

# Role of methoxide species in *isobutene* formation from CO and H<sub>2</sub> over oxide catalysts

## Methoxide species in *isobutene* formation

Ken-ichi Maruya<sup>a,\*</sup>, Akihiro Takasawa<sup>a</sup>, Takashi Haraoka<sup>a</sup>, Kazunari Domen<sup>a</sup>,  
Takaharu Onishi<sup>b</sup>

<sup>a</sup> Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

<sup>b</sup> Advanced Polytechnic Center, 3-1-2 Wakaba, Mihama-ku, Chiba 261, Japan

Received 26 March 1996; accepted 28 May 1996

### Abstract

The role of methoxide species in selective formation of *isobutene* from CO and H<sub>2</sub> over ZrO<sub>2</sub> was investigated by means of <sup>13</sup>C tracer method. Analysis of <sup>13</sup>C–<sup>13</sup>C coupling in the formed *isobutene* showed that <sup>12</sup>CO hydrogenation over ZrO<sub>2</sub> pretreated with <sup>13</sup>CO and H<sub>2</sub> formed <sup>12</sup>CH<sub>2</sub>=<sup>13</sup>C(<sup>12</sup>CH<sub>3</sub>)<sub>2</sub>, while <sup>13</sup>CO hydrogenation over (<sup>12</sup>CH<sub>3</sub>)<sub>2</sub>O-adsorbed ZrO<sub>2</sub> formed <sup>13</sup>CH<sub>2</sub>=<sup>12</sup>C(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>. It was proposed from these results that methoxide species gave central carbon of *isobutene*, while the other carbons came from gas phase CO. A reaction path through methoxide species was proposed.

**Keywords:** CO hydrogenation; Oxide catalysts; *Isobutene* formation; <sup>13</sup>C tracer study

### 1. Introduction

CO hydrogenation over oxide catalysts selectively forms branched-chain compounds such as *isobutane* [1], *isobutene* [2], *isoprene* [3], 2-methylpropanal [1,4], and *isobutanol* [4]. ZrO<sub>2</sub> catalyst is especially selective for *isobutene* formation [2]. The in situ IR measurements of ZrO<sub>2</sub> at 523 and 673 K showed the presence of only methoxide and formate species on the surface [5]. <sup>13</sup>C CP MAS NMR measurements of ZrO<sub>2</sub> treated with a mixture of CO and H<sub>2</sub> at 523 and 653 K, rapidly cooled by liquid nitrogen, and then slowly warmed under vacuum

confirmed the surface species [6]. The chemical trapping of the surface species on the same ZrO<sub>2</sub> with a vapor of diluted aqueous HCl solution at room temperature and of dimethyl sulfate at 553 K formed only methanol and methyl formate, respectively [6]. The addition of dimethyl ether to a mixture of CO and H<sub>2</sub> enhanced the formation of hydrocarbons maintaining the high selectivity of *isobutene* [7]. These results indicate the participation of methoxide species in the formation of *isobutene*.

Regarding the formation of *isobutanol* from CO and H<sub>2</sub> over oxide catalyst, Mazanec proposed the mechanism of CO insertion into the M–C bond of a surface-bound aldehyde [8]. Chain-branching mechanism on *isobutene* formation over ZrO<sub>2</sub> proposed by Ekerdt and

\* Corresponding author.

coworkers consisted of two paths (i) CO insertion into the zirconium–carbon bond of adsorbed aldehydic intermediate and (ii) condensation between  $\eta$ -enolate and methoxide species [9]. On the other hand, it is well known that methanol synthesis catalysts can produce *isobutanol* from CO and H<sub>2</sub>, which has the same carbon framework with *isobutene*. Nunan and coworkers have studied in detail the formation mechanism of higher alcohols from CO and H<sub>2</sub> over methanol synthesis catalysts, where the CO hydrogenation was carried out in the coexistence of <sup>13</sup>C-labeled oxygenates such as <sup>13</sup>CH<sub>3</sub>OH, <sup>12</sup>CH<sub>3</sub><sup>13</sup>CH<sub>2</sub>OH, and <sup>13</sup>CH<sub>3</sub>OH–<sup>12</sup>CH<sub>3</sub><sup>12</sup>CH<sub>2</sub>OH. The conclusions were as follows: (i) dominant source of both carbons of ethanol was methanol [10], (ii) branched primary alcohols were formed through addition of C<sub>1</sub> species to  $\beta$ -position of C<sub>n</sub> surface species [11], and (iii) linear primary alcohols were given through C<sub>1</sub> addition steps at the alcohol end of the growing chain [11]. Ueda and coworkers showed that the reaction of ethanol or propanol with methanol over modified MgO catalysts formed propanol and *isobutanol*, respectively, although the reaction of methanol alone over the same catalyst gave no higher alcohols [12]. In our previous papers, it was shown that CeO<sub>2</sub> forms 2-methylpropanal at 523 K as the second main product, while the addition of In<sub>2</sub>O<sub>3</sub> to CeO<sub>2</sub> lead to the hydrogenation product of *isobutanol* from 2-methylpropanal as a main product at the same temperature [4]. Since CeO<sub>2</sub> gives *isobutene* at 673 K as a main product, the branched C<sub>4</sub> oxygenates at the lower temperatures are likely to be precursors of *isobutene*. Our purpose in this paper is to demonstrate the role of methoxide species for the formation of *isobutene* by means of <sup>13</sup>C tracer method.

## 2. Experimental

Zirconium was prepared according to the previous papers [2,7]. CO hydrogenation with <sup>13</sup>C tracer was carried out in a glass vacuum system

equipped with a gas circulation pump. Total volume of the circulation system was 470 ml, in which volume of the reactor was 55 ml. The reactor was able to be *isolated* from the gas circulation line for changing the reaction gas.

<sup>12</sup>CO hydrogenation on ZrO<sub>2</sub> catalyst pretreated with a mixture of <sup>13</sup>CO and H<sub>2</sub> (1/3) was carried out as follows. ZrO<sub>2</sub> (4.0 g) was evacuated at 973 K for 3 h. After the reaction of <sup>13</sup>CO and H<sub>2</sub> at 643 K and 67 kPa for 3 h, the gas in the circulation line except a small volume of reactor was changed to <sup>12</sup>CO and H<sub>2</sub> while keeping the temperature of the reactor, and then <sup>12</sup>CO hydrogenation at the same temperature and pressure started. The products were collected at liquid nitrogen temperature. After the <sup>12</sup>CO hydrogenation in a given time, the catalyst was heated at 773 K for 1 h in air and evacuated at 973 K for 30 min. The treatment with <sup>13</sup>CO and H<sub>2</sub> followed by the reaction with <sup>12</sup>CO and H<sub>2</sub> restarted. This reaction cycle was repeated 8 times for the collection of products enough to obtain clear <sup>13</sup>C NMR spectra.

<sup>13</sup>CO hydrogenation on dimethyl ether (180 Torr)-adsorbed ZrO<sub>2</sub> (4.0 g) was carried out at 643 K for 20 min. The products were collected at liquid nitrogen temperature.

<sup>13</sup>CO with 99.3% purity was obtained from MSD isotopes. <sup>12</sup>CO was purified by a trap at liquid nitrogen temperature. H<sub>2</sub> was purified by a deoxo and a liquid nitrogen temperature.

<sup>13</sup>C NMR spectra were recorded at room temperature on a JEOL-GX-500 as a CDCl<sub>3</sub> solution using TMS as an internal standard. The assignment of carbons of *isobutene* was carried out using the products from the reaction of <sup>13</sup>CO and H<sub>2</sub> over ZrO<sub>2</sub>. The assignments of carbons of ethylene and propylene were carried out using unenriched ethylene and propylene.

## 3. Results

### 3.1. Estimation of <sup>13</sup>C concentration

The concentration of <sup>13</sup>C tracer in three kinds of carbons of *isobutene* was estimated as an

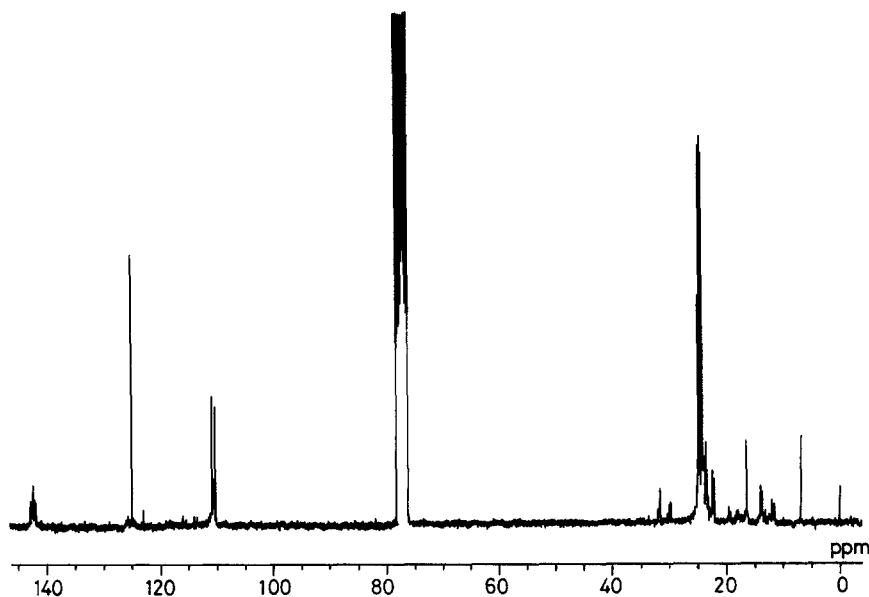


Fig. 1.  $^{13}\text{C}$  NMR spectrum of the products formed from  $^{12}\text{CO}$  and  $\text{H}_2$  at 643 K for the initial 20 min over  $\text{ZrO}_2$ , which was treated with  $^{13}\text{CO}$  and  $\text{H}_2$  at 643 K for 3 h.

approximate value from the coupling spectra because of inadequate peak splitting of  $^1\text{H}$  NMR spectra and NOE effect of  $^{13}\text{C}$  NMR spectra. Methylene, central, and methyl carbons in *isobutene* are denoted as **C(a)**, **C(b)**, and **C(c)**, respectively.

Fig. 1 shows the  $^{13}\text{C}$  NMR spectrum of products in  $^{12}\text{CO}$  hydrogenation at 643 K for initial 20 min over  $\text{ZrO}_2$  pretreated with  $^{13}\text{CO}$  and  $\text{H}_2$  at the same temperature for 3 h. The  $^{13}\text{C}$  NMR spectrum of *isobutene* formed in  $^{13}\text{CO}$  hydrogenation over a fresh  $\text{ZrO}_2$  indicated that the peaks of 142.40, 110.45, and 24.10 ppm were due to **C(b)**, **C(a)**, and **C(c)**, respectively, and the coupling constants of  $^1J(\text{C(a)}-\text{C(b)})$ ,  $^1J(\text{C(c)}-\text{C(b)})$ , and  $^1J(\text{C(a)}-\text{C(c)})$  were 71.72, 41.20, and 3.05 Hz, respectively. A singlet at 124.85 and a triplet at 77.21 ppm in Fig. 2 correspond to  $\text{CO}_2$  and  $\text{CHCl}_3$ , respectively. Therefore, Fig. 1 shows that the products consist mainly of *isobutene*. Fig. 2 shows that the singlet of **C(a)** is smaller than the doublet due to the coupling with  $^{13}\text{C(b)}$ . The ratio of peak area of the doublet to the singlet would give ratio of the concentration of  $^{13}\text{C}$  to  $^{12}\text{C}$  in **C(b)**.

The same ratio could be estimated also from the peaks of **C(c)**.

The calculation of  $^{13}\text{C}$  concentration in **C(a)** and **C(c)** was more complexed because of the coupling of  $^{13}\text{C(b)}$  with one  $^{13}\text{C(a)}$  and two  $^{13}\text{C(c)}$ s. When all combinations of the couplings are perfectly separated, there should be 15 peaks.

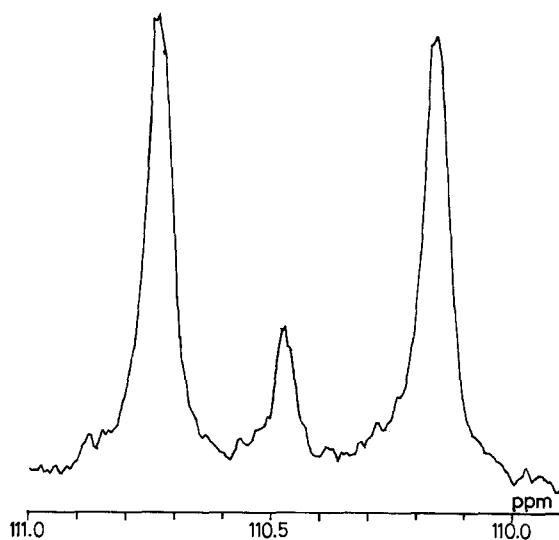


Fig. 2. Enlarged  $^{13}\text{C}$  NMR spectrum of the **C(a)** region of Fig. 1.

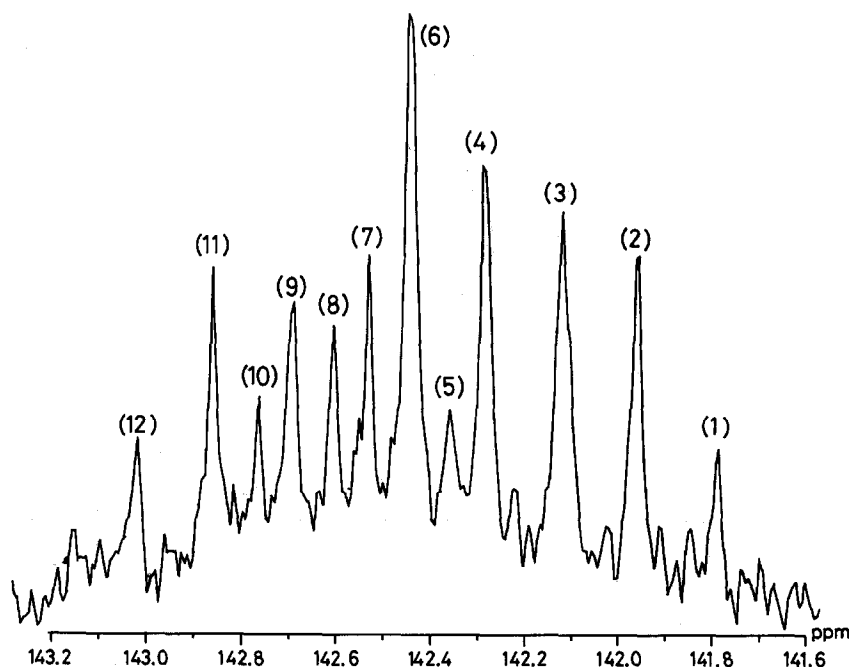


Fig. 3. Enlarged  $^{13}\text{C}$  NMR spectrum of the C(b) region of Fig. 1.

However, Fig. 3 shows the overlapping in the lower field and the separation in the higher field. The peak assignment of  $^{13}\text{C}$ -containing compound would be as follows:

Compound	Peak assignment
$  \begin{array}{c}  ^{13}\text{CH}_3 \\    \\  ^{13}\text{CH}_2 = ^{13}\text{C} - ^{13}\text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $	$\Longrightarrow$ (1), (3), (5), (6), (9), and (12)
$  \begin{array}{c}  \text{CH}_3 \\    \\  ^{13}\text{CH}_2 = ^{13}\text{C} - ^{13}\text{CH}_3 \\    \\  ^{13}\text{CH}_3  \end{array}  $	$\Longrightarrow$ (2), (4), (7), (11)
$  \begin{array}{c}  ^{13}\text{CH}_3 \\    \\  \text{CH}_2 = ^{13}\text{C} - ^{13}\text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $	$\Longrightarrow$ (3), (6), and (10)
$  \begin{array}{c}  \text{CH}_3 \\    \\  ^{13}\text{CH}_2 = ^{13}\text{C} - \text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $	$\Longrightarrow$ (3) and (8)
$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{CH}_2 = ^{13}\text{C} - ^{13}\text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $	$\Longrightarrow$ (4) and (7)
$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{CH}_2 = ^{13}\text{C} - \text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $	$\Longrightarrow$ (6)

where carbons without superscript 13 stand for  $^{12}\text{C}$  and figures in parentheses correspond to the

position in Fig. 3. Thus, the concentrations of  $^{13}\text{C}$  in C(a) and C(c) could be estimated.

### 3.2. $^{12}\text{CO}$ hydrogenation over $\text{ZrO}_2$ treated with $^{13}\text{CO}$ and $\text{H}_2$

$^{12}\text{CO}$  hydrogenation over  $\text{ZrO}_2$  pretreated with a mixture of  $^{13}\text{CO}$  and  $\text{H}_2$  was carried out using  $\text{ZrO}_2$  of 4.0 g at 643 K, at which the selectivity and the yield of *isobutene* were higher than those at 673 K. Fig. 4 shows the time course of  $^{13}\text{C}$  concentrations in C(a), C(b), and C(c) carbons, which were obtained as described above. The data of the reaction time of 10 min were obtained from the products collected for the initial 20 min. Similarly, the reaction times of 30, 90, and 150 min refer to the product collection from 20 to 40, from 60 to 120, and from 120 to 180 min, respectively. C(b) was higher in  $^{13}\text{C}$  concentration than C(a) and C(c).  $^{13}\text{C}$  concentrations of C(a) and C(c) were almost the same, showing the fast *isomerization* of double bond.  $^{13}\text{C}$  concentration in

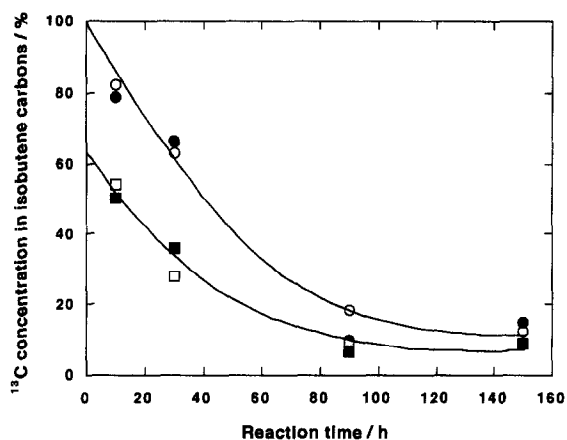


Fig. 4. Time course of  $^{13}\text{C}$  concentration in each carbon of *isobutene* produced from  $^{12}\text{CO}$  and  $\text{H}_2$  at 643 K over  $\text{ZrO}_2$ , which was treated with  $^{13}\text{CO}$  and  $\text{H}_2$  at 643 K for 3 h.  $\square$ : C(a),  $\circ$  and  $\bullet$ : C(b) estimated from coupling with C(c) and C(a), respectively, and  $\blacksquare$ : C(c).

C(b) carbon was nearly 90 and 75% at 10 and 30 min, respectively, while those of C(a) and C(c) were less than 60 and 40%, respectively.

### 3.3. $^{13}\text{CO}$ hydrogenation over $^{12}\text{CH}_3\text{O}$ -pre-adsorbed $\text{ZrO}_2$

Fig. 5 shows  $^{13}\text{C}$  NMR spectrum of the products from  $^{13}\text{CO}$  hydrogenation over  $^{12}\text{C}$ -dimethyl ether-adsorbed  $\text{ZrO}_2$ . Since the spectrum was measured under off-resonance condition, the coupling between H and  $^{13}\text{C}$  appeared clearly. Methyl of *isobutene* is quartet at 24.1 ppm due to coupling only with proton, and therefore, there was no coupling of methyl carbon with  $^{13}\text{C}(\text{b})$  carbon. Similarly, methylene was a triplet at 110.45 ppm. No peak due to C(b) was observed around 142.4 ppm.

A quartet at 18.7 ppm is due to a methyl group of propylene. Although methylene of propylene is observed as a triplet at 115.4 ppm, there is no doublet due to methine. A triplet due to methylene of ethylene was observed at 122.8 ppm.

Although  $^{13}\text{C}$ -H couplings are observed, no  $^{13}\text{C}$ - $^{13}\text{C}$  coupling was detected.

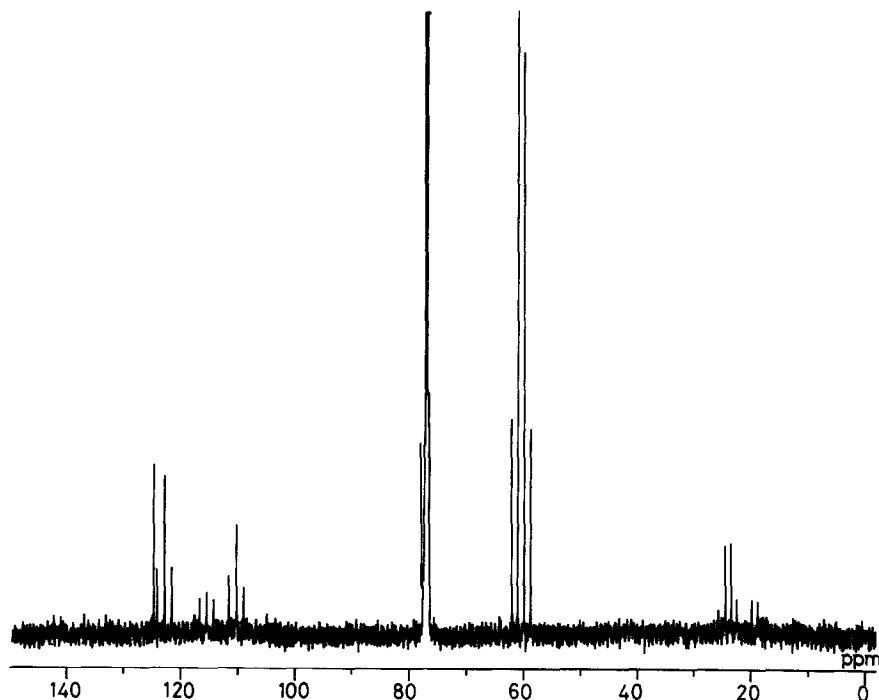
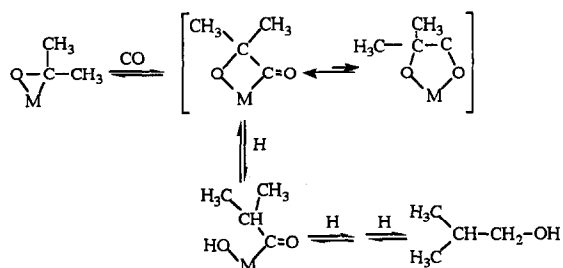


Fig. 5.  $^{13}\text{C}$  NMR spectrum of the products formed from  $^{13}\text{CO}$  and  $\text{H}_2$  at 643 K for 20 min over  $\text{ZrO}_2$ , which was treated with dimethyl ether at room temperature and 180 Torr.

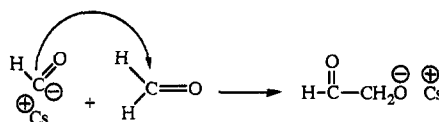
## 4. Discussion

### 4.1. Chain branching mechanism

*Isobutene* has been thought to be formed through dehydration of *isobutanol*, which is given by the hydrogenation of 2-methylpropanal [6–9]. Aldol-condensation-type reaction of propanal with  $C_1$  oxygenate and carbonylation at carbon of carbonyl of  $\eta^2$ -adsorbed acetone have been proposed for chain branching to form 2-methylpropanal. Mazanec proposed the mechanism as shown in Scheme 1, where chain branching occurs through CO insertion at carbon of  $\eta^2$ -acetone. Nunan and coworkers have studied the formation mechanism of higher alcohols from CO and  $H_2$  over Cs-doped and undoped Cu/ZnO catalysts in detail [11]. The reaction of CO and  $H_2$  in the presence of  $^{13}C$ -labeled methanol or ethanol revealed that lower alcohols were incorporated into the synthesis to form higher alcohols and that carbon chain growth occurred in a step-wise manner dominated by the addition of oxygenated  $C_1$  intermediates at the  $\beta$  carbons of the oxygenated  $C_n$  ( $n \geq 2$ ) intermediates, although the formation mechanism of  $C_2$  to  $C_3$  alcohols depends on the presence and absence of Cs dopant. Thus, the chain branching and the chain growth are explained by the aldol-condensation type reaction. On the other hand, Ekerdt and coworkers proposed the mechanism for the formation of branched hydrocarbons over  $ZrO_2$  catalyst, which consists of both the carbonylation similar to Scheme 1 and the aldol-con-



Scheme 1. Proposed mechanism for carbon chain branching [8].



Scheme 2. The mechanism of  $C_2$  oxygenate formation through two  $C_1$  oxygenates reaction by Ref. [10].

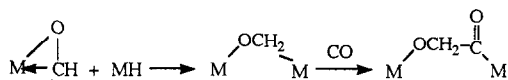
denation of aldehyde with methoxide species [9]. We have proposed [6,13] the aldol-condensation type reaction for the chain branching over oxide catalysts based on that (i) addition of basic additives such as NaOH to  $ZrO_2$  promoted the formation of *isobutene* [14] and (ii) cofeeding of acetaldehyde or acetaldehyde dimethylacetal to CO and  $H_2$  remarkably enhanced the formation of *isobutene* [7]. The present low pressure conditions of less than 1 atm could prefer the aldol-condensation-type reaction to carbonylation at the carbon of carbonyl double bond. It is also known that  $Cp_2Zr(\eta^2\text{-acetone})$  intermediate formed from  $Cp_2Zr(CH_3)_2$  and CO underwent carbonylation at the carbon atom of carbonyl group, while the reaction of the similar Zr complex with ketones or aldehydes under CO atmosphere gave only their enediolate-coordinated Zr complex but not the carbonylation product [15]. This may indicate the difficulty of carbonylation at the carbon atom of carbonyl double bond.

### 4.2. The role of methoxide species

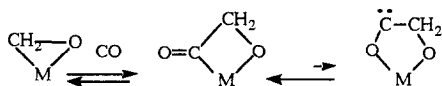
Nunan and coworkers reported the detailed investigation using  $^{13}C$ -enriched methanol and ethanol on the higher alcohol synthesis from syngas over modified methanol synthesis catalysts [10,11]. One of their conclusions is that ethanol is formed by coupling of oxygenated  $C_1$  intermediates originating from methanol as in Scheme 2. The similar mechanism was first proposed by Fox and coworkers for the higher alcohol synthesis from methanol but not syngas [16] and was also presented by Foratti and coworkers [17]. This means that no carbons of higher alcohols are incorporated into the products without passing the path from CO to

methanol and that the mechanism is similar to higher alcohol synthesis from methanol and ethanol over MgO-based catalysts [12]. On the other hand, the results of Figs. 4 and 5 show that *isobutene* from CO hydrogenation over ZrO<sub>2</sub> catalyst is composed of central carbon from surface methoxide species and methyl and methylene carbons from gaseous CO. The spectrum in Fig. 5 shows that there are no carbon–carbon couplings between two carbons of ethylene and between central carbon and methyl and methylene carbons of propylene. Different from the reaction over methanol synthesis catalyst, the results in Figs. 4 and 5 mean that (i) one carbon of ethylene comes from methoxide species and the others from gas phase CO, (ii) the central carbon of propylene originates from methoxide species and methyl and methylene carbons from gaseous CO, and (iii) methyl and methylene carbons of *isobutene* come from gaseous CO and the central carbon from methoxide species. These seem to indicate that the CO–H<sub>2</sub> reaction over oxide catalysts is different from that over methanol synthesis catalysts.

Two mechanisms have been proposed for the formation of C<sub>2</sub> species from CO and H<sub>2</sub>. One is CO insertion into μ<sup>2</sup>-formaldehyde [8] and μ<sup>2</sup>-formyl species [13] as in Scheme 3. CO insertion products in Scheme 3 undergo either (a) hydrogenation to afford acetaldehyde or (b) hydrogen shift by carbene-like character of carbonyl carbon to form enediolate dimer as in the reaction of Zr [18,19] and Th complex [20].



(a) CO insertion into μ<sup>2</sup>-formyl species by Reference 13

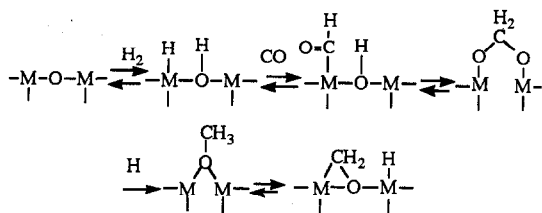


(b) CO insertion into μ<sup>2</sup>-formaldehyde species by Reference 8

Scheme 3. Mechanism of formation of C<sub>2</sub> oxygenate through CO insertion. (a) CO insertion into μ<sup>2</sup>-formyl species by Ref. [13]. (b) CO insertion into μ<sup>2</sup>-formaldehyde species by Ref. [8].

The two carbons of enediolate dimer formed by the hydrogen shift can not be distinguished from each other. Therefore, the present result that each carbon of *isobutene* formed from CO and H<sub>2</sub> over ZrO<sub>2</sub> has the clear history as shown in Figs. 4 and 5 would eliminate this mechanism. The second path of acetaldehyde root (Scheme 3(a)) can not be denied by the present results if formyl comes from methoxide species. In this case the acetaldehyde formed is to consist of methyl given from formyl species and formyl from gaseous CO. In our previous paper, we reported that the reaction of CO and H<sub>2</sub> over ZrO<sub>2</sub> forms paraformaldehyde type adsorbed species even at room temperature [21], while methoxide species slowly appears at 373 K [22]. ZrO<sub>2</sub> at 473 and 523 K began to form methanol after induction time of 20 and 3 h, respectively [7]. These results would indicate that formyl and formaldehyde are in equilibrium with gas phase CO and H<sub>2</sub>, while methoxide is not. Therefore, if η<sup>2</sup>-formaldehyde species in Scheme 3(a) is a precursor of the methyl group in acetaldehyde, the species must be given from methoxide but not directly from formaldehyde which is in equilibrium with the gas phase.

On the other hand, it has been reported that zirconium–hydride complex undergoes carbonylation to yield η<sup>2</sup>-formaldehyde complex [18,19,23], which can be converted to methyl species by the reaction with zirconium–hydride complex [24], and thermolysis of the similar trimeric (η<sup>2</sup>-formaldehyde)zirconocene complex at 473 K results in the cleavage of three CO-derived –CH<sub>2</sub>– groups to form the ‘Cp<sub>2</sub>Zr oxide’ trimer [23]. These suggest that η<sup>2</sup>-formaldehyde species can be transformed to methyl or methylene species. The similar mechanism was also reported in the reaction of tantalum hydride complex with CO at low temperatures to form μ-methylene complex [25]. If this kind of reaction should be possible on the ZrO<sub>2</sub> surface, the mechanism for the formation of η<sup>2</sup>-formaldehyde intermediate could be proposed in Scheme 4. On the other hand, the direct cleavage of methyl–oxygen bond of alkoxide cluster



Scheme 4. Proposed mechanism of  $\eta^2$ -formaldehyde intermediate formation.

is reported for the formation of methyl–metal species [26]. Since  $\text{ZrO}_2$  is one of the difficult-to-reduce oxides [27] and even the  $\text{H}_2$ -treatment at 973 K showed no ESR signal due to  $\text{Zr}^{3+}$ , it may be proposed that the formation of methyl and methylene species from  $\eta^2$ -formaldehyde species would be preferred to the direct formation of methyl species from methoxide species. Thus, methoxide species would be the direct precursor of  $\eta^2$ -formaldehyde species, which is transformed to methyl or methylene–metal species of the precursor of  $\text{C}_2$  oxygenates.

## 5. Conclusions

$^{12}\text{CO}$  hydrogenation over  $\text{ZrO}_2$  treated with a mixture of  $^{13}\text{CO}$  and  $\text{H}_2$  and  $^{13}\text{CO}$  hydrogenation over  $^{12}\text{C}$ -dimethyl ether-adsorbed  $\text{ZrO}_2$  showed that central carbons of propylene and *isobutene* stemmed from methoxide species and the other carbons from gas phase  $\text{CO}$  produced  $^{13}\text{CH}_2=\text{CH}_2$ ,  $^{13}\text{CH}_2=\text{CH}-^{13}\text{CH}_3$ , and  $^{13}\text{CH}_2=\text{C}(^{13}\text{CH}_3)_2$ . From these results was proposed the reaction path which consists of the sequence of (i) conversion of methoxide species to  $\eta^2$ -formaldehyde species, (ii) formation of methyl or methylene species from the  $\eta^2$ -formaldehyde species by hydrogenation or thermalolysis, (iii) carbonylation of the methyl or methylene species to form  $\text{C}_2$  oxygenate, (iv) aldol-condensation type reaction to form branched  $\text{C}_4$  oxygenates, and (v) formation of branched hydrocarbons from the hydrogenation followed by dehydration. It was proposed that

the role of methoxide species was to form the  $\eta^2$ -formaldehyde species, which was not given directly from formaldehyde in equilibrium with gas phase  $\text{CO}$  and  $\text{H}_2$ .

## References

- [1] H. Pichler and K.H. Ziesecke, *Brennst. Chem.* 30 (1949) 13.
- [2] T. Maehashi, K. Maruya, K. Domen, K. Aika and T. Onishi, *Chem. Lett.* (1984) 747.
- [3] K. Maruya, K. Ito, K. Kushihashi, Y. Kishida, K. Domen and T. Onishi, *Catal. Lett.* 14 (1992) 123.
- [4] K. Maruya, T. Arai, K. Domen and T. Onishi, *Catal. Sci. Tech.*, S. Yoshida, N. Takezawa and T. Ono (Eds.), Vol. 1 (Kodansha, Tokyo, 1990) p. 457.
- [5] H. Abe, K. Maruya, K. Domen and T. Onishi, *Chem. Lett.* (1984) 1875.
- [6] K. Maruya, A. Takasawa, M. Aikawa, T. Haraoka, K. Domen and T. Onishi, *J. Chem. Soc. Faraday Trans.* 90 (1994) 911.
- [7] K. Maruya, T. Fujisawa, A. Takasawa, K. Domen and T. Onishi, *Bull. Chem. Soc. Jpn.* 62 (1989) 11.
- [8] T.J. Mazanec, *J. Catal.* 98 (1986) 115.
- [9] S.C. Tseng, N.B. Jackson and J.G. Ekerdt, *J. Catal.* 109 (1988) 284; N.B. Jackson and J.G. Ekerdt, *J. Catal.* 126 (1990) 31, 46.
- [10] J.G. Nunan, C.E. Bodgan, K. Klier, K.J. Smith, C.-W. Young and R.G. Herman, *J. Catal.* 113 (1988) 410.
- [11] J.G. Nunan, C.E. Bodgan, K. Klier, K.J. Smith, C.-W. Young and R.G. Herman, *J. Catal.* 116 (1989) 195.
- [12] W. Ueda, T. Oshida, T. Kuwabara and Y. Morikawa, *Catal. Lett.* 12 (1992) 97.
- [13] K. Maruya, *J. Jpn. Petrol. Inst.* 37 (1994) 246.
- [14] K. Maruya, T. Maehashi, T. Haraoka, S. Narui, Y. Asakawa, K. Domen and T. Onishi, *Bull. Chem. Soc. Jpn.* 61 (1988) 667.
- [15] P. Hofmann, P. Stauffert, M. Frede and K. Tatsumi, *Chem. Ber.* 122 (1989) 1559.
- [16] J.R. Fox, F.A. Pesa and B.S. Curatolo, *J. Catal.* 90 (1984) 127.
- [17] P. Foratti, E. Tronconi and I. Pasquon, *Catal. Rev. Sci. Eng.* 33 (1991) 109.
- [18] P.T. Wolczanski and J.E. Bercaw, *Acc. Chem. Res.* 13 (1980) 121.
- [19] S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc.* 105 (1983) 1690.
- [20] E.A. Maatta and T.J. Marks, *J. Am. Chem. Soc.* 103 (1981) 3576; P.J. Fagan, K.G. Moloy and T.J. Marks, *J. Am. Chem. Soc.* 103 (1981) 6959.
- [21] T. Onishi, H. Abe, K. Maruya and K. Domen, *J. Chem. Soc., Chem. Commun.* (1986) 103.
- [22] H. Abe, K. Maruya, K. Domen and T. Onishi, *Chem. Lett.* (1984) 1975.
- [23] G. Erker, *Acc. Chem. Res.* 17 (1984) 103.
- [24] G. Erker, U. Dorf, J.L. Atwood and W.E. Hunter, *J. Am. Chem. Soc.* 108 (1986) 2251.



- [25] R.L. Miller, R. Toreki, R.E. LaPointe, P.T. Wolczanski, G.D. Van Duyne and D. Christopher Roe, *J. Am. Chem. Soc.* 115 (1993) 5570.
- [26] A. van Asselt, B.J. Burger, V.C. Gibson and J.E. Bercaw, *J. Am. Chem. Soc.* 108 (1986) 5347; G. Parkin, E. Bunel, B.J. Burger, M.S. Trimmer, A. van Asselt and J.E. Bercaw, *J. Mol. Catal.* 41 (1987); J.E. Nelson, G. Parkin and J.E. Bercaw, *Organometallics* 11 (1992) 2181.
- [27] E.M. Cohn, *Catalysis*, P.H. Emmett (Ed.), Vol. 4 (Reinhold, New York, 1956) p. 443.