1.3	95
ZrO_2–CeO_2	0	100	1.8	1.1	1.0	2.9	1.2	+	82
	0.5	20	34.89	7.3	7.3	49.3	13.1	33.4	
(1:1)	1.0	15	38.5	7.7	6.2	47.7	15.4	37.0	97
ZrO_2–CeO_2–CoO	0	125	6.3	5.7	6.8	31.9	4.6	1.7	93
	0.5	24	61.9	8.8	10.5	63	17.5	15.8	
(10:10:1)	1.0	12	61.3	8.8	10.5	63.0	17.5	15.8	96
ZrO_2–CeO_2–Fe_2O_3	0	158	12.2	3.7	4.3	31.1	6.1	3.7	88
	0.5	71	311.1	24.2	4.0	48.5	8.1	4.0	
(10:10:1)	1.0	69	505.6	12.2	6.1	54.8	12.2	18.5	79

[a] Catalyst: 2.0 g, reaction temperature: 643 K, flow rate: $CO/H_2/N_2 = 40/40/20$ ml min^{-1}.

that in the absence, except for ZrO_2–CeO_2–Fe_2O_3 catalyst, as shown in the last column. Thus, the five catalysts investigated can be divided into the following three groups: (i) the increase in formation rate of hydrocarbons with high isobutene selectivity and a large decrease of CO_2 (ZrO_2, ZrO_2–CeO_2, ZrO_2–CeO_2–CoO), (ii) nearly no effect (CeO_2), and (iii) the remarkable increase of only methane and the moderate increase of the other hydrocarbons. This is accompanied by a lower rate of formation of CO_2 and lower selectivity for isobutene (ZrO_2–CeO_2–Fe_2O_3). The effects of methoxy species are most significant for catalyst in group (i). Oxygenated products, which account for the decrease in CO_2 formation, are observed as methanol as shown in Table 2. Therefore, one of the roles of DME is possibly to convert surface hydroxyl groups to methoxy species and methanol.

The rate of hydrocarbon formation and the distribution of products with CeO_2 catalysts are influenced very little by addition of DME. There are two possibilities for this: (1) DME cannot react with hydroxyl species on CeO_2, and (2) the amount of hydroxyl species available to react with DME is low compared with ZrO_2. Table 3 shows the dependence of the CO_2:H_2 ratio on the space velocity. The ratio of CO_2:H_2O formed at 673 K approaches the equilibrium value, and further increase of the velocity, i.e., decrease of gas contact time results in the decrease of the CO_2:H_2O ratio, indicating that CO_2 are formed by the water gas shift reaction. This indicates that the reaction of DME with hydroxyl species on CeO_2 is slower than that of CO, as illustrated in Scheme 1. It has been shown that CeO_2 is partially reduced under the reaction conditions and the reduced CeO_2 is active for the hydrogenation of CO [11]. The reduced and oxygen-deficient cerium ion has d-electron density available for back-donation to CO. ZrO_2 is less easily reduced; the active site is Zr^{4+}, which has no d-electrons. Thus, Zr–OH reacts faster DME than with CO, while the opposite holds true for Ce–OH.

2.2. Difference between ZrO_2 and CeO_2 for the reactivity of methoxy species

From the chemical trapping experiments, the amounts of methoxy species on ZrO_2 during CO hydrogenation were observed to be 140 and 30 μmol g^{-1} at 523 and 643 K, respectively [5]. These amounts were estimated to occupy 40 and 9% of surface Zr ions where the surface area of ZrO_2 was 50 m^2 g^{-1}. The lattice parameters used in the estimations were obtained from

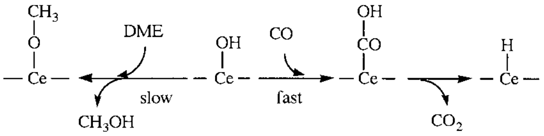
Table 2
Formation of methanol by the addition of DME

Catalyst (atomic ratio)	DME feed rate (ml min^{-1})	Rate of formation (μmol h^{-1} g^{-1})	
		Total hydrocarbon	Methanol
ZrO_2–CeO_2–CoO	0	57	0
	0.5	182	486
(10:10:1)	1.0	175	792
ZrO_2–CeO_2–Fe_2O_3	0	61	0
	0.5	404	289
(10:10:1)	1.0	609	555

Table 3
Dependence of ratio of CO_2 to H_2O on the cantact time[a]

Space velocity (10^3 h^{-1})	At equilibrium	0.48	0.97	3.95	19.9
CO_2:H_2O ratio	3.7	3.5	3.9	3.3	2.3

[a] Catalyst: 1.5 g, reaction temperature: 673 K, $H_2/CO = 3$.

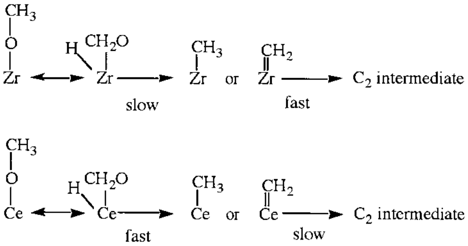


Scheme 1. The reaction of Ce–OH with CO and DME.

tetragonal phase of ZrO_2. Similarly, the amounts of methoxy species on CeO_2 were 0.36 and 0.18 μmol g^{-1} at 523 and 673 K, respectively [5]. These amounts are small, even considering the lower surface area. The predominant feature of the CeO_2 catalyst is that chemical trapping of intermediates species gave 0.47 and 0.23 μmol g^{-1} of methane from the catalysts at 523 and 673 K, respectively [5]. This suggests that there are methyl or methylene species on the CeO_2 surface; the amounts of these species exceed those of methoxy species. To investigate whether the DME preadsorption results in the increase of hydrocarbons like ZrO_2 catalyst or not, CO hydrogenation on CeO_2, on which DME was preadsorbed, was carried out. The preadsorption of DME results only in the increase of methane and the retardation of the other hydrocarbons, as shown in Run 2 in Table 4. This suggests that with the CeO_2 catalyst, the transformation of DME to methyl or methylene species is fast, while the carbon–carbon bond formation reaction is slower. Thus, the reactivity of methoxy species on ZrO_2 and CeO_2 can be described as represented in Scheme 2.

2.3. Reaction path from methoxy to methyl and / or methylene species

Studies on the conversion of methoxy species to methyl or methylene species have been reported. Cp_2ZrCl-substituted dimethyl ether, $Cp_2Zr(Cl)CH_2OCH_3$, is hydrogenated with H–Zr complex to yield the corresponding methyl–Zr complex [12], while its thermolysis at 200°C gives ethene [13]. Upon treatment of binuclear μ, η^2-formaldehyde Cp_2ZrCl complex with suspension of hydridozirconocene chloride at 55°C, the complex is slowly consumed to form $(Cp_2ZrCl)_2O$ and $Cp_2Zr(CH_3)Cl$ in a equimolar ratio [14]. μ-Hydride complex and dinuclear complex of Ta react with CO to form η-CHO and η-CH_2, respectively [15]. It is reported that methoxy complex of Cp_2^*Ta is in an equilibrium with the η^2-formaldehyde hydride complex, which is further transformed to form the corresponding oxo methyl complex by the rearrangement [16,17].



Scheme 2. The difference of reactivity of methoxy species on ZrO_2 and CeO_2.

Since the above literatures show that η^2-formaldehyde-type species can be intermediates in the formation of hydrocarbons from CO and H_2, CO hydrogenation over CeO_2 pretreated with dimethyl acetals of aldehydes was carried out. The preadsorption of dimethoxymethane (Run 3) leads to a marked increase in ethene production, even in comparison to the reaction without the preadsorption (Run 1). This suggests that dimethoxymethane converts to η^2-formaldehyde species, which form methylene species. On the other hand, it is known that there are terminal and bridging types of methoxy species on ZrO_2 during CO hydrogenation [18] and it was suggested from the reaction of methoxy species on CeO_2 that there are methoxy species that adsorbed three Ce ions [19,20]. Therefore, the conversion of methoxy species to methyl and/or methylene species could proceed through a species coordinated to two or three Ce ions. If a bridging or a three-coordinate methoxy species converts to η^2-formaldehyde and hy-

Table 4
Effect of oxygenate preadsorption on product formation rate over CeO_2 catalyst[a]

Run	Compound preadsorbed	Rate of H.C.[c] formation/carbon (μmol g^{-1} h^{-1})	Selectivity[b] (%)					
			C_1	C_2	C_3	C_4	C_5	C_{6+}
1	–	62	78	21	2	1	N.D.[c]	N.D.[c]
2	CH_3OCH_3	21	95	3	1	1	N.D.	N.D.[c]
3	$CH_2(OCH_3)_2$	46	66	25	3	4	4	N.D.
4	$CH_2CH(OCH_3)_2$	118	19	14	13	21	15	17
5	$CH_3CH_2CH(OCH_3)_2$	87	26	4	10	24	15	21
6	in steady state (CeO_2)	43	25	29(96)	9(84)	21	8	8
7	in steady state (ZrO_2)	10	5	6(64)	1(90)	77	5	trace

[a] Catalyst (2.0 g) was evacuated at 973 K for 3 h, followed by hydrogen treatment at 773 K and 66 kPa for 16 h before the reaction. The preadsorption of oxygenates was carried out at 5 pKa and evacuated soon after the treatment at 673 K. Products were collected for initial 10 min.

[b] C_2 and C_3 hydrocarbons formed in preadsorption experiments consisted of alkenes with almost 100% selectivity. Figures in parentheses in C_2 and C_3 in steady states stand for alkene selectivity of the corresponding hydrocarbons.

[c] H.C. = hydrocarbons, N.D. = not detected.

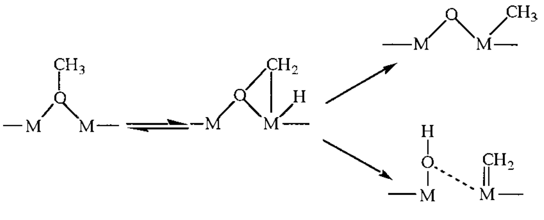
dride species, the reaction path could be depicted as in Scheme 3.

With ZrO_2 catalyst the selectivity of ethene in C_2 hydrocarbons is lower than that of propene in C_3 hydrocarbons (Table 4, Run 7), while with CeO_2 the order of selectivity is reverse (Table 4, Run 6). For alkene, ethene is hydrogenated faster than propene. Therefore, if an alkane is a hydrogenation product from an alkene, the selectivity of ethene should be lower than that of propene. The higher selectivity of ethene with the CeO_2 catalyst would seem to suggest that there is an another path to form ethene alone. The coupling reaction of methylene species in Scheme 3 could explain both the selective formation of C_2 hydrocarbons and the higher selectivity of ethene. The difference between ZrO_2 and CeO_2 catalysts could relate to the fact that ZrO_2 is less easily reduced than CeO_2 [21,22].

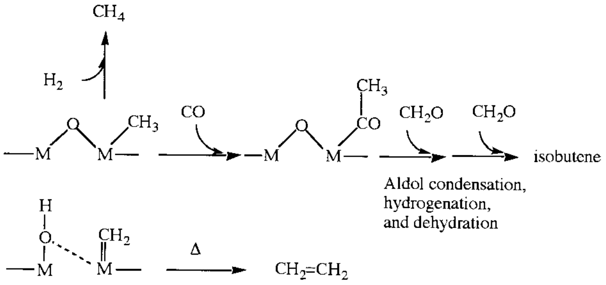
The formation of C_2 species derives from the carbonylation of methyl–Zr species, although we have no clear evidence at present. The results that ^{12}CO hydrogenation on $^{13}CH_3O$-preadsorbed ZrO_2 formed $^{12}CH_2={}^{13}C(^{12}CH_3)_2$ [6] and that the insertion of CO into a methyl–Zr bond is fast at room temperature [23] would support the carbonylation path, depicted in Scheme 4. The formation of isobutene is explained by the aldol condensation from acyl species.

2.4. The role of Co and Fe ions in the three-component catalysts

XRD analyses of the three component catalysts before and after CO hydrogenation showed only broad peaks due to $Ce_{1-x}Zr_xO_2$ or its mixture with CeO_2, along with shoulders due to ZrO_2. No peaks were observed for CoO and Fe_2O_3, indicating the fine dispersion of the oxides. XPS measurements showed peaks due to Zr^{4+}, Ce^{4+}, and small peaks due to Ce^{3+}, but no peaks due to Co and Fe ions. This indicates that concentrations of Co and Fe ions on the surface are much lower than those estimated from their atomic ratios in the catalyst preparation because the cross sections of $2P_{3/2}$'s of Co and Fe are between 4.3 of Zr $3d_{5/2}$ and 28 of Ce $3d_{5/2}$. The product distribution with ZrO_2–CeO_2–CoO in Table 1 and the above results with XRD and XPS show that the Co in this catalyst is in a higher oxidation rather than the metallic state. The rate of hydrogenation in the absence of DME with this catalyst system is higher than that with ZrO_2 and ZrO_2–CeO_2, while the rate in the presence of DME is slightly higher. Therefore, the role of Co ion could be to increase the amount of methoxy species on the catalyst and the effect on the acceleration of transformation from methoxy to methyl and/or methylene could be low.



Scheme 3. Proposed reaction path of methoxy species to methyl and methylene species.



Scheme 4. The formation of C_2 compounds.

On the other hand, ZrO_2–CeO_2–Fe_2O_3 becomes a selective methanation catalyst by the addition of DME, as shown in Table 1. This may mean that Fe_2O_3 is reduced to metal or that iron oxide promotes the formation of methane. Since the results of XRD and XPS showed no peaks due to iron compounds, the state of iron is not clear yet.

With the Co-containing catalysts, the rate of formation of hydrocarbons is much less than those of CO_2 (Table 1) and of methanol (Table 2), indicating the formation of carbonaceous or carbide species on the catalyst surface. Table 1 shows that the formation of such surface carbon species seems to occur on the present catalyst systems. On the other hand, with the Fe-containing catalyst, the rate of hydrocarbon formation is much less than that of CO_2, and little more than that of methanol, indicating that the reaction in the presence of DME proceeds without forming the surface carbon species, but CO hydrogenation without DME is similar to that with the Co-containing catalyst. Thus, it is concluded that the role of iron oxide in Fe-containing catalysts is to accelerate the formation of methyl and/or methylene species and also the hydrogenation of the C_1 species.

3. Experimental

Oxides were prepared according to the literatures [1,3,4]. Reactions were carried out in a conventional flow system under atmospheric pressure. Catalysts were calcined at 723 K under N_2 for 3 h, followed by lowering to a given temperature to start the CO hydrogenation. CO hydrogenation on oxygenate-preadsorbed CeO_2 was carried out in a glass vacuum system equipped with a gas circulation pump. CeO_2 catalyst was evacuated at 973 K for 3 h, treated with H_2 at 773 K for 16 h, and evacuated again at the temperature before the CO hydrogenation reaction. The hydrogen treatment was done before oxygenate preadsorption because CeO_2 is partially reduced under the reaction conditions. Treatments of CeO_2 with oxygenates were carried out at 673 K and at 50 Torr for few minutes, followed by evacuation at the temperature for few minutes. Products were determined by the on-line GC equipped with adsorb P-1 for hydrocarbons and CO_2 and VZ 10 for C_4 and C_5 isomers.

4. Summary

(i) The selective formation of isobutene from CO and H_2 over oxide catalysts is explained by the paths: (1) formation of methoxy species from CO and H_2, (2) conversion of methoxy species to methyl species, (3) insertion of CO into a methyl–metal bond, and (4) aldol condensation of C_2 oxygenates with formaldehyde.

(ii) ZrO_2 catalyst has the rate-determining step shown in path (2) and faster steps shown in (3) and (4).

(iii) CeO_2 is fast in step (2) but slow in step (3).

(iv) Co in ZrO_2 catalyst accelerates step (1), but has almost no effect on the other steps. Fe accelerates only hydrogenation of methyl species to form methane.

Acknowledgements

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References

[1] H. Pichler, K.H. Ziesecke, Brennst.-Chem. 30 (1949) 13.
[2] R. Kieffer, J. Varela, A. Deluzarche, J. Chem. Soc., Chem. Commun. (1983) 763.
[3] T. Maehashi, K. Maruya, K. Domen, K. Aika, T. Onishi, Chem. Lett. (1984) 747.
[4] K. Maruya, A. Inaba, T. Maehashi, K. Domen, T. Onishi, J. Chem. Soc., Chem. Commun. (1984) 487.
[5] K. Maruya, A. Takasawa, M. Aikawa, T. Haraoka, K. Domen, T. Onishi, J. Chem. Soc., Faraday Trans. 90 (1994) 911.
[6] K. Maruya, A. Takasawa, T. Haraoka, K. Domen, T. Onishi, J. Mol. Catal. A: Chemical 112 (1996) 143.
[7] K. Maruya, K. Ito, K. Kushihashi, Y. Kishida, K. Domen, T. Onishi, Catal. Lett. 14 (1992) 123.
[8] C. Li, K. Domen, K. Maruya, T. Onishi, J. Catal. 141 (1993) 540.
[9] R.B. Anderson, J. Feldman, H.H. Storch, Ind. Eng. Chem. 44 (1952) 2418.
[10] J.G. Nunan, C.E. Bogdan, K. Klier, K.J. Smith, C.-W. Young, R.G. Herman, J. Catal. 113 (1988) 410.
[11] T. Arai, K. Maruya, K. Domen, T. Onishi, J. Catal. 141 (1993) 533.
[12] G. Erker, R. Schlund, C. Kruger, J. Chem. Soc., Chem. Commun. (1986) 1403.
[13] G. Erker, C. Kruger, R. Schlund, Naturforsch. B12 (1987) 1009.
[14] G. Erker, U. Dorf, J.L. Atwood, W.E. Hunter, J. Am. Chem. Soc. 108 (1986) 2251.
[15] R. Toreki, R.E. LaPointe, P.T. Wolczanski, J. Am. Chem. Soc. 109 (1987) 7558.
[16] A.V. Asselt, B.J. Burger, V.C. Gibson, J.B. Bercaw, J. Am. Chem. Soc. 108 (1986) 5347.
[17] G. Parkin, E. Bunel, B.J. Burger, M.S. Trimmer, A. van Assalt, J.E. Bercaw, J. Mol. Catal. 41 (1987) 21.
[18] F. Ouyang, J.N. Kondo, K. Maruya, K. Domen, J. Chem. Soc., Faraday Trans. 93 (1997) 169.
[19] M. Hara, M. Kawamura, J.N. Kondo, K. Domen, K. Maruya, J. Pht. Chem. 100 (1996) 14462.
[20] A. Badri, C. Binet, J.-C. Lavalley, J. Chem. Soc., Faraday Trans. 93 (1997) 1159.
[21] E.M. Cohn, in: P.H. Emmett (Ed.), Catalysis, Vol. 4, Reinhold, New York, 1956, p. 443.
[22] K. Otsuka, M. Hatano, A. Morikawa, J. Catal. 79 (1983) 493.
[23] J.M. Manriquez, D.R. McAlister, R.D. Sanner, J.E. Bercaw, J. Am. Chem. Soc. 100 (1978) 2716.