# The mechanism of higher alcohol formation on ZrO₂-based catalyst from syngas

**Yingquan Wu[*,**], Hongjuan Xie[*], Yongli Kou[*,**], Noritatsu Tsubaki[***], Yizhuo Han[*], and Yisheng Tan[*,†]**

*State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences,
Taiyuan, Shanxi 030001, China
**University of the Chinese Academy of Sciences, Beijing 100039, China
***Department of Applied Chemistry, University of Toyama, Toyama 930-8555, Japan

**Abstract**−A chain growth scheme for the synthesis of alcohols from carbon monoxide and hydrogen is proposed based on the chemical enrichment method on ZrO₂-based catalyst. Methanol addition has no obvious effect on the STY of $C_{2+}$ alcohols, indicating that COH→CCOH is a slow initial growth step. Addition of ethanol and propanols can enhance the STY of isobutanol, especially n-propanol, revealing that n-propanol is largely the precursor of isobutanol. Results of large alcohols addition further reveal the relationship between small alcohols and large alcohols of formation. Also, addition of aldehydes has a similar effect on the formation of higher alcohols, indicating that alcohols exist in the form of aldehydes before desorption. Anisole are introduced into syngas for confirmation of predicted intermediates and the result indicates that formyl species is participated both in the formation of methanol and higher alcohols. Reaction temperature has a significant effect on the chain growth of alcohols synthesis. Under low temperature, chain growth occurs with CO insertion and alcohols are linear products. Isobutanol appears and becomes the main product during $C_{2+}$ alcohols undergo an aldo-condensation reaction at high temperature.

Keywords: Mechanism, Syngas, Enrichment, Higher Alcohol, Isobutanol

## INTRODUCTION

The synthesis of mixed alcohols from CO and $H_2$ has attracted great attention due to the possibility of synthesis gas generation from a variety of carbon sources including biomass, coal, and natural gas by gasification and/or reforming [1,2]. The formed mixed alcohols could be used for octane enhancers and environmentally friendly fuel additives, and this application may be a feasible approach to "coal substitute for oil" [3-5]. Isobutanol, one product of alcohol generation, is an important organic chemical material that would be the raw material of pharmaceutical and chemical products, such as anti-oxygen, paint solvents, flavoring agents, plasticizers, and synthetic rubber [6]. Furthermore, the isobutanol has been approved as gasoline additives by U.S. Environmental Protection Agency (EPA) in 2010 [7].

To promote the selectivity of isobutanol among the whole alcohol products, the reaction pathways leading to it from syngas should be understood deeply. Many pathways of isobutanol formation from syngas have been proposed based on the specific alcohol distribution during which methanol and isobutanol were the primary products. Negishi [8] tried to explain the high selectivity of isobutanol in alcohol products and proposed a mechanism in which dimethyl ether as an intermediate reacted with ethanol to produce isobutanol. Stiles [9,10] suggested a mechanism that the addition of methylene species to the surface-adsorbed aldehydes was the key step for chain growth. He also suggested that the reaction site

is a lattice-deformity site rather than a metallic (or crystalline) site. But this mechanism is unable to explain why i-BuOH and n-PrOH are the major reaction products in most of the higher alcohol synthesis processes. Then he proposed another mechanism for his Cu/Mn/Zn/Co/Cr/K+Cs catalyst composition, test conditions, and products. This mechanism combines several probable growth pathways, including α-and β-addition of methylene groups to surface-bound aldehydes and condensation of two surface alkoxy species. Smith and Anderson [11,12] reported a dehydration hypothesis based on the quantification of the distribution of higher alcohols in the HAS product on Cu/ZnO/Al₂O₃ catalysts. Chain growth of COH→CCOH is a slow initial step, and isobutanol is formed from β-addition of CCCCOH. Vedage [13] found that branched alcohol (isobutanol) appeared under high reaction temperature (>280 °C) on CuZnO catalyst. They proposed a mechanism that isobutanol was formed from formyl species and propanal. Mananec [14] reported a primary pathway for the construction of higher alcohols over metal oxide catalysts. Hydrogen is transferred to coordinated CO stepwise and chain growth is achieved by inserting the CO into a metalcarbon bond of a surface-bonded aldehyde. During this mechanism, n-$C_3$ intermediate is first formed, then converted to i-$C_3$ through isomerization, followed by CO insertion to produce isobutanol. Hilmen [15] added ethanol and n-propanol to syngas and found that chain growth occurred predominantly by the aldol-type addition of methanol-derived $C_1$ species to ethanol and higher alcohols, which followed the rules of base-catalyzed aldol condensations. Artyukh [16] and Beretta [17] added methanol and other $C_{2+}$ alcohols to syngas and found that n-propanol could enhance the yield of isobutanol greatly. So, they deduced that n-propanol was an intermediate over isobutanol formation. An et al. [18] found that isobu-

tanol is formed from C$_1$ $\beta$-addition to CCCOH on modified methanol synthesis catalyst (K-Zn/Cr). Tao [19] studied the mechanism of carbon chain growth for higher alcohol synthesis from syngas over Zn-Cr catalyst in supercritical fluid by chemical enrichment, and also found that isobutanol is formed from C$_1$ $\beta$-addition to CCCOH. Daiping He [20] studied the mechanism of isobutanol formation on Zr-based catalyst, and found that $\alpha$-insertion of COH to CCOH was the initial chain growth. Then continuous $\beta$-addition to CCOH occurred to produce the n-propanol and isobutanol.

Based on these studies, there is still controversy over some important issues, particularly the concrete existence form of C$_1$ or C$_{2+}$ intermediates during isobutanol formation. Besides, for the formation of isobutanol, it is widely accepted that isobutanol is from reaction of C$_1$ and C$_3$ directly. But, the pathway of $\beta$-addition of C$_1$ to C$_3$ or CO insertion of C$_1$ to C$_3$ is also not clear.

We investigated isobutanol synthesis from CO/H$_2$ over ZrO$_2$-based catalyst at 360 $^\circ$C under 10 MPa with 3,000 h$^{-1}$ syngas. A mechanism of higher alcohols synthesis was proposed based on the chemical-enrichment method. Methanol, ethanol and other C$_{2+}$ alcohols, aldehydes and ether were introduced to syngas at different reaction conditions.

## EXPERIMENTAL

### 1. Catalyst Preparation

Preparation of the Cu/Zn/La/ZrO$_2$ catalyst and its physical and chemical properties have been described in the previous work [21]. The Cu/Zn/La/ZrO$_2$ catalyst was prepared by co-precipitation of a solution (1 mol/L) of Cu(NO$_3$)$_2$·3H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, La(NO$_3$)$_3$·6H$_2$O and ZrO(NO$_3$)$_2$·2H$_2$O (Cu : Zn : La : Zr=1 : 1.5 : 0.2 : 4, mole ratio) with KOH (1 mol/L) at 60 $^\circ$C, pH 11, in a well-stirred thermostated container. The precipitate was settled at room temperature for 3 h, then washed to pH=7 with deionized water. After drying at 120 $^\circ$C for 12 h, the precursor was calcined at 450 $^\circ$C. Calcined catalyst was powdered and impregnated with 1 wt% K as a promoter by KOH with incipient wetness method, then it was dried at 120 $^\circ$C for 12 h and calcined at 450 $^\circ$C. Finally, the promoted catalyst was pressed and broken in 30 to 40 mesh.

### 2. Catalytic Performance Testing

The catalytic reactions were carried out in a stainless fixed-bed reactor with 5 ml catalyst. A feed gas of H$_2$ and CO (V/V, 2.3 : 1) was introduced into the reactor at a space velocity of 3,000 h$^{-1}$ by a mass flow controller. A wet test meter was used to measure the flow rate of exit gas. The catalyst was reduced using a mixture of H$_2$/N$_2$ (10 : 90) according to a designed temperature program from room temperature to 380 $^\circ$C over 12 h. The typical composition of syngas was as follows: H$_2$, 67.2%; CO, 30.6%; CH$_4$, 0.7%; and CO$_2$, 1.5%. Products passed through a condenser for separation. Alcohols and water were collected in liquid products. The flow rate of vent gas was read with a wet flowmeter. The reactions were run at 360 $^\circ$C, 10 MPa. The product stream was analyzed on a GC 4000 gas chromatograph. Syngas and exit gas were analyzed using a carbon sieves column and a thermal conductivity detector (TCD) for H$_2$, CH$_4$, CO and CO$_2$. CHx mixtures were analyzed by using a GDX-403 column and detected using flame ionization. Water and methanol were detected with a column of GDX-401 and a TCD.
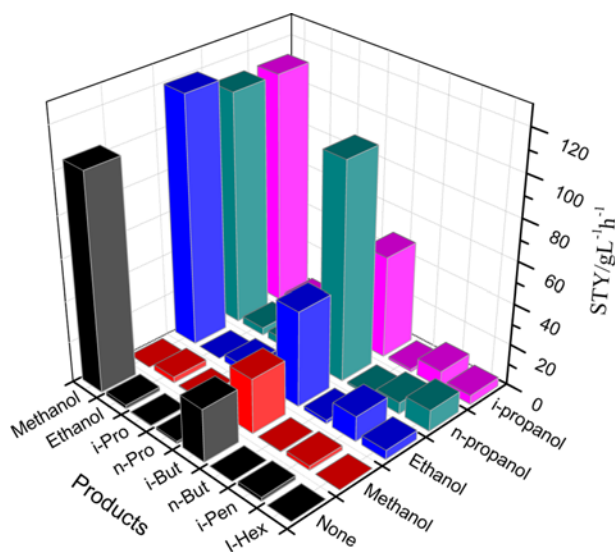


**Fig. 1. Distribution of alcohols with and without addition of alcohols (T=360 $^\circ$C, P=10 MPa, GHSV=3,000 h$^{-1}$, H$_2$ : CO=2.3 : 1, feed rate of additives=1 ml/h).**

The mixtures of alcohol products were analyzed by another GC-7A gas chromatograph using a Chromosorb 101 column and a flame ionization detector (FID). Anisole and alcohol additives were introduced into the syngas with a pump at 1 ml/h.

## RESULTS AND DISCUSSION

### 1. Addition of Methanol, Ethanol, n-Propanol and i-Propanol

The addition of an alcohol to the reactant of HAS can increase the surface concentration of a particular alcohol precursor, which increases the yield of alcohols produced from this particular precursor. These observations may lead to a technique for determining if the chain growth steps in this work are consistent, and may also have some practical advantage.

Fig. 1 shows the composition of the alcohol distribution on ZrO$_2$-based catalyst with and without additives. The STY of alcohol added in syngas as an additive is not considered here, so, its STY is listed out as 0 in the figure. Methanol and isobutanol are the primary products without any additives. After addition of methanol to syngas, no obvious influence on the distribution of alcohol products is observed. Smith and Anderson [12] found that addition of methanol to the syngas on K-Cu/ZnO catalyst could double the ethanol and 1-propanol yields. Artyukh [16] found that addition of methanol only led to a slight increase in the amount of ethanol and propanols at 653 K, but had an inhibiting effect on all the alcohols from C$_2$ and higher at 693 K on the K-Zn/Cr catalyst. An [18] found that, on the K-Zn/Cr catalyst, addition of methanol led to an increase of n-propanol and isobutanol yields 2 and 0.6 times compared with none addition. Daiping He [20] found that methanol addition could enhance the STY of isobutanol, but there was an optimum amount of methanol. More methanol addition has no more increase on STY of isobutanol. So, the C$_1$ intermediate from methanol on surface of catalyst has relationship with isobutanol formation. Meanwhile, the present ZrO$_2$-based catalyst surface has

enough $C_1$ species for the synthesis of methanol and $C_{2+}$ alcohols. Large methanol selectivity indicates that COH→CCOH is a slow initial growth step.

Ethanol addition has an obvious effect on the STYs of all alcohol products, especially the isobutanol and i-$C_5$ alcohol. Meanwhile, n-butanol appears with low content. 1-propanol addition has similar effects on the STY of all alcohol products as ethanol. Increased STY of ethanol further confirms that n-propanol comes from $C_2$ intermediates of ethanol. The significant increase of isobutanol indicates that $C_3$ species derived from n-propanol is largely the precursor of isobutanol. Besides, the STY of i-$C_6$ alcohol also increases with an obvious concentration.

Alcohol STYs also increase remarkably with the addition of i-propanol to syngas. Artyukh [15] thought that the secondary alcohols could convert to the primary alcohols at the surface of the catalyst. So, the increased STY of n-propanol could be attributed to the isomerization of i-propanol. Increased STY of isobutanol is related to increased amount of n-propanol.

Based on the results of small alcohols addition, isobutanol formation is related to $C_2$ and $C_3$ species. Smith and Anderson [12] verified their mechanistic scheme of HAS over K-doped Cu/ZnO catalysts by injecting $C_1$-$C_4$ oxygenates. In particular, the results of these experiments proved that the formation of ethanol, propanol, and isobutanol occurs sequentially. Beretta [17] thought that alcohols do not participate directly in HAS but are related through hydrogenation-dehydrogenation reactions to the true reacting species in the chain growth, namely, the corresponding aldehydes and ketones. Thus, the apparent reactivity of ethanol was properly due to the evolution of acetaldehyde, of which the added alcohol represented a sort of reservoir. Ethanol added to syngas dehydrogenated to aldehyde which is a nucleophilic reactant in normal aldol condensations with $C_1$, $C_2$, and $C_3$ species. N-propanol, n-butanol and i-$C_5$ alcohol increase. In the same way, addition of n-propanol increases the STY of isobutanol, i-$C_5$ and i-$C_6$.

## 2. Addition of Methanal, Ethanal and Propanal

As discussed, alcohols are related through hydrogenation-dehydrogenation reactions to the aldehyde species in the chain growth. Morgan and Hardy [22] hypothesized that higher alcohols (and aldehydes) arose from lower aldehydes by the consecutive reactions of aldol condensation, dehydration, and hydrogenation. Stiles [10] found a substantial amount of aldehydes on their newly developed catalyst system (Cu/Mn/Zn/Co/Cr/K+Cs=4/3/1/0.028/15%/4.0%). In our work, no aldehyde was detected due to the high ratio of $H_2$/CO. To determine the precursor intermediates of alcohols, various kinds of aldehydes were introduced to syngas.

Fig. 2 shows the alcohol products and their STYs produced by HAS with aldehydes added to syngas. The addition of methanal to the syngas slightly affects the STYs of all alcohol products. Ethanal addition more or less increased the STYs of all the alcohol products. Obvious increase occurs on the STY of isobutanol. In addition, the STY of i-$C_5$ alcohol increases greatly. N-butanol also appears with addition of ethanal. Propanal addition increases the STYs of alcohol products too, but n-butanol was not observed. The propanal added in syngas can be converted to n-propanol through hydrogenation. The strikingl increasing in isobutanol STY is caused by the increased amount of n-propanal.
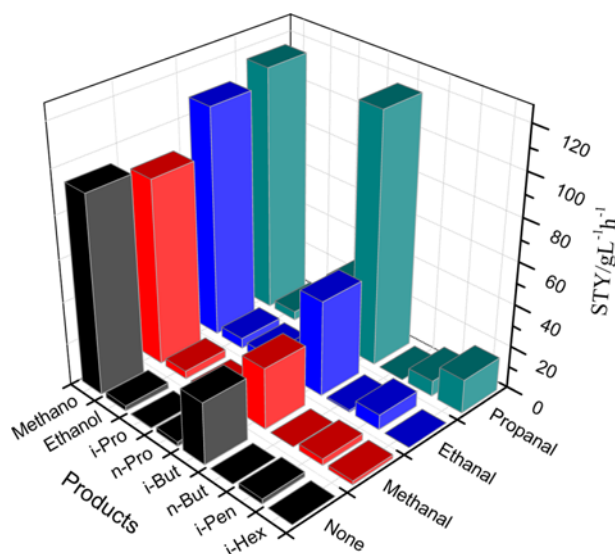
**Fig. 2. Distribution of alcohols with and without addition of aldehydes (T=360 °C, P=10 MPa, GHSV=3,000 $h^{-1}$, $H_2$:CO= 2.3:1, feed rate of additives=1 ml/h).**

The reaction products produced with addition of methanal, ethanal and propanal are similar to these produced with addition their alcholates, respectively. This indicates that alcohols exist in the form of aldehydes before desorption.

## 3. Addition of Isobutanol, n-Butanol and n-Pentanol

Methanol and isobutanol are the primary products of HAS using syngas without any additive. Methanol addition results indicate that COH→CCOH is a slow step, so a large amount of methanol remains in the reaction product. To test further addition reaction on isobutanol, isobutanol was added to syngas. Meanwhile, n-butanol and n-pentanol were also introduced to observe the formation
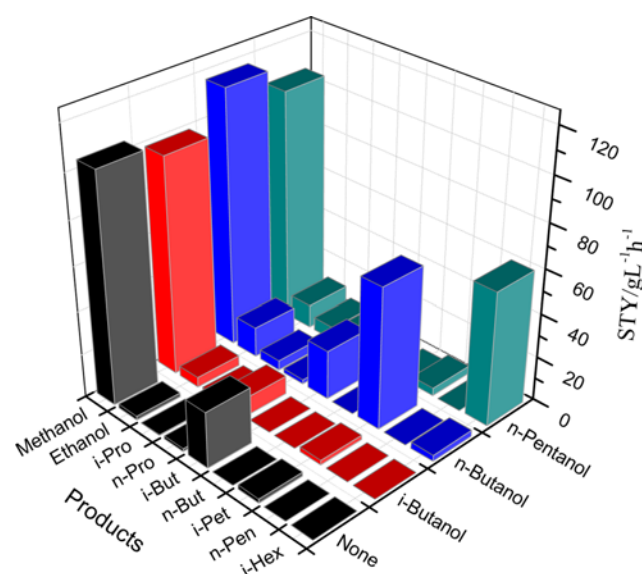


**Fig. 3. Distribution of alcohols with and without addition of large molecular alcohols (T=360 °C, P=10 MPa, GHSV=3,000 $h^{-1}$, $H_2$:CO=2.3:1, feed rate of additives=1 ml/h).**

of the C$_5$ and C$_6$ alcohols.

Fig. 3 shows the composition of the reaction products using the syngas with and without additives. No new alcohol is formed with addition of isobutanol. The STY of methanol decreases slightly, while the STYs of ethanol and n-propanol increase, indicating that isobutanol is related to C$_2$ and C$_3$ intermediates in another way. Chain growth does not happen on isobutanol because no obvious increase is observed on C$_{4+}$ alcohols. This is why isobutanol exists in large amount, except methanol during the alcohol products.
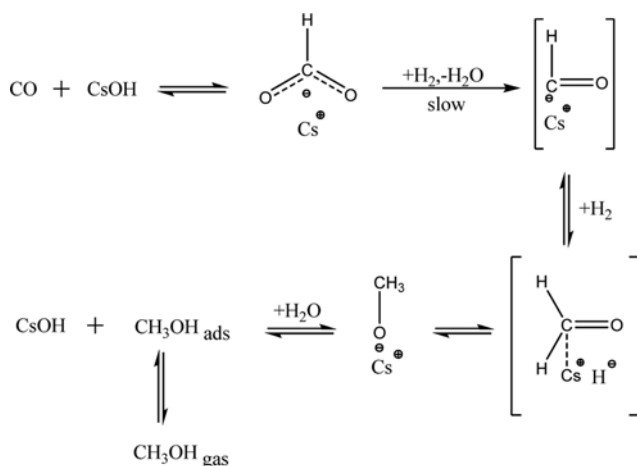
The STYs of alcohol products with n-butanol and n-pentanol addition are also listed in Fig. 3. Addition of n-butanol and n-pentanol causes a significant increase in the STY of i-C$_5$ and i-C$_6$ alcohols, respectively. This result reveals that linear alcohols favor reacting with C$_1$ species to form 2-methyl-branched alcohols on the ZrO$_2$-based catalyst. That is why linear alcohols exist in low selectivity in alcohol products, such as ethanol, n-propanol et al.
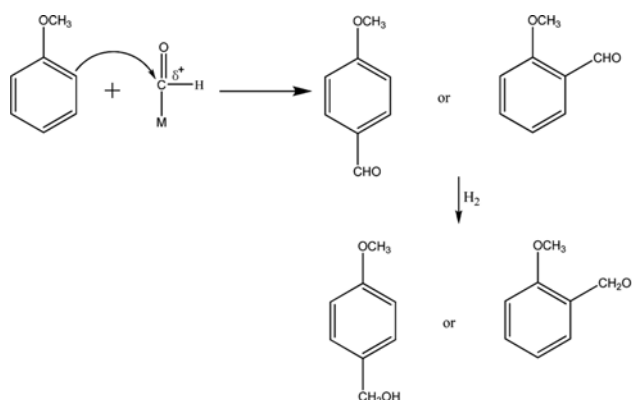
**4. Addition of Anisole**

The first step in syngas reaction is to activate reactants with catalysts. Hydrogen undergoes heterolytic cleavage on ZnO surface, which produces Zn-H and Zn-OH groups as detected by infrared spectroscopy [23,24]. Other metal oxide catalysts for alcohol synthesis can activate hydrogen in the same way: for example, the heterolytic cleavage of H$_2$ on ZrO$_2$ results in Zr-H and Zr-OH groups [25].

Adsorption of CO on metal oxides has been well studied. Recent spectroscopic analysis shows that CO is adsorbed on ZnO through the bond of carbon to Zn$^{2+}$ ion. The C-O vector makes a 30$^\circ$ angle on the surface and the bound CO has a stronger C-O bond than free CO [26].

Co-adsorption of CO and H$_2$ changes their individual adsorption behaviors on these oxides, probably through the formation of surface complexes [27]. Infrared measurements and chemical trapping experiments have confirmed the existence of several species on ZnO, and one of them is formyl [28]. Thereafter, many mechanisms for HAS have proposed that formyl is a C$_1$ intermediate [29-33]. It is unknown if formyl species is related to higher alcohols formation directly. Based on chemical trapping, $^{13}$C label flow, and spectroscopic analysis as well as quantum chemical calculation,

Scheme 2. Equation of formyl species.

Nun et al. [30] proposed that adsorbed formyl is a reactive nucleophile that forms C-C bond by attacking the positive carbon of adsorbed formaldehyde or methanol. But the intermediates associated with Cs$^+$ in square brackets are unproved and the existence of these intermediates was only deduced from their reaction patterns with higher alcohols, aldehydes, ketones, and amines (Scheme 1).

To test the function of formyl species in alcohol synthesis, the following reaction equation is proposed with anisole as a probe molecular (Scheme 2). If formyl species were formed during the alcohol formation and were related to the methanol and higher alcohol synthesis, methoxybenzaldehyde or Methoxybenzyl alcohol would be detected. Meanwhile, yield of alcohol would be affected for trapping of formyl species by anisole.

Fig. 4 shows the distribution of alcohol products with and without anisole added. Methanol and isobutanol are the primary products without anisole. Only small amounts of other C$_{2+}$ alcohols are produced. After the addition of anisole, the STY of all alcohols
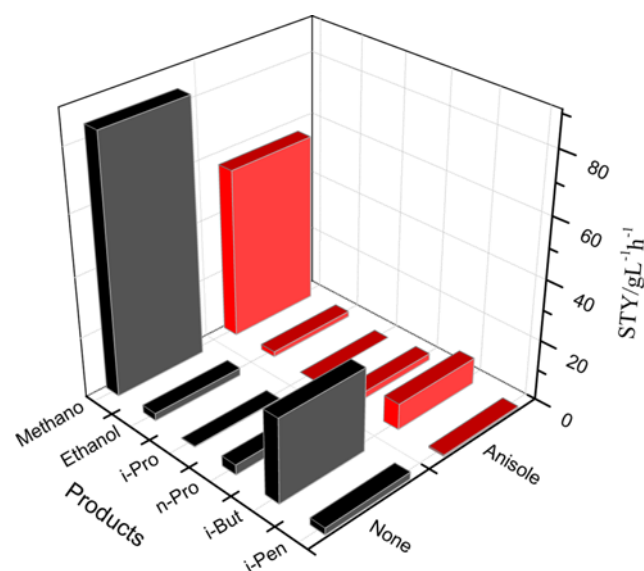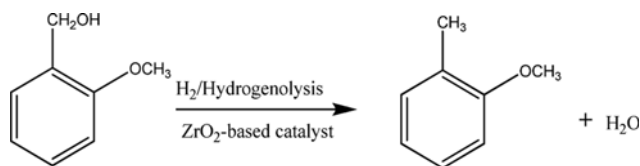
Scheme 1. Methanol synthesis.

Fig. 4. Distribution of alcohols with and without addition of anisole (T=360 $^\circ$C, P=10 MPa, GHSV=3,000 h$^{-1}$, H$_2$:CO=2.3:1, feed rate of anisole=1 ml/h).

**Scheme 3. Hydrogenolysis of 2-methoxybenzyl alcohol.**

decreases obviously, indicating that intermediates react with anisole. Oil products were also detected by GC/MS. In addition to unreacted anisole, 2-methylanisole and 2,6-dimethylanisole were found in the product. 4-Methylanisole was not detected in the oil products. No methoxybenzaldehyde or Methoxybenzyl alcohol was detected in the products. In our opinion, methoxybenzaldehyde is hydrogenated to Methoxybenzyl alcohol, then converts to methylanisole by hydrogenolysis (Scheme 3) on the catalyst containing Cu [34]. Some ring compounds, such as cyclohexylcarbinol and 2,6-dimethylcyclohexylcarbinol, were also detected, indicating that anisole is hydrogenated to some degree. This further indicates that the $ZrO_2$-based catalyst has strong hydrogenation ability.

To verify the hypothesis of hydrogenolysis, 2-methoxybenzyl alcohol was introduced into the reactor just like anisole, and syngas was replaced by $H_2$ as the carrier gas. After analysis of the liquid products, a large amount of 2-methylanisole was found, and no aromatic compounds with -$CH_2OH$ group were found.

These results indicate that formyl species are largely the $C_1$ intermediates of alcohol synthesis. Namely, formyl species participate in both methanol and higher alcohols synthesis. In another study, over a $CuO/ZnO/Al_2O_3$ catalyst, Elliott and Pennella [35] suggested on the basis of experimental results in which they used labeled methanol that the precursor for the formation of methanol and ethanol is the same. The mechanism they suggested shows that syngas (CO and $H_2$) or methanol could form an adsorbed $C_1$ species that serves as a common precursor for both methanol and ethanol. But they do not mention the composition of $C_1$ species.

**5. Addition of Ethanol and Propanol under Lower Reaction Temperature**

Catalysts for higher alcohol synthesis have been studied extensively, and the distribution of alcohols has had a great difference based on different catalysts. In general, there are two types of distribution which obey the ASF or not. Comparing the reaction temperature, alcohol distribution obeys the ASF mainly under a relative low reaction temperature (around 300 °C) [36-38], and the one does not obey the ASF under a high reaction temperature (≥400 °C) [39, 40]. Linear alcohol formation mainly is from linear chain growth (carbonylation) pathway [15], but the branched alcohol (isobutanol) is formation through the aldo-condensation reaction [30].

Fig. 5 shows the results of alcohol distribution under different temperature and effects of ethanol and n-propanol addition under low reaction temperature on alcohol distribution. Methanol and isobutanol are the primary products in alcohol products with little other alcohols at 360 °C. When the reaction temperature decreases to 290 °C, methanol is the main product with little $C_{2+}$ alcohols. Compared to the results under 360 °C, the yield of ethanol and n-butanol increases and an obvious decrease is observed in the yield of isobutanol and i-$C_5$, indicating that β-addition reaction is inhib-



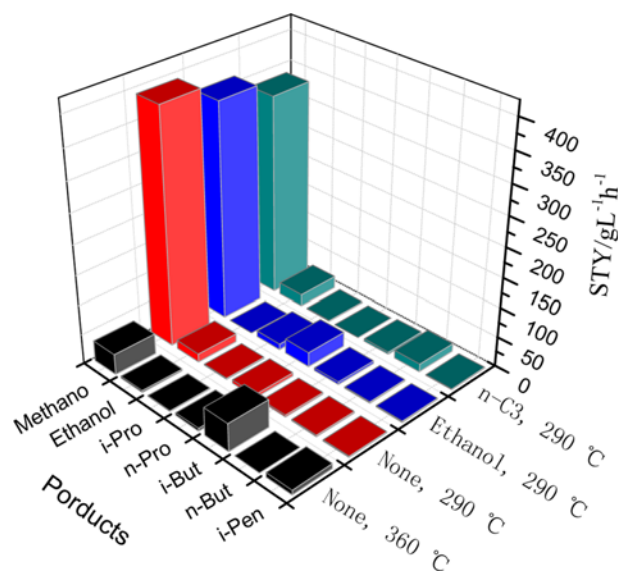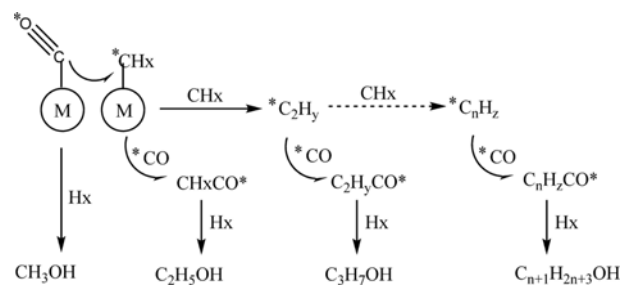**Fig. 5. Distribution of alcohols with and without addition of ethanol and n-propanol under different reaction temperatures (P=10 MPa, GHSV=3,000 h$^{-1}$, H$_2$:CO=2.3:1, feed rate of additives=1 ml/h).**
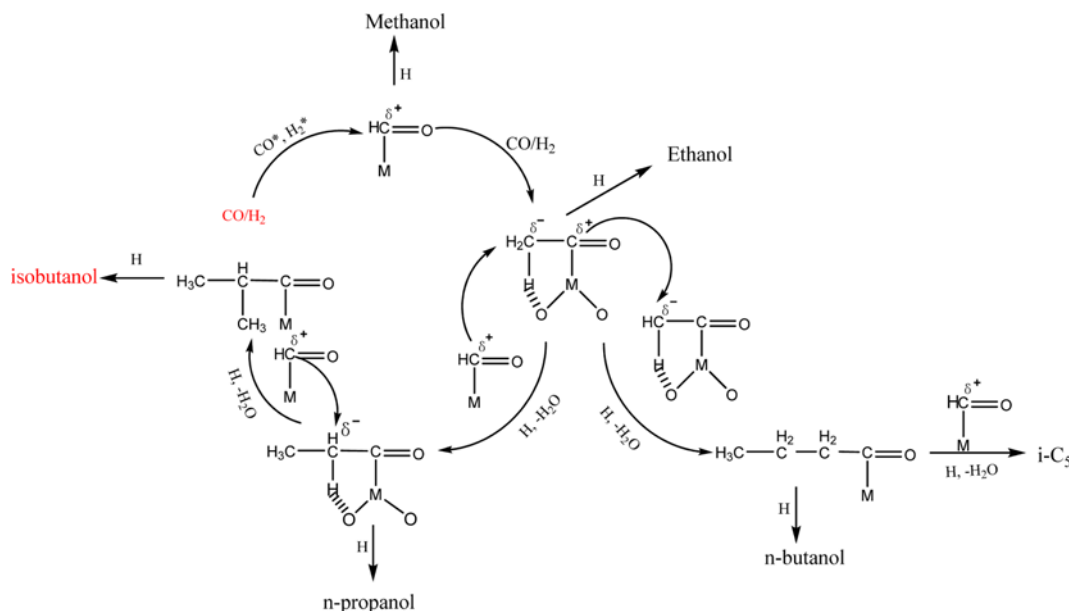
ited under low temperature. Introduction of ethanol and n-propanol into syngas has an obvious effect on the distribution of alcohols under 290 °C. Yield of n-propanol increases with ethanol addition and n-butanol increases with n-propanol addition, though the increase is not much. Yield of isobutanol has no obvious change. It is different from the results with addition of ethanol and n-propanol under high reaction temperature (360 °C, Fig. 1). This reveals that linear chain growth is the main way for high alcohol formation under low reaction temperature on the $ZrO_2$-based catalyst.

As discussed above, two kinds of chain growth exist in the synthesis of higher alcohols on the $ZrO_2$-based catalyst, linear chain growth and branch chain growth. The two pathways are significantly influenced by the reaction temperature. Under low reaction temperature, chain growth occurs through CO insertion [15,41,42] and linear alcohols are the primary products. When reaction temperature is raised, chain growth mainly happens with aldo-condensation in step of linear growth. Branched alcohols (mainly isobutanol) become the primary alcohols during the $C_{2+}$ alcohols. A mechanism for higher alcohols synthesis on the $ZrO_2$-based catalyst is proposed below:

Linear chain growth (under low reaction temperature):



**Scheme 4. Formation of linear alcohols.**

**Scheme 5. Formation of branched alcohols.**

Branched chain growth (under high reaction temperature):

## CONCLUSION

A chain growth scheme for the synthesis of alcohols from carbon monoxide and hydrogen is proposed based on the chemical enrichment method on ZrO₂-based catalyst. Methanol, ethanol and propanols addition to syngas have different influence on the distribution of alcohol products, especially the isobutanol. But n-propanol is related to the formation of isobutanol directly. Methanal, ethanal and propanal addition has a similar effect on the formation of higher alcohols, indicating that alcohols exist in the form of aldehydes before desorption. Anisole are introduced into syngas for confirmation of predicted intermediates, and the result indicates that formyl species is participated both in the formation of methanol and higher alcohols. Reaction temperature has a significant effect on the chain growth of alcohols synthesis. Under low temperature, chain growth occurs with CO insertion and alcohols are linear products. Isobutanol appears and becomes the main product during $C_{2+}$ alcohols undergoing an aldo-condensation reaction at high temperature.

## ACKNOWLEDGEMENTS

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