Effect of co-feed species on methanol conversion over Cu/ZnO/Al$_2$O$_3$ and its possible mechanism

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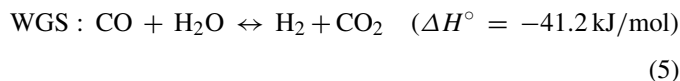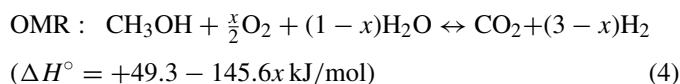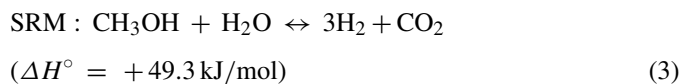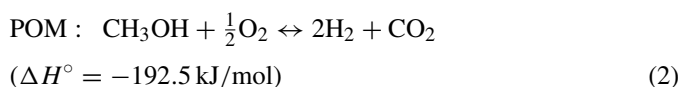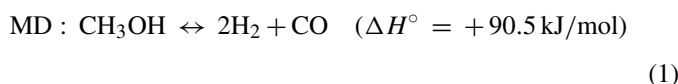Available online 25 July 2007

Abstract

Methanol (MeOH) conversion over a commercial Cu/ZnO/Al$_2$O$_3$ catalyst was investigated with different co-feed gas, namely, He, H$_2$, H$_2$O or O$_2$ from 423 to 573 K. In-situ XRD results indicate that oxidic Cu was mostly reduced during the MeOH conversion reactions, except in the presence of O$_2$, when the Cu state seems to depend on the pretreatment. The steady-state activity follows: MeOH + O$_2$ > MeOH > MeOH + H$_2$ > MeOH + H$_2$O. In the presence of H$_2$, a sequential H-abstraction of MeOH is indicated by the fact that formaldehyde (FAL) was produced at low MeOH conversion and CO dominated at high conversion. In the absence of H$_2$, no FAL was produced while CO dominated and some methyl formate (MF) was observed. Oxygen and water in the feed promoted CO$_2$ formation and suppressed the formation of CO and MF. A reaction scheme involving mainly H-abstraction and O-addition steps is proposed.
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Keywords: Methanol; Cu/ZnO/Al$_2$O$_3$; Steady-state; Selectivity; In-situ XRD

1. Introduction

Using methanol as the feed stock to produce hydrogen has received great attention due to an anticipated hydrogen energy era [1]. Hydrogen can be used as a clean energy source for fuel in combustion engines or to generate electricity with fuel cells. The reaction pathways from MeOH to H$_2$ are typically classified as: (1) methanol decomposition (MD), (2) partial oxidation of methanol (POM), (3) steam reforming of methanol (SRM), and (4) oxidative methanol reforming (OMR) which is also called the autothermal reaction. The OMR pathway (4) is a combination of POM (2) and SRM (3) while the MD (1) plus a water gas shift (WGS) pathway (5) constitute the SRM (3).

$$\text{MD}: \text{CH}_3\text{OH} \leftrightarrow 2\text{H}_2 + \text{CO} \quad (\Delta H^\circ = +90.5\,\text{kJ/mol}) \tag{1}$$

$$\text{POM}: \text{CH}_3\text{OH} + \tfrac{1}{2}\text{O}_2 \leftrightarrow 2\text{H}_2 + \text{CO}_2$$
$$(\Delta H^\circ = -192.5\,\text{kJ/mol}) \tag{2}$$

$$\text{SRM}: \text{CH}_3\text{OH} + \text{H}_2\text{O} \leftrightarrow 3\text{H}_2 + \text{CO}_2$$
$$(\Delta H^\circ = +49.3\,\text{kJ/mol}) \tag{3}$$

$$\text{OMR}: \text{CH}_3\text{OH} + \tfrac{x}{2}\text{O}_2 + (1-x)\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + (3-x)\text{H}_2$$
$$(\Delta H^\circ = +49.3 - 145.6x\,\text{kJ/mol}) \tag{4}$$

$$\text{WGS}: \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2 \quad (\Delta H^\circ = -41.2\,\text{kJ/mol}) \tag{5}$$

Although these MeOH-to-H$_2$ reactions have been examined in many studies with many different techniques [2–15], the mechanism is still not well understood. Even which reaction pathway among (1)–(5) is involved seems ambiguous. For example, Peppley et al. proposed that three pathways, i.e., MD, SRM, and WGS must be included in their kinetic analysis of the SRM reaction [5,6]. This may be because these reaction pathways (1)–(5) are oversimplified in describing the MeOH conversion mechanism. A comprehensive mechanism could be beneficial for improving the efficiency of H$_2$ generation. Pepply et al. [5,6] proposed a Langmuir-Hinshelwood mechanism and the rate equation was

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derived to fit their data measured in transient experiments. Transient reaction data may be sensitive to experimental conditions, and their results may not be applicable to steady-state conditions. Differences between transient and steady-state performance can be found, for example, in Navarro et al. [14]. They showed that initially, a calcined CuO/ZnO had a lower methanol conversion and a higher CO_2 selectivity than a reduced Cu/ZnO, but that the consecutive second and later temperature-programmed reaction became almost identical as the reduced Cu/ZnO. It clearly shows that transient activity can be dependent on the initial state, i.e., the pretreatment of the catalyst. The steady-state performance data would allow for the discovery of better applications and provide a better insight to the reaction mechanism. Thus, this study is devoted to the steady-state reaction evaluation.

The Cu/ZnO/Al_2O_3 catalyst has long been used to catalyze the methanol synthesis (MS) reaction and was also found to be applicable to the MeOH-to-H_2 conversions, especially MD (1) [1,3]. The MD (1) is the reverse reaction of MS. This implies the possible existence of a microreversible reaction scheme. Furthermore, the difference in the reaction pathways (1)–(4) can be considered to be due to the presence of different co-feed species. If a microreversible reaction scheme exists, the co-feed species is expected to participate in surface reaction steps and consequently alter the overall reaction performance. This possibility is supported by the fact that the same methoxy adspecies is found present in (1)–(4) [2,4,6–10]. Few earlier studies tried to compare the effect of co-feed species from this approach. Most analyses were focused on the effect of concentration of oxygen and/or water, i.e., reactions (2)–(4), in order to increase hydrogen production and to suppress CO generation [2,6–10]. From them, it was shown that one role that a co-feed species, e.g., O_2 or H_2O, plays is to provide surface oxygen for converting CO into CO_2. Since the oxygen on Cu can be removed by passing H_2, it would be interesting to include H_2 in the feed to quench the role of surface oxygen. Consequently, this study compares the effect of co-feed species, namely, H_2, H_2O, and O_2, on the MeOH conversion over a commercial Cu/ZnO/Al_2O_3 catalyst. A reaction scheme for methanol conversions is proposed accordingly.

2. Experimental

2.1. Sample preparation

A commercial Cu/ZnO/Al_2O_3 catalyst (Nissan Girdler G66B; CuO: 30, ZnO: 60, Al_2O_3: 10 wt%) was used throughout this study. The catalyst was grounded and particles of 80–120 mesh were used. The measured BET surface area was 65.3 m^2/g and no other impurity was detected in an EDX analysis. The catalyst was calcined in O_2 at 573 K for 1 h (the calcined CuO/ZnO) and then reduced in-line with H_2 at 473 K for 1hr (the reduced Cu/ZnO) before test. The estimated particle size of CuO in the calcined catalyst and that of Cu^0 in the reduced catalyst was 12.3 and 8.8 nm, respectively, based on the XRD peak width analysis.

2.2. Methanol reactions

The methanol reaction was performed at 423–573 K and atmospheric pressure in a fixed-bed reactor system with online GC (Shimadzu 8A, with TCD). A heated Teflon line was used to connect the effluent from the pyrex reactor to GC in order to prevent condensation and side reactions. The U-tube reactor has an inner diameter of 6.2 mm in which catalyst bed is supported by quartz wool and a K-type thermocouple is attached next to catalyst bed. Typically, 0.3 g of catalyst is used and the catalyst bed height is around 4 mm which is positioned in the middle point of 25-cm-long heating zone. We checked the temperature uniformity across the bed and thermal equilibration is achieved and confirmed by the observation of steady state performance at isothermal reaction tests. A four-way valve was used to connect the reactor to the system such that the feed gas composition could be checked and the material balance of the reactor effluent analyzed. The catalyst was pretreated in-line before reaction. The MeOH (Merck, 99.9%, soaking with dehydrated molecular sieve) was fed with a syringe pump into the preheated fore line and was carried by He to the reactor at a WHSV (weight hourly space velocity, g MeOH/g catalyst/h) from 0.11 to 15 h^{-1}. The reaction used a MeOH partial pressure of 26.7 kPa (200 Torr), with or without co-feed species such as H_2, H_2O, or O_2 (balanced with He). The molar ratios of H_2, H_2O, and O_2 to MeOH were 2, 0.3, and 0.3, respectively. All He, H_2 and O_2 were of 99.995% purity. Both He and H_2 were flown through drying columns and Oxytrap columns before entering the system, while O_2 was flown through only a drying column. When the temperature effect was studied, MeOH was fed only at constant-temperature segments during a stepwise temperature-ramping sequence, in which steady-state conversion and product selectivity were observed typically after 30 min onstream. The reported data are averaged from data of onstream time from 30 to 60 min at each temperature. Additionally, the MeOH reaction maintaining at 473 K was also examined while switching co-feed species. In this case, the pretreated Cu/ZnO catalyst was exposed to a feed condition at 473 K until the steady state was attained, then purged with He for 15 min and a new feed was introduced.

2.3. In-situ XRD analysis

The XRD analysis was performed using a Cu Kα radiation with a commercial instrument (Shimadzu XRD-6000). Typically, the spectrum was taken at 298 K and a scan rate of 1 deg/min covering a 2θ range of 25–75°. An XRD cell (Anton Paar, TTK-450) was used to carry out in-situ analysis during the MeOH reaction at 473 K, in which the scan was taken every 5 min at 2 deg/min for 2θ of 37–45° in order to cover Cu(1 1 1), Cu_2O(2 0 0), and CuO(2 0 2) signals at 43.3, 42.3, and 38.8°, respectively.

2.4. Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) study

Infrared spectra were collected by using a commercial instrument (Nicolet Magna-IR 550) equipped with a MCT detector

and a DRIFTS accessory (Thermo Spectra-Tech). The spectrum was collected at a resolution of $4\,cm^{-1}$ and was averaged from 64 scans. The reference spectra were taken at the reaction temperature under He flow after the sample was pretreated in-line. Methanol was carried into the DRIFTS system by flowing the feed gas through a bubbler containing dehydrated MeOH. The temperature of the bubbler was controlled by a thermostat. After the MeOH reaction reached steady-state, the gas phase was purged with He at the reaction temperature for 15 min. Thereafter, a spectrum was collected.

3. Results

3.1. Methanol conversion with different co-feed species

MeOH reaction was examined at 473 K with different co-feed species over the calcined CuO/ZnO, in order to understand how the steady state MeOH conversion is affected by co-feed species. Fig. 1 shows the MeOH conversion and product yields as a function of cumulated on-stream time. Initially, water was found but it disappeared after the steady state was attained. At steady state under MeOH + He, methyl formate (MF) is the minor product while the dominant products are CO and H_2 (not shown). No significant deactivation was found for 5 h on-stream.

When H_2O was introduced in the feed at $H_2O/MeOH = 0.3$, the MeOH conversion dropped and CO_2 was produced exclusively. No CO or MF was found after a new steady state was reached. The molar ratio of H_2O consumption to that of MeOH was very close to 1, which is the stoichiometric ratio in SRM (3). When H_2O was removed from the feed, the reaction switched back to the steady state under MeOH + He.

Thereafter, O_2 was fed at $O_2/MeOH = 0.3$. A new steady state was established at more than two times the steady-state conversion under MeOH + He. Again, CO_2 was the dominant product and H_2O became obvious in the effluent. Small amounts of CO

and formic acid (FA) were found in the effluent. After stopping O_2, the reaction performance once again switched back to the steady state under MeOH + He.

Fig. 1 demonstrates that the steady-state MeOH conversion over Cu/ZnO catalyst is determined by co-feed species and that the steady-state performance can be repeatedly attained. This suggests the presence of a reversible MeOH reaction scheme in which co-feed species can participate to change the product formation. The product CO_2 was favored over CO in the presence of H_2O or O_2 and also at the initial transient period in Fig. 1. This indicates that O-containing species like H_2O, O_2, and lattice oxygen can contribute oxygen to convert CO to CO_2. The involvement of lattice oxygen in MeOH conversions is consistent with (i) the isotope study of the CO_2 formation from O-labeled $Cu/ZnO/Al_2O_3$ catalyst by Vanderborgh et al. [16], (ii) the proposed in-situ reduction of Cu/ZnO during SRM by Choi and Stenger [7] based on the weight change of the catalyst before and after reaction, and (iii) the temperature-programmed methanol oxidation over Cu/ZnO reported by Navarro et al. [14].

3.2. In-situ XRD analysis

In-situ XRD tests were used to examine the Cu state of Cu/ZnO under steady-state reactions at 473 K with different co-feed species. Fig. 2 shows the evolution of the signal intensity of Cu(1 1 1), $Cu_2O(2 0 0)$ and CuO(2 0 2) starting with calcined CuO/ZnO in a reaction sequence of MeOH + O_2, MeOH + H_2O, MeOH, and MeOH + H_2 at 473 K. Fig. 3 shows the evolution of these signals starting with reduced Cu/ZnO in a sequence of MeOH + H_2, MeOH, MeOH + H_2O, and MeOH + O_2 at 473 K. No change in the ZnO diffraction signals was observed throughout these in-situ XRD tests. The calcined catalyst in Fig. 2 maintained mainly as CuO under MeOH + O_2 at 473 K, though some Cu_2O structure developed. The subsequent MeOH + H_2O
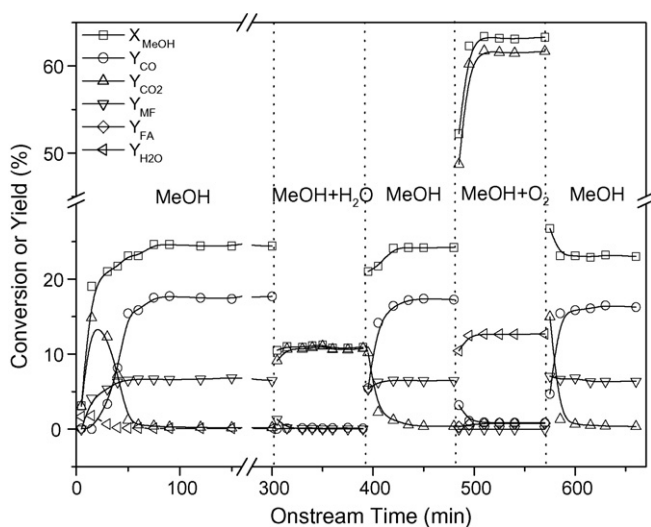

Fig. 1. The effects of co-feed gas on the MeOH conversion over the calcined Cu/ZnO, at WHSV = $2.1\,h^{-1}$, $P_{MeOH} = 26.7$ kPa, and 473 K. The reactant H_2O is not plotted during the $H_2O/MeOH$ feed (at 0.3 molar ratio), whereas the product H_2O is shown during the $O_2/MeOH$ feed (at 0.3 molar ratio).
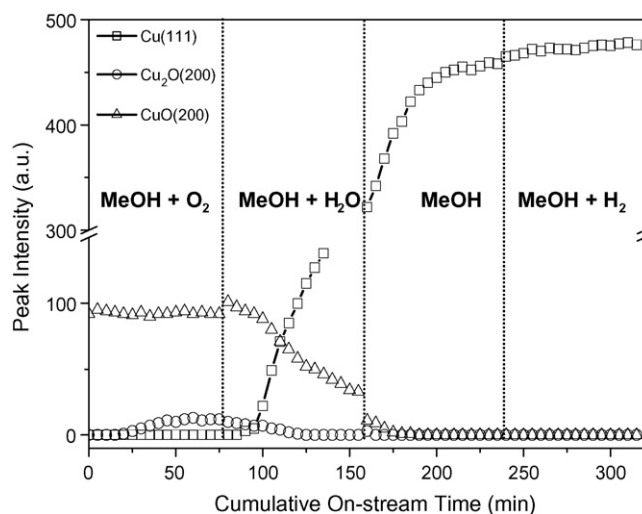

Fig. 2. The XRD peak intensities of Cu(1 1 1), $Cu_2O(2 0 0)$, and CuO(2 0 0) during a series of MeOH reactions at 473 K over the calcined CuO/ZnO. The catalyst was subjected to He purging when switching reaction conditions. All peaks were recorded at 473K within an in-situ XRD cell.
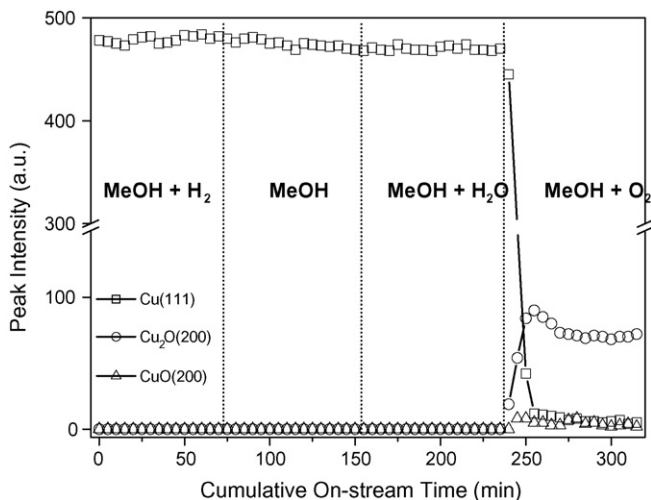
Fig. 3. The XRD peak intensities of Cu(1 1 1), $Cu_2O(2\,0\,0)$, and CuO(2 0 0) during a series of MeOH reactions at 473 K over the reduced Cu/ZnO. The catalyst was subjected to He purging when switching reaction conditions. All peaks were recorded at 473K within an in-situ XRD cell.

reaction progressively reduced both CuO and Cu_2O and the Cu^0 peak intensity increased correspondingly. The intensity of the Cu^0 peak became stronger in the following MeOH and MeOH + H_2 reactions while CuO and Cu_2O disappeared completely. The finial intensity of the Cu^0 peak is very close to that of the in-line reduced Cu/ZnO shown initially in Fig. 3. On the other hand, the reduced Cu/ZnO in Fig. 3 retained the Cu^0 state during MeOH + H_2, MeOH and MeOH + H_2O reactions at 473K, though a slight decrease in Cu^0 diffraction intensity was indicated during MeOH and MeOH + H_2O sequences. The introduction of O_2 at O_2/MeOH = 0.3 resulted in a sharp decrease in the Cu^0 signal with a concomitant increase, more in Cu_2O and less in the CuO diffraction signal.

Figs. 2 and 3 indicate that Cu tends to be at reduced state under steady-state reaction conditions at 473 K, except when O_2 is included in the feed. The reducing power of reaction conditions follows: MeOH + H_2 ≥ MeOH > MeOH + H_2O > MeOH + O_2. The Cu state under MeOH + O_2 seems to depend on the initial state and the test procedure. The MeOH + H_2O reaction, though producing mainly CO_2, shows significant reducing power. Although the in-situ XRD analysis is insufficient to explain surface morphology, it clearly shows that Cu has a high tendency to be reduced during MeOH conversion at 473 K. The exchange of surface oxygen and lattice oxygen can occur during the transient period of MeOH reaction and while in the presence of O_2.

Both the involvement of lattice oxygen and the reduction of oxidic Cu observed in Figs. 2 and 3 implies that Cu^0 is the active site at steady-state reaction conditions. Similar proposition of Cu^0 as the active site can be found in MD (1) [17], in SRM (3) [18,19], and in POM (2) [20] over Cu catalysts. Günter et al. [19] showed that CuO can be transformed to Cu metal under MeOH + H_2O at 523K. Reitz et al. [10] reported that Cu^{2+} was the dominant species of Cu/ZnO in OMR (4) at low oxygen conversion at 470–533 K but Cu^{2+} was reduced to Cu metal at high oxygen conversion.
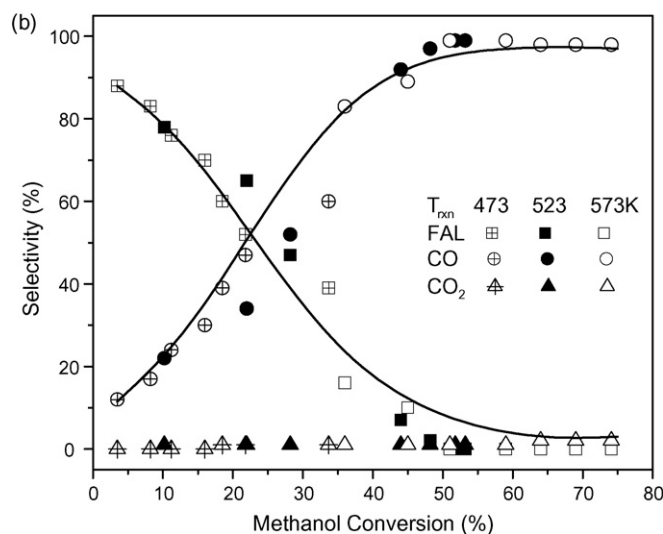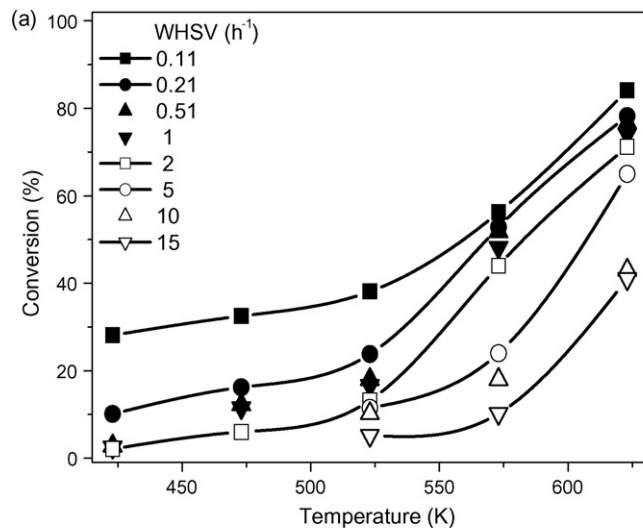

Fig. 4. The effect of space velocity on (a) the conversion and (b) the product selectivity of the MeOH + H_2 reaction over the completely reduced Cu/ZnO/Al_2O_3, at P_{MeOH} = 26.7 kPa and H_2/MeOH = 2.

3.3. Effect of space velocity on MeOH + H_2 reaction

Since the MeOH + H_2 reaction shows the highest reducing power, it is expected that the role of surface oxygen in MeOH conversion would be suppressed consequently. The effect of MeOH space velocity at H_2/MeOH = 2/1 over the reduced Cu/ZnO was examined and is shown in Fig. 4. Only CO and formaldehyde (FAL) were found as products. No condensation product (e.g., MF) or more oxidized product (e.g., CO_2 or FA) was found. Such a reaction pathway without a condensation product (MF formation) had not been observed over supported Cu catalysts before, but it is typical over Group VIII metal catalysts [21,22]. The selectivity-conversion diagram shows that FAL is favored at lower MeOH conversions and CO is favored at higher conversions. A serial reaction scheme is implied. The decrease in FAL selectivity was accompanied by an increase in CO selectivity. The FAL product can be expected from the H-abstraction of methoxy, which is the adspecies of MeOH
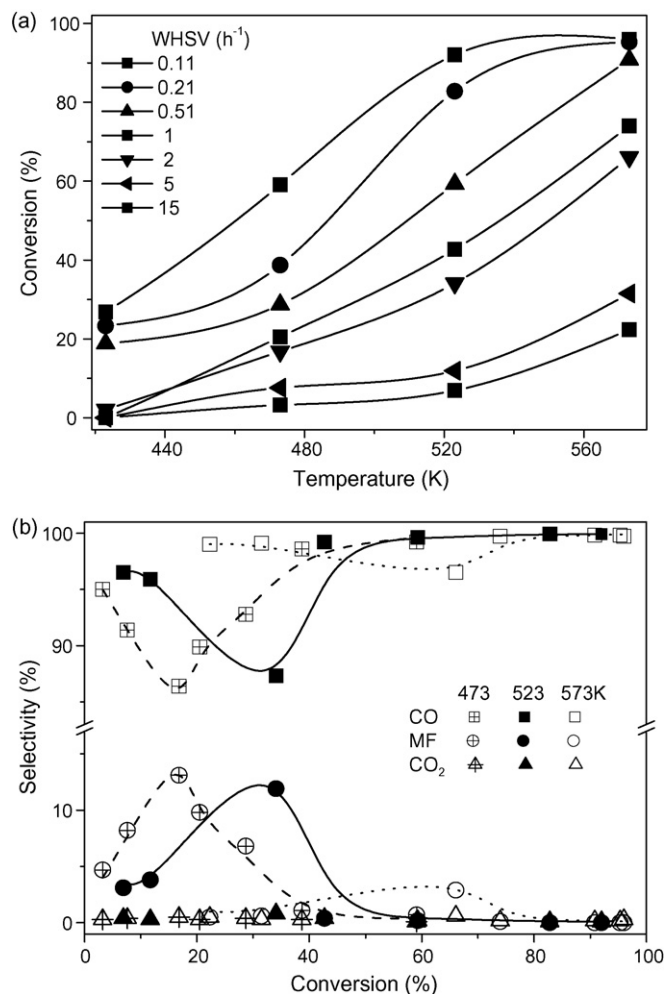
Fig. 5. The effect of space velocity effect on (a) the conversion and (b) the product selectivity of the MeOH reaction over the completely reduced $Cu/ZnO/Al_2O_3$, at $P_{MeOH} = 26.7$ kPa.
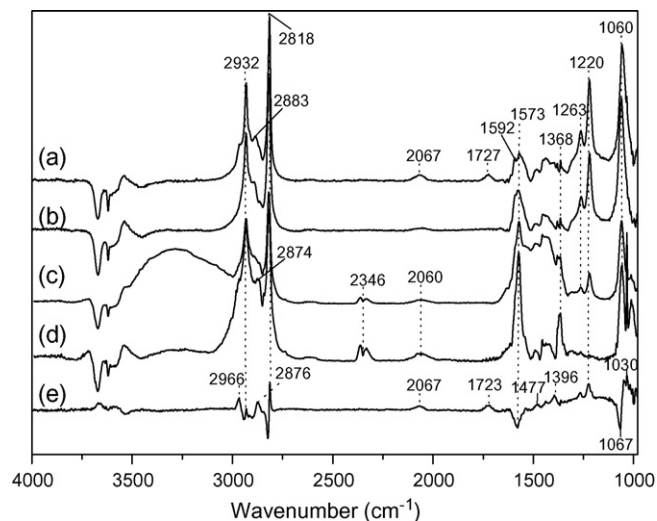

Fig. 6. Infrared spectra collected during exposure to a stream of different co-feed molecular with MeOH (26.7 kPa) in He at 30 cm³/min for 15 min at 473 K and at atmospheric pressure, and then after exposure to He to remove the signal of gas phase on (a) MeOH + H_2, (b) MeOH, (c) MeOH + H_2O, (d) MeOH + O_2 and (e) the spectrum of spectra (a) subtract from spectrum (b).

it decreases rapidly as the reaction temperature increases from 473 to 573 K.

3.5. In-situ DRIFTS analysis

In-situ DRIFTS is used to analyze the surface species over the reduced Cu/ZnO at 473 K during a sequence of MeOH + H_2,

on Cu [2,7,23–26]. A surface formyl from the H-abstraction of FAL can result in CO desorption, which is expected by the reverse of the H-assisted CO adsorption on Cu/ZnO [27]. The sequential H-abstraction of MeOH is indicated as $CH_3OH_{(g)} \rightarrow CH_3O_{(a)} \rightarrow CH_2O_{(a)} \rightarrow CHO_{(a)} \rightarrow CO_{(g)}$. Fig. 4b shows that the reaction temperature did not change the relative selectivity of FAL to CO. It implies that the activation energy is similar for the two H-abstraction steps leading to FAL and then to CO.

3.4. Effect of space velocity on MeOH + He reaction

Comparatively, the effect of MeOH space velocity under MeOH + He over the reduced Cu/ZnO catalyst is shown in Fig. 5. Products contain mainly CO and some MF; no FAL was found. Comparing data of the same MeOH WHSV in Fig. 5 and Fig. 6, the MeOH conversion was lowered by the presence of hydrogen. For example, the MeOH conversion in the absence of H_2 was about 1.5 times of that in the presence of H_2 at 573 K and WHSV = 2.1 h⁻¹. From the selectivity-conversion diagram, the MF selectivity shows a maximum versus MeOH conversion and

Table 1
The surface species assignment of methanol adsorbed on reduced Cu/ZnO after different feed gas and then helium purging at 473 K

MeOH + Co-feed gas	Feature wavenumber (cm⁻¹)	Assignment	Ref./comment
MeOH + H_2[a]	2931, 2817, 1060	Methoxy	[28–34]
	2883, 1592	m-F	[30,35,36]
	2067, 1727, 1220	FAL	[37–39]
MeOH[b]	2931, 2817, 1060	Methoxy	[28–34]
	1573, 1368	m-F	[30,35,36]
MeOH + H_2O[c]	2931, 2817, 1060	Methoxy	[28–34]
	2346	CO_2	–
	2060	CO	–
	1573, 1368	m-F	[30,35,36]
MeOH + O_2[d]	2931, 2817, 1060	Methoxy	[28–34]
	2874, 1368	b-F	[26]
	2346	CO_2	–
	2060	CO	–
	1573, 1368	m-F	[30,35,36]
(MeOH + H_2)–MeOH[e]	2817	Methoxy	[28–34]
	1573	m-F	[30,35,36], Negative signal
	2966, 2876, 2067, 1723, 1396, 1220, 1030	FAL	[37–39]

[a–e] i.e. Spectra of Fig. 6(a)–(e), m-F: monodentate formate; b-F: bidentate formate.

MeOH + He, MeOH + H_2O, and MeOH + O_2; Fig. 6 shows the spectrum taken at 473 K under He after each reaction. The assignments are summarized in Table 1. In the presence of H_2, surface methoxy, m-F (monodentate formate), and FAL species are found in Fig. 6a, in consistent with the reaction product analysis. It should be noted the $CHO_{(a)}$ (formyl) can be equivalent to m-F species if the adsorption site is O on the surface. When H_2 is removed from the feed, methoxy and m-F remains on the surface but the signals of FAL disappear. The difference spectrum in Fig. 6e shows a decrease in FAL signals and an increase in m-F signals. It suggests that the $CH_2O_{(a)} \rightarrow CHO_{(a)}$ is promoted when H_2 is removed from the feed, consistent with the reaction data. When H_2O is present in the feed, surface H_2O is indicated by bands around 3600–3100 and 1600–1300 cm^{-1}. The surface m-F signals become stronger, and CO_2 and CO signals appear. Finally, the signals of surface m-F, CO, and CO_2 all increased significantly when the MeOH conversion proceeded in the presence of oxygen.

4. Discussion

The effect of co-feed species on the steady-state MeOH reaction over Cu/ZnO is found to (i) change the MeOH conversion rate and (ii) change the product selectivity. The steady-state conversion can be attained repeatedly while switching back and forth between the co-feed species (Fig. 1). This indicates the presence of a microreversible MeOH reaction mechanism. The different product selectivity with different co-feed species (Figs. 1, 4 and 5) indicates that the surface reaction pathway is affected by co-feed species.

The presence of a sequential H-abstraction route is indicated during the MeOH + H_2 reaction in this study. Such a H-abstraction sequence of: $MeOH_{(g)} \rightarrow$ methoxy $\rightarrow$ FAL $\rightarrow$ formyl $\rightarrow CO_{(g)}$ was proposed by Espinosa et al. [40] but no evidence of the presence of FAL or formyl was provided. Many infrared studies suggested that formate is the key intermediate in MeOH-to-H_2 [2,4–6,9,41] or in MS [4,42,43]. Very little of the literature on methanol synthesis mentions the presence of FAL or formyl [44–46]. We observed FAL in the presence of H_2 as shown in DRIFTS (Fig. 6) and in reaction study. Surface formyl can be difficult to distinguish from surface formate, as mentioned earlier, if the formyl is adsorbed on an O-site on the surface.

In addition to H-abstraction steps, O-addition steps are present, as CO_2 is selectively produced in the presence of H_2O or O_2. Ovesen et al. [47,48] have proposed a so-called microkinetic model in which water can dissociatively adsorb on Cu to form surface hydroxyl OH_{ad} and O_{ad}. Reduced Cu is known to chemisorb O_2 [49–51]. In the initial unsteady-state period of Fig. 1, CO_2 and H_2O were formed with excess O in the product stream relative to the feed which was revealed by an oxygen balance analysis. It suggests that lattice oxygen also participated in the O-addition step.

The surface reaction scheme for MeOH conversions over Cu/ZnO from the above discussion is summarized in Scheme 1, where the mechanistic steps are mainly H-abstraction and O-addition. MeOH adsorbs as surface methoxy on Cu [23,24,52], oxides [53,54], and Cu catalysts [2,7,21,22,25,26,52–54], regardless of the type of co-feed species, as revealed in Fig. 6 and in earlier studies. Wachs and Madix [23] showed that methoxy on O-covered Cu(1 1 0) decomposes to yield FAL. It supports the H-abstraction of methoxy. FAL adsorption is reported on clean Cu(1 1 0) [55], O-covered Cu(1 1 0) [55,56], and supported Cu catalysts [2,57]. The adsorbed FAL on clean Cu(1 1 0) can desorb as CO, whereas FAL on O-covered Cu(1 1 0) resulted in surface formate, which decomposes to form CO_2 [55]. Thus, surface FAL can proceed via either an H-abstraction or an O-addition step depending on the availability of surface oxygen. Both CO and MF were suppressed when CO_2 was formed, irrespective of whether the labile oxygen was from lattice oxygen, H_2O or O_2 (Fig. 1). The O-addition step is clearly the competitive route to CO and MF formation. An O-addition to surface FAL and surface formyl can result in formic acid [58,59] and surface formate [2,5,6,11], respectively. Fig. 1 shows the occurrence of formic acid in the presence of O_2, in agreement with an earlier report [14]. Formic acid can give off H to form surface formate [60] and surface formate decomposes to yield CO_2. [41,61] This suggests that surface formate can come from either formyl + O or FAL + O followed by a H-abstraction.

With H_2 in the feed, Fig. 4b indicates that FAL and CO are formed in serial steps having similar activation energy. Surface methoxy seems to be the more abundant species, as indicated by IR (Fig. 6). Without H_2, no FAL desorbs and CO is the main product. It implies that H_2 can suppress the FAL $\rightarrow$ formyl $\rightarrow$ CO route. The MeOH conversion is lower when in the presence of H_2. It is attributable to a lower methoxy
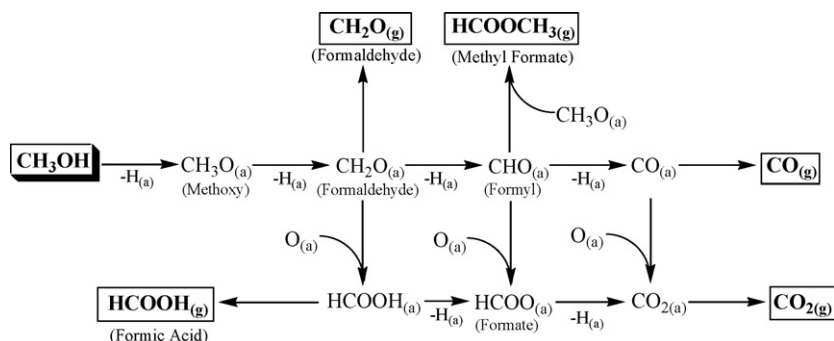
Scheme 1. The proposed reaction scheme of the MeOH conversions over Cu/ZnO (see text for details).

concentration in the presence of H_2, if the methoxy decomposition to FAL is assumed as the rate determining step (rds). The fact that no FAL is desorbed in the absence of H_2 implies that the H-abstraction of FAL is relatively enhanced. The rds would remain as the methoxy to FAL step. The more abundant surface species would thus contain methoxy and formyl, whose condensation can lead to MF formation as observed in Fig. 1.

Theoretical calculation indicates that the rds of POM (2) over Cu surfaces is still the methoxy to FAL step. [62] It seems that the same rds prevails in the MeOH conversions over Cu with different co-feed species. It is supported by an observed MeOH reaction order of 0.5 or lower in MD [63], SRM [64], and ORM [65] over Cu catalysts. The 0.5 order is attributable to the dissociative adsorption of MeOH. Following the hypothesis of the same rds, the surface coverage of methoxy could determine the overall MeOH conversion rate (activity) with different co-feed species. This serves as an explanation why the observed MeOH conversion is suppressed by H_2O but it is enhanced by O_2 as shown in Fig. 1. It is attributable to a lowered methoxy surface coverage due to H_2O competitive adsorption [8] but an enhanced methoxy surface coverage by oxygen [23,24,66]. Thus, Scheme 1 can be viewed as the possible microreversible mechanism for the MeOH conversions over Cu as it qualitatively explains all the observed reaction performances. However, Scheme 1 needs future extension to identify how surface species like H_{ad}, O_{ad}, OH_{ad} are involved.

The MeOH conversion reaction to produce H_2 has gained a lot of attention recently. For fuel cell applications, it requires low CO and high H_2 production at high MeOH conversion. Thus, the O-addition steps in Scheme 1 are desirable. Fig. 1 demonstrates that the lattice oxygen and O_2 in the feed tend to perform less-selective oxidation, as evidenced by the enhancement of both CO_2 and H_2O production. Water in the feed is more selective because H_2O was found to be consumed, leading to extra H_2 production. When considering the MeOH conversion, the presence of H_2O suppressed while O_2 enhanced the MeOH conversion compared to that from a feed of MeOH alone (Fig. 1). The optimal H_2 production thus seems to require a combination of H_2O and O_2 as co-feed species.

5. Conclusions

The steady-state MeOH reaction over $Cu/ZnO/Al_2O_3$ catalyst was attained with or without the presence of co-feed species such as O_2, H_2O, and H_2. The steady-state activity and product selectivity can be shifted back and forth by changing co-feed species. This indicates the presence of a microreversible reaction mechanism. Both the reaction study and in-situ XRD analyses show that the Cu/ZnO is more in the reduced state (Cu^0) during the MeOH + H_2, MeOH or MeOH + H_2O reactions; whereas oxidic Cu is present during the MeOH + O_2 reaction. Through the introduction of H_2, the MeOH reaction over Cu/ZnO is found to follow a stepwise H-abstraction to FAL and then to CO. The presence of surface FAL and formyl is indicated. That no MF was found in the presence of H_2 suggests that MF is not from surface FAL.

Without H_2, the steady-state MeOH reaction over reduced Cu/ZnO produced CO and some MF. That no FAL was found in product stream is assumed to mean that the H-abstraction of FAL to formyl and CO is relatively promoted. This would consequently make formyl and methoxy the more abundant surface species, whose condensation lead to MF formation. When surface oxygen is available from H_2O and O_2 in the feed or from lattice oxygen, O-addition to surface FAL and formyl can lead to formate, whose decomposition yields CO_2. This is confirmed by the steady-state MeOH reaction in the presence of H_2O or O_2 or starting the reaction with calcined CuO/ZnO.

A MeOH reaction scheme involving H-abstraction and O-addition steps is proposed, in which the rds is considered as the methoxy decomposition to FAL. The effect of co-feed species on the MeOH conversions over Cu catalysts involves affecting (i) the surface concentration of methoxy, which would affect the reaction rate, and (ii) the availability of surface oxygen, which would change the product selectivity. The steady-state reaction results observed in this study can be explained accordingly.

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