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Methanol to Long-chain Oxygenates Over Mg/Al Mixed Oxides Supported Cu Catalysts

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Abstract The synthesis of long-chain oxygenates (C_{2+}) from methanol is examined at atmospheric pressure and 523–673 K. The Cu–ZnO/d-HT (decomposed hydrotalcite) catalyst shows ca. 10% yield of C_{2+} at 573 K and a weight hourly space velocity of 0.2 h^{-1}; whereas, no C_{2+} is formed over Cu/d-HY, Cu–MgO/Al_2O_3, Cu–ZnO/Al_2O_3, or a commercial Cu/ZnO methanol synthesis catalyst. The role of the synergistic effect of Cu, ZnO and the basicity of d-HT and the possible reaction intermediates for the C_{2+} synthesis are discussed.

Keywords Methanol · Oxygenates · Hydrotalcite · Cu · ZnO

1 Introduction

Petroleum has been the main source of energy and also petrochemicals during the past century. Since petroleum supply is diminishing and its price becomes more expensive, the pressure to find a substitute for petroleum is increasing. Both hydrogen-economy and methanol-economy are praised as a possibility in post-petroleum era. Methanol is cheap and easier to be transported or stored than hydrogen. It can be obtained from non-petroleum sources and has a wide variety of applications. Consequently, methanol can play an indispensable role as a substitute for petroleum.

Methanol as an energy carrier has received considerable attention. It can be used as a direct fuel for fuel cells, i.e., DMFCs (direct methanol fuel cells), as an additive to current fuels, or as a feedstock to produce hydrogen, biodiesels, chemicals such as acetic acid [1], or other fuel additives or substitutes such as methyl tertiary butyl ether (MTBE) [2, 3], methyl formate (MF) [4, 5], dimethyl ether (DME) [6, 7], etc. Furthermore, existing processes can produce long-chain chemicals from methanol, e.g., the methanol-to-gasoline (MTG) [8–10], the methanol-to-olefins (MTO) [11–13], or the methanol-to-hydrocarbons (MTH) processes [14–19]. Zeolites are usually used as catalysts at temperatures from 623 to 723 K. However, products from these processes lose the oxygen of methanol and water is formed. The transformation of oxygen to water causes lower energy efficiency. Long-chain oxygenates as products from methanol conversion can have higher energy efficiency than MTG, MTO, and MTH processes. Oxygenates also provide good potentials for further conversion to specialty chemicals. Comparatively, the synthesis of long-chain oxygenates from methanol attracts relatively low attention because very low selectivity is observed in previous work [20], but it may be a useful synthesis route when appropriate process is developed.

Methanol is industrially produced from syn-gas using Cu catalysts [21], i.e., the methanol synthesis (MS) process. When Cu catalysts are modified by base additives such as Na, K, Cs, and Zr [22–28], higher alcohols are formed and the process is known as the higher-alcohol synthesis (HAS) [29]. Products of HAS from syn-gas typically contains CO_2, methanol, higher (C_{2+}) oxygenates (e.g., DME, MF, and higher alcohols), and some hydrocarbons. Methanol is usually the major product. To selectively produce higher alcohols has been a challenge in this HAS process. The mechanism of C–C bond formation in HAS has been discussed extensively [30–32]. The formation of the first C–C bond to make ethanol is considered as the critical step

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because higher oxygenates can be generated subsequently through aldol-condensation of ethanol. Nunan et al. [30] and Elliot and Pennella [31] mixed labeled methanol with syn-gas during HAS and proposed that ethanol can be formed from formaldehyde and formyl C1 intermediates whereas reaction between methanol (methoxy) and CO yields MF. Calverley and Smith [33] found later that both methanol and CO are incorporated in the formation of ethanol, i.e., the first C–C bond. Xu and Iglesia [34, 35] concluded that parallel pathways exists in the formation of initial C–C bond in ethanol, i.e., coupling of MeOH-derived C1 intermediates and reactions of CO to form methyl acetate. Though the exact route of ethanol formation in HAS is not unambiguously concluded, all these studies indicate that C1 intermediates in the following simplified scheme lead to the initial C–C bond formation.

$$\begin{array}{c} CO + H_2 \leftrightarrows C_1 \text{ intermediates} \leftrightarrows MeOH \\ \downarrow\uparrow \\ \text{Higher oxygenates } (C_{2+}) \end{array} \quad (1)$$

Most HAS studies used syn-gas or MeOH-syn-gas mixture as the reaction feed. However, there are very few reports on using MeOH alone as the feed to generate C_{2+} oxygenates although Scheme indicates that is possible. Gines and Iglesia [36] showed by isotope technique that methanol decomposed into CO and H_2 over $Cu/MgCeO_x$ but methanol could react with ethanol via aldol condensation to form propionaldehyde and higher oxygenates. Lietti et al. [20] made a first report of the synthesis of C_{2+} oxygenates from MeOH at atmospheric pressure and 573–678 K using a K–Zn–Cr-oxide catalyst, and the products include alcohols, aldehydes and ketones from C_4 to C_7 but the yield of C_{2+} oxygenates is very low. No better catalyst has been reported after Lietti et al. [20] to the best of our knowledge. In this study, we report a Cu catalyst that can catalyze the synthesis of C_{2+} oxygenates from MeOH with a significantly improved yield at mild conditions. Although significant amount of CO is observed in the product stream during this methanol reaction, no C_{2+} oxygenates were found when the methanol feed is replaced by CO/H_2 [37]. This suggests that the formation of C_{2+} cannot be considered as owing to methanol decomposition to syngas and a subsequent HAS route. Based on the reaction results, the route of C_{2+} formation is discussed.

2 Experimental

2.1 Catalyst Preparation

We used two commercial supports for catalyst preparation, namely, hydrotalcite (HT, Condea, Pural MG 50) and γ-Al_2O_3 (Condea, Puralox SCCa-150/155n). An impregnation or co-impregnation method was used to prepare catalysts from aqueous solution containing selected precursors of $Cu(NO_3)_2 \cdot 3H_2O$ (Merck, 99.5%), $Mg(NO_3)_2 \cdot 6H_2O$ (Aldrich, 99.8%), and $Zn(NO_3)_2 \cdot 6H_2O$ (Aldrich, 99.8%). The prepared catalysts were vacuum-dried for overnight at room temperature and stored in desiccators for later uses. Only $Cu(OH)_2$ and hydrotalcite structures are indicated from XRD analysis at this stage. A commercial MS catalyst $Cu/ZnO/Al_2O_3$ (Nissan Girdler, G-66B) is compared in this study and is referred to as Cu/ZnO hereafter. All catalysts are subjected to calcinations at 573 K and subsequently reduced in-line with H_2 at 523 K. Since HT decomposes to mixed oxides after calcinations at 523 K and above [38], catalysts prepared from HT in this study are denoted as Cu/d-HT or Cu–ZnO/d-HT.

2.2 Characterization

Brunauer–Emmett–Teller (BET) surface area is analyzed with N_2 adsorption at 77 K over 573 K-calcined catalysts using Micromeritics (ASAP-2000, USA). A N_2O-decomposition method [39] is used to determine the copper surface area of reduced catalysts, from which the percentage dispersion and Cu particle size can be determined [40, 41]. Energy dispersive X-ray (EDX) analysis of the catalyst shows no element other than Cu, Zn, Mg, Al, and O elements.

2.3 Catalytic Reaction Test

The methanol reaction was performed at atmospheric pressure with a methanol partial pressure of 26.7 kPa (200 Torr), balanced with helium; the WHSV (weight hourly space velocity, in g MeOH/g catalyst/h) covered from 0.1 to 15 h^{-1}. The catalyst was loaded into a pyrex reactor and pretreated inline by first calcining at 573 K and followed by hydrogen-reduction at 523 K. Both He and H_2 gases were 99.995% pure and were passed through drying and Oxytrap columns before entering the system. Methanol (Merck, spectroscopy grade, 99.95%) was dehydrated by soaking with molecular sieves, then fed into a heated foreline using a syringe pump and carried into the reactor by helium. The reactor was subjected to a stepwise temperature-ramp sequence in which methanol was fed only at constant-temperature segments. The reactor effluent was carried to inline GC (Shimadzu 8A, using TCD detector) via a heated Teflon line to prevent condensation or side reactions. A 4-way valve was used to connect the reactor to the system such that the feed composition can be examined. The reaction conversion is calculated from the percentage of methanol remained in the effluent. The selectivity is defined as the ratio of the fractional methanol conversion to

a specific product to the total methanol conversion, i.e., carbon selectivity. The yield reported in this study is calculated by multiplying conversion with selectivity. Typically, both the activity and the selectivity approach steady state after 30 min on-stream at each test temperature. The reported data are averaged from on-stream time from 30 to 60 min at each temperature. An ice-water bath was installed after GC sampling port to collect condensates for GC-MS (Angilent, 6890N/5973N) analysis.

3 Result and Discussion

Table 1 shows the target composition, BET area, Cu surface area, and the calculated dispersion and Cu particle size of samples used in this study. The BET area of prepared catalysts is lower than that of supports. High Cu dispersion is achieved in most prepared catalysts. Comparatively, the commercial $Cu/ZnO/Al_2O_3$ catalyst has a lower Cu dispersion.

Table 2 summarizes results of the methanol reaction at 523 K over different catalysts tested in this study. Three types of catalysts were examined, namely, Al_2O_3-supported, d-HT-supported, and a commercial Cu/ZnO catalyst. Blank supports showed no activity under the conditions of this study. The Al_2O_3-supported Cu catalysts show high methanol conversion and CO, CO_2, and DME are formed. The MgO additive causes lower methanol conversion and higher DME selectivity. The ZnO additive increases methanol conversion and slightly reduces DME selectivity. Neither ZnO nor MgO additive to Cu/Al_2O_3 results in the formation of C_{2+} oxygenates. The commercial methanol synthesis catalyst, Cu/ZnO, appears to be a good methanol decomposition catalyst showing high MeOH conversion and high CO selectivity, but no C_{2+} is formed. Copper catalysts supported on d-HT resulted in lower methanol conversion than Al_2O_3-supported Cu catalysts or the Cu/ZnO commercial catalyst under the same conditions. However, the Cu–ZnO/d-HT catalyst shows very different product selectivity. Significant amounts of formaldehyde (FAL) and long-carbon-chain compounds (C_{2+}) are observed in the effluent with Cu–ZnO/d-HT. The ZnO/d-HT catalyst has no activity. On the other hand, Cu/d-HT does not produce FAL or C_{2+} although it shows somewhat higher MeOH conversion than Cu–ZnO/d-HT. The different product selectivity between Cu–ZnO/d-HT and Cu/d-HT suggests a synergistic effect between Cu and ZnO for the formation of C_{2+} when supported on d-HT. Furthermore, the basicity of d-HT obviously plays a role in the formation of C_{2+} because neither $Cu–ZnO/Al_2O_3$ nor commercial Cu/ZnO catalyst produces C_{2+}. Therefore, the formation of C_{2+} oxygenates is tentatively attributed to the synergistic effect of Cu, ZnO and the basicity of d-HT. The synergistic effect between Cu and ZnO has been known to promote the methanol synthesis (MS) from syngas [42–45]. The basicity enhancement, usually by alkali-modification, of MS catalysts can lead to the formation of higher alcohols from syngas [27, 28, 46]. However, only a K–Zn–Cr-oxide catalyst [20] was reported previously to produce C_{2+} oxygenates from methanol at a selectivity significantly lower than that of Cu–ZnO/d-HT catalyst in this study.

The formation of C_{2+} at 523 and 573 K is illustrated in Fig. 1 as steady-state production. Table 3 lists the analysis of C_{2+} products from the condensed liquid collected during the reaction test shown in Fig. 1. The C_{2+} products include: ketones, aldehydes, esters, ethers, and alcohols from C_2 to C_9. Alcohols, ketones and aldehydes comprise almost 79% of the higher oxygenates products whereas ethers and esters take up only 18%, and the others are about 3%. The yield to C_{2+} oxygenates, excluding esters and ethers, is around

Table 1 The target composition, BET surface area, Cu surface area and Cu particle size of catalysts in this study

Catalyst	$Cu/ZnO/MgO/Al_2O_3$ (wt%)	BET (m^2/g)	S^c_{Cu} (m^2/gCu)	Cu_s/Cu (%)	P.S.[d] (nm)
Al_2O_3	–/–/–/100	157[b]	–	–	–
Cu/Al_2O_3	4/–/–/96	133	400	62	1.7
$Cu–MgO/Al_2O_3$	4/–/5/91	115	387	60	1.7
$Cu–ZnO/Al_2O_3$	4/4/–/92	130	420	64	1.6
HT	–/–/51/49	228[b]	–	–	–
Cu/d-HT	4/–/48/48	191	272	42	2.4
ZnO/d-HT	–/5/48/47	179	–	–	–
Cu–ZnO/d-HT	4/4/46/46	182	190	29	3.5
$Cu/ZnO/Al_2O_3$[a]	30/60/–/10	128	61	9	11

[a] Commercial methanol synthesis catalyst

[b] BET area listed on Condea catalogue

[c] Specific surface area of Cu determined by N_2O decomposition method

[d] Particle size, calculated by P.S. (nm) = 6000/ ($S_{Cu}\cdot\rho_{Cu}$) [33, 34], in which ρ_{Cu} is the density of copper (8.92 g/cm^3)

Table 2 Methanol conversion and product selectivity of the methanol reaction over different catalysts at 523 K and WHSV = 0.2 h^{-1}

Cu-catalyst	Conversion (%)	S_{CO} (%)	S_{CO_2} (%)	S_{MF} (%)	S_{FAL} (%)	S_{DME} (%)	S_{C2+} (%)
Cu/Al_2O_3	87	50	25	–	–	25	–
$Cu–MgO/Al_2O_3$	82	38	30	–	–	32	–
$Cu–ZnO/Al_2O_3$	99	54	23	–	–	23	–
Cu/d-HT	72	84	8	–	–	8	–
ZnO/d-HT	0	–	–	–	–	–	–
Cu–ZnO/d-HT	65	47	18	0.2	13	2	20
$Cu/ZnO/Al_2O_3$	100	99	1	0.3	–	–	–

S_{CO}: selectivity to CO; MF: methyl formate; FAL: formaldehyde; DME: dimethyl ether; C_{2+}: long-carbon-chain compounds

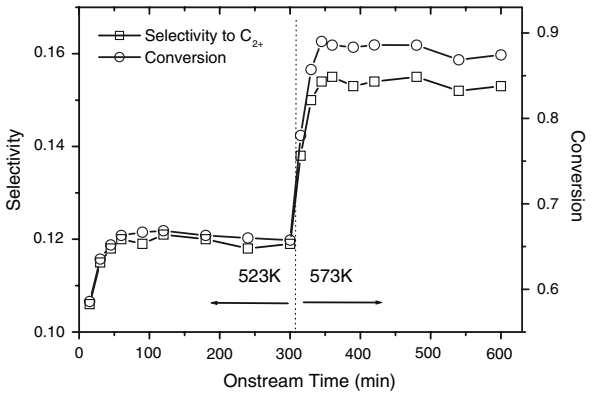


Fig. 1 The yield of long-chain oxygenates during the methanol conversion over Cu–ZnO/d-HT at 523 and 573 K with WHSV = 0.2 h^{-1}, P_{MeOH} = 26.7 kPa

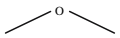
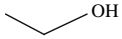
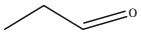
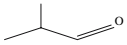
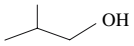
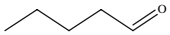
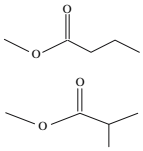
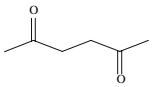
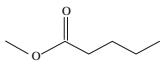
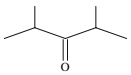
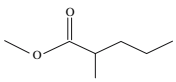
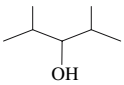
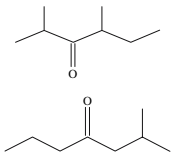
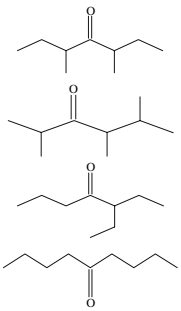
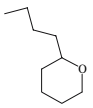
8–10% based on methanol consumption over Cu–ZnO/d-HT at a weight hourly space velocity of 0.2 h^{-1}, 523–573 K, and atmospheric pressure. This is about 2–3 orders higher than the previously reported synthesis of C_{2+} oxygenates from methanol over K–Zn–Cr-oxide at 573 K and atmospheric pressure [20]. Although the formed oxygenates spread over a wide variety and further improvement in product selectivity is needed, this Cu–ZnO/d-HT catalyst demonstrates an unprecedented high selectivity to C_{2+} oxygenates from methanol and potentials for future industrial applications.

The influence of reaction temperature on the product selectivity of Cu–ZnO/d-HT is shown in Fig. 2. The main product is CO over the range of reaction temperature tested. In order to verify if the C_{2+} formation is from CO and H_2 (resulted from MeOH decomposition), we examined the reaction with CO+H_2 as the feed instead of methanol over Cu–ZnO/d-HT catalyst. No C_{2+} product was observed and the CO conversion was low at 523–673 K. Furthermore, products from HAS typically contain MeOH, linear and branch higher alcohols; whereas, C_{2+} products in this study contain mainly aldehydes and ketones which seems like products obtain from aldol condensation of mixed alcohols over $Cu/MgCeO_x$ [36]. This indicates that the formation of C_{2+} in this study cannot be considered as owing to MeOH decomposition followed by a HAS route. It is more likely to occur via the condensation of certain intermediate(s) during MeOH decomposition. Methanol adsorbs on Cu catalysts as methoxy [47–50] whose dehydrogenation leads to formaldehyde (FAL). Sequential dehydrogenation of FAL to formyl then to CO is known to occur over Cu/ZnO [35]. The steady-state selectivity to higher oxygenates shows a maximum at around 600 K in Fig. 2, and similar trend is found in the selectivity to FAL and CO_2. This maximum selectivity corresponds to the minimum in CO selectivity, suggesting that the formation of CO, CO_2, FAL and C_{2+} compete for the same surface intermediate. As CO is formed from surface formyl, this implies that formyl and/or its precursor intermediate (FAL), is involved in the formation of C_{2+}.

The effect of methanol space velocity on the product selectivity of Cu–ZnO/d-HT at 523 K is shown in Fig. 3. The selectivity to CO decreases with increase of methanol conversion. At higher methanol conversion, the sequential dehydrogenation of methoxy is expected to shift from adsorbed FAL to more formyl and more CO should have formed. The lower CO selectivity at higher MeOH conversion implies that formyl participates in a reaction route competing with its decomposition into CO. Fig. 3 also indicates that the selectivity to formaldehyde has a maximum which seems to correspond to the rise in C_{2+} selectivity. This trend seems coincide with a serial reaction scheme from methanol to FAL then to C_{2+}, implying that formaldehyde may be the key C_1 intermediate to the initial C–C bond formation of C_{2+}. Results from the temperature effect and the space velocity effect (Figs. 2 and 3) suggest that formyl and FAL are involved in the C–C formation. This seems consistent with previous proposition [29, 30, 32] that the initial C–C bond of C_{2+} in HAS is formed by a reaction between formyl and adsorbed FAL.

At present, the mechanism from methanol to higher oxygenate cannot be confirmed, but it seems to involve methanol dehydrogenation to formaldehyde and formyl

Table 3 Product distribution of collected condensate from the methanol reaction on Cu-ZnO/d-HT at 523 and 573 K with WHSV = 0.2 h^{-1} and P_{MeOH} = 26.7 kPa

C_n	Mole %	Aldehyde or Ketone (%)	Ester (%)	Ether (%)	Alcohol (%)
C_2	12.1	2.1 	2.2 	7.4 	0.4 
C_3	12.9	12.9 	–	–	–
C_4	3.7	3.0 	–	–	0.7 
C_5	5.7	3.3 	0.6 	1.8 	–
C_6	6.1	3.0 	1.1 	2.0 	–
C_7	15.9	12.5 	0.5 	1.7 	1.2 
C_8	14.4	14.4 	–	–	–
C_9	26.1	25.1 	–	1.0 	–
Total		76.3	4.4	13.9	2.3

and a subsequent condensation. Furthermore, the active morphology in Cu–ZnO/d-HT responsible for the C_{2+} formation is not known and is under investigation. However, basicity is required for the proposed chain growth via coupling of MeOH-derived C_1 intermediates to form the initial C–C bond (ethanol) as stated for HAS [22–25, 27, 28, 34, 35, 46], for the aldol condensation of methanol with higher alcohols [34–37], and for Guerbet reaction to produce higher alcohols from smaller alcohols [51, 52]. It is very likely that the basicity from d-HT is involved in C_{2+}

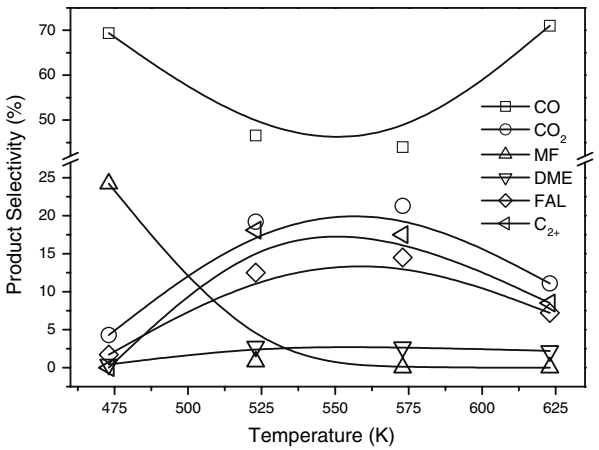


Fig. 2 Effect of reaction temperature on the methanol conversion over Cu–ZnO/d-HT with WHSV = 0.2 h^{-1}, P_{MeOH} = 26.7 kPa

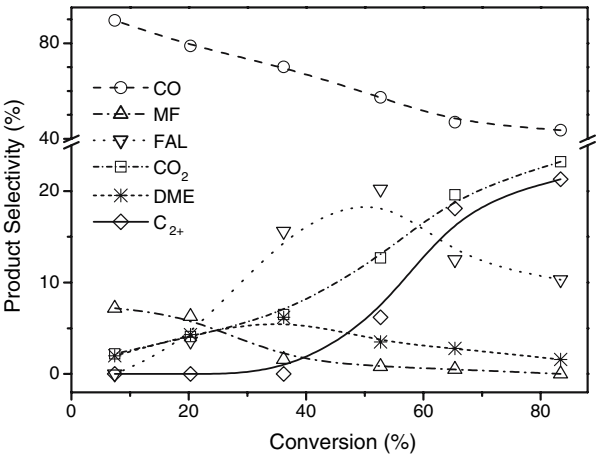


Fig. 3 Effect of space velocity on the methanol conversion over Cu–ZnO/d-HT at 523 K with WHSV = 0.1–15 h^{-1}, P_{MeOH} = 26.7 kPa

formation in this study, but only basicity is insufficient for the formation of C_{2+} oxygenates as indicated by the absence of C_{2+} products over Cu/d-HT or over Cu–MgO/Al_2O_3. On the other hand, Cu is the main active species as neither d-HT nor ZnO/d-HT showed any activity under the conditions of this study. This suggests that the formation of C_{2+} oxygenates can be attributed to a combination of Cu–ZnO and basicity from d-HT.

This study illustrates the possibility of a methanol-to-oxygenate process using the Cu–ZnO/d-HT catalyst at mild conditions. Catalysts derived from hydrotalcites such as Cu–Zn–Al [53] or Cu–Mg–Al [54] have been tested for the production of hydrogen from methanol or the catalytic combustion of methane, but no formation of long-chain compounds was reported. The formation of higher alcohols from lower alcohols is possible to occur through aldol condensation and through Guerbet reaction. Liquid-phase reactions of these two reactions are known to be base-catalyzed and catalysts derived from HT are reported [55, 56]. Gas-phase Guerbet reaction to prepare isobutanol from methanol and propanol using HT-derived catalysts are also reported [51, 52]. However, it is noteworthy that the formation of higher oxygenates from MeOH alone has not been reported via aldol-condensation or via Guerbet reaction. This is because methanol contains no α-hydrogen. Consequently, the methanol-to-higher-oxygenates reported in this study by using Cu–ZnO/d-HT catalyst illustrates a new possibility to make higher oxygenates.

4 Conclusion

This study illustrates a methanol-to-oxygenate process over Cu–ZnO/d-HT catalyst at mild conditions. The Cu–ZnO/d-HT catalyst can form C_{2+} oxygenates with a yield of 8–10% at a weight hourly space velocity of 0.2 h^{-1}, 523–573 K, and atmospheric pressure. The produced oxygenates include alcohols, ketones, aldehydes, esters, and ethers from C_2 to C_9 in which alcohols, ketones and aldehydes comprising 79% of the total oxygenates under the conditions of this study. Reaction studies on the effect of temperature and space velocity suggest that the first C–C bond formation from formyl and formaldehyde can explain the formation of long-chain oxygenates. The synergistic effect of Cu, ZnO and the basicity of d-HT is likely responsible for the synthesis of C_{2+} oxygenates from methanol.

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