



In situ DRIFTS study on the methanol oxidation by lattice oxygen over Cu/ZnO catalyst

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ABSTRACT

Previous research shows that lattice oxygen of Cu catalyst participates in the methanol conversion. In this study, Cu/ZnO catalyst was pretreated to become fully oxidized, partially reduced, or completely reduced. In situ diffuse-reflectance infrared Fourier-transformed spectroscopy (DRIFTS) was used to analyze the methanol (MeOH) adsorption at 393 K and a following stepwise temperature-programmed desorption (sTPD). In addition to methoxy and formates appeared after MeOH adsorption, Cu/ZnO catalyst had formaldehyde but no CO₂ while the Cu was completely reduced. When the Cu was in the oxidized or partially reduced states, CO₂ formed and more formate appeared. Lattice oxygen participated in the MeOH conversion, and the reactivity was higher in the partially reduced Cu/ZnO than in the oxidized Cu/ZnO. This suggests that reduced Cu catalyzes the reaction between MeOH adspecies and lattice oxygen.

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1. Introduction

Copper catalysts, especially Cu/ZnO, are widely used in many traditional applications such as the water–gas shift reaction (WGS) [1,2], methanol synthesis (MS) [3–7], higher alcohol synthesis (HAS) [8–10], methanol decomposition (MD) [11–15], partial oxidation of methanol (POM) [16–18], and steam reforming of methanol (SRM) reaction [19–21]. Researchers have recently focused on the POM (MeOH + O₂), SRM (MeOH + H₂O), or oxidative methanol reforming (OMR, MeOH + O₂ + H₂O) reaction [17–23] in an effort to produce CO-free hydrogen for fuel cells. These reactions are very complex and sometimes interrelated. The best example appears in Peppley et al. [22,23], who pointed out that MD, SRM, and WGS reactions must all be included in the kinetic analysis of the SRM. The working state of Cu/ZnO during reactions remains unclear, and may change with different reaction conditions. For MD and SRM, Cu⁰ is generally accepted as the active state of the Cu/ZnO catalysts [12,19,24]. Reitz et al. [25] suggested that Cu²⁺ was the dominant species of Cu/ZnO in OMR at low oxygen conversion (470–533 K); however, Cu⁰ from the reduction of Cu²⁺ dominated at high oxygen conversion conditions and the pathway shifted to SRM. Alejo et al. [26] proposed that Cu⁰ is involved in the formation of CO₂ and H₂ in POM, Cu¹⁺ sites favor the formation of CO and H₂O, and Cu²⁺ is relatively inactive in OMR. These examples illustrate the controversy

regarding the states of the Cu catalysts during methanol conversion, and suggest that the Cu state varies under different conditions.

Using the MD reaction as a reference, we reported previously that co-feed species like H₂O and O₂ can change not only the MeOH conversion activity and selectivity, but also the Cu state [27]. We also examined differently reduced Cu/ZnO catalyst (the pretreatment effect) for the MD reaction [28]. The lattice oxygen in the incompletely reduced catalysts can take part in the reaction, leading to CO₂ formation. To gain more insight to this pretreatment effect, this study examined the surface species or intermediates after methanol adsorption on the differently pretreated Cu/ZnO catalysts by in situ diffuse-reflectance infrared Fourier-transformed spectroscopy (DRIFTS) analysis. Previous studies [29–31] show that absorbance band positions from methanol adsorption over Cu catalysts could change in reducing or oxidic environments. The C–H stretching bands of the methoxy adspecies on Cu/SiO₂ shifted from 2923 and 2816 cm⁻¹ to 2935 and 2823 cm⁻¹ after the reduced catalyst was re-oxidized [29]. Mudalige and Trenary [31] reported a red shift in the OCO vibration mode from 1340 to 1317 cm⁻¹ when the Cu(100) surface was precovered with O. These results indicate that the vibration modes of surface species can vary as the state of Cu changes. However, no researchers have tried to illustrate the effect of lattice oxygen on the evolution of MeOH adspecies as the temperature increases. This study reports the DRIFTS results from MeOH adsorption over Cu/ZnO catalysts at different extents of Cu reduction and discusses how the lattice oxygen may have participated in MeOH conversion.

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2. Experimental

2.1. Sample preparation

The experiments in this study involved a commercial Cu/ZnO catalyst (Nissan Girdler G66B; CuO: 30, ZnO: 60, Al₂O₃: 10 wt%). The catalyst was ground and particles of 80–120 mesh were used in this study. Reference samples include powders of metallic Cu (Cerac, 99.999%, ~100 mesh), Cu₂O (Cerac, 99%, ~200 mesh), Cu₂O (Merck, 99%), and ZnO (Fluka, 99%).

2.2. In situ DRIFTS study

Infrared spectra were collected using a Nicolet Magna-IR 550 with MCT detector and a diffuse reflectance FT-IR (DRIFT) accessory (Thermo Spectra-Tech). The spectra were collected at a resolution of 4 cm⁻¹ and an accumulation of 64 scans. The reference spectra were taken after the sample was pretreated and cooled to the experimental temperature under flowing helium. The H₂ and He gases used in this study were obtained from San-Fu Gas Co. Ltd. High purity (>99.99%) gases of H₂ and He were used after flowing through dryer and deoxygen columns. Methanol (Merck >99.9%, soaking with dehydrated molecular sieve) was carried into the system by a helium flow through a bubbler, whose temperature was controlled by a thermostat. Catalyst powders were packed in the sample holder of the in situ cell, subsequently calcined at 573 K for 1 h, and then reduced by H₂ at different temperatures for 30 min when needed. After feeding methanol at the desired adsorption temperature, methanol gas phase and reversibly adsorbed species were purged by helium until the spectra stabilized. A stepwise temperature-programmed desorption (sTPD) process was then carried out under He flow to 473 K, and spectra were collected at each predetermined temperature.

2.3. Temperature-programmed reduction (TPR)

Temperature-programmed reduction was performed at a heating rate of 5 K/min using 10% hydrogen in nitrogen and a TCD detector. Samples of Cu/ZnO were pretreated by calcination at 573 K for 1 h with/without a subsequent hydrogen reduction at selective temperature for 30 min, cooled down to room temperature, and then analyzed with TPR. The reduction degrees of the catalysts with different pretreatments were calculated according to the quantitative hydrogen consumption of TPR results. The effect of methanol adsorption and a following sTPD on the reduction degrees of the catalysts with different pretreatments were also examined. The pretreatment, methanol adsorption, and sTPD procedures prior to TPR analyses were kept exactly the same as those used in DRIFT analyses.

3. Results

3.1. Methanol adsorption on Cu, Cu₂O, CuO, and ZnO

To illustrate the interaction between MeOH and different Cu species, this study uses DRIFTS to determine MeOH adsorption on Cu, Cu₂O, CuO, ZnO, and differently pretreated Cu/ZnO catalysts. Fig. 1 shows the DRIFTS spectra of MeOH adsorption at 393 K for four reference compounds: Cu, Cu₂O, CuO, and ZnO. The Cu powders showed absorbances at 2935, 1064, and 1030 cm⁻¹, attributable to the C–H stretching, the C–O stretching, and the CH₃ rocking mode of methoxy (MeO), respectively [30,32–38]. In addition to MeO, Cu₂O powders contained absorbance attributable to mono-dentate formate (m-F) at 1584 ($\nu_{as}(\text{OCO})$) [30,39,40]. This implies that MeO interacted with surface oxygen to yield formate. Both CuO and ZnO showed stronger IR absorption than Cu and

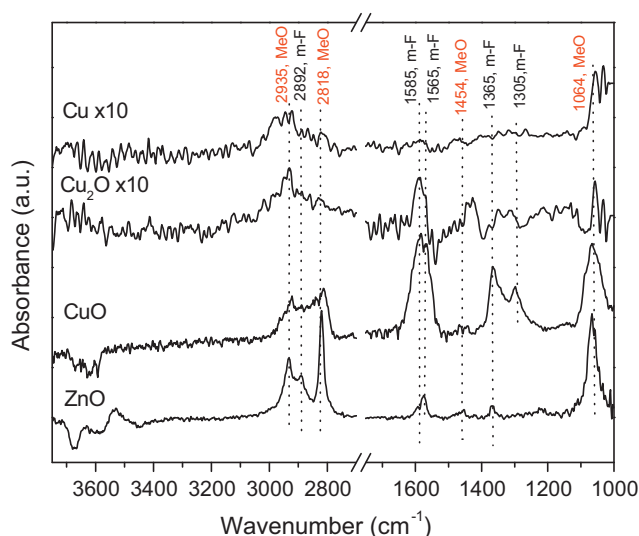


Fig. 1. DRIFTS spectra of MeOH adsorption over Cu, Cu₂O, CuO, and ZnO, after exposure to a stream of 26.7 kPa methanol in He at 30 cm³/min for 15 min at 393 K and at atmospheric pressure, and then purge with He to remove gas phase MeOH. MeO: methoxy, m-F: monodentate formate.

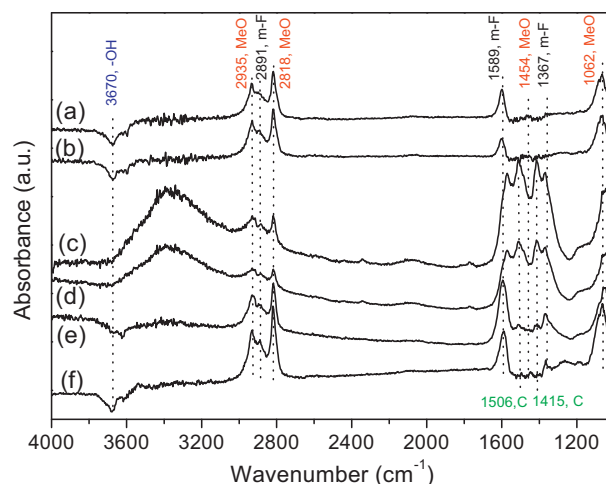


Fig. 2. DRIFTS spectra of the MeOH adsorption over the Cu/ZnO after (a) calcination at 573 K, and then reduction at (b) 423, (c) 450, (d) 463, (e) 473, and (f) 493 K, after exposure to a stream of 26.7 kPa methanol in He at 30 cm³/min for 15 min at 393 K and at atmospheric pressure, and then purge with He to remove gas phase MeOH. MeO: methoxy, m-F: monodentate formate, C: carbonate.

Cu₂O. This suggests a relatively lower MeOH uptake on the reduced Cu surface than the oxidized surface. The absorption bands over CuO and ZnO can be assigned to MeO and m-F adspecies. However, shifts in band position were apparent compared to those over Cu and Cu₂O. In addition, the ratio of methoxy (~2818 cm⁻¹) to formate (~1575 cm⁻¹) was different. ZnO showed higher intensity of methoxy than formate, but CuO showed higher intensity of formate than methoxy.

3.2. Effect of pretreatment on the MeOH adsorption over Cu/ZnO

Fig. 2 shows the DRIFTS spectra of MeOH adsorption at 393 K over the Cu/ZnO catalyst pretreated at different conditions. The calcined catalyst had a DRIFTS spectrum containing MeO and m-F absorbances. The ratio of MeO to m-F lies between that of CuO and ZnO, suggesting a combined contribution from both CuO and ZnO. After H₂ reduction at 423 K, the catalyst showed very similar DRIFTS spectrum as the calcined catalyst. This reduction tempera-

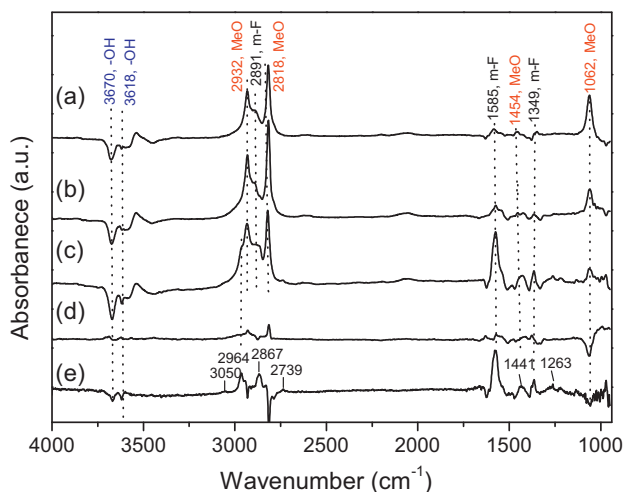


Fig. 3. DRIFTS spectra of (a) MeOH adsorption at 393 K over ZnO and the subsequent stepwise TPD to (b) 433 and (c) 473 K. The difference spectra include (d) 433–393 K and (e) 473–433 K. MeO: methoxy, m-F: monodentate formate.

ture was too low to cause any change in the oxidation state of the catalyst, which agreed with previous TPR findings [28]. The DRIFTS spectra from MeOH adsorption at 393 K changed as the reduction temperature increased to 450 and 463 K, with a significant increase in water-related absorbance at 3000–3500 and at 1300–1600 cm^{-1} . This indicates the formation of H_2O during MeOH adsorption over partially reduced Cu/ZnO catalyst. Ellis and Wang [41] reported that MeOH adsorption on O-preadsorbed Cu(100) yielded H_2O via a 2-step process. The adspecies over the partially reduced Cu/ZnO catalyst included MeO, formate, and carbonates. Absorbances at 1415 and 1506 cm^{-1} indicate the presence of carbonates. Weigel et al. [42] reported that surface carbonates appeared between 1700 and 1200 cm^{-1} on Cu/ZrO₂, which has a similar band shape to that in Fig. 2. The feature at 1506 cm^{-1} could be assigned to the OCO asymmetrical stretching mode of bidentate carbonate, whose ν_{as} and ν_{s} were at 1512 and 1325 cm^{-1} respectively [40], while that at 1415 cm^{-1} could be assigned to polydentate carbonate [37] or uncoordinated carbonate [40]. The absorbances related to water and carbonates disappeared as the reduction temperature increased to 473 and 493 K, while the MeO and m-F absorbances became stronger. This suggests that Cu/ZnO catalysts with more reduced Cu had more MeO and formate adspecies (Fig. 2(e) and (f)). The relatively higher intensity of MeO compared to m-F suggests that ZnO contributed more than Cu to the observed spectra over the reduced Cu/ZnO.

3.3. The MeOH sTPD over Cu/ZnO

An analysis of MeOH adsorption on ZnO is a prerequisite to understand the interaction of MeOH with a Cu/ZnO catalyst. Fig. 3 shows the infrared spectra of the MeOH adsorption at 393 K, the following stepwise TPD (sTPD) over ZnO to 433 and 473 K, and their difference spectra. The adsorbed species at 393 K contained MeO and m-F. The negative peaks at the OH band position (3670 and 3618 cm^{-1}) in Fig. 3 suggest that the hydroxyl groups interacted with the adsorbed species, as the background spectra were the same sample at the same temperatures before MeOH adsorption. DFT calculations [43] suggest that MeOH interacted with the hydroxyl group of ZnO to generate MeO and H_2O . Similar species appeared during sTPD to 433 and 473 K, but some bands shifted position. The difference spectrum between that at 433 and that at 473 K (Fig. 3(e)) shows the disappearance of MeO and the appearance of bi-dentate formate (b-F). The features at 2964, 2867, and

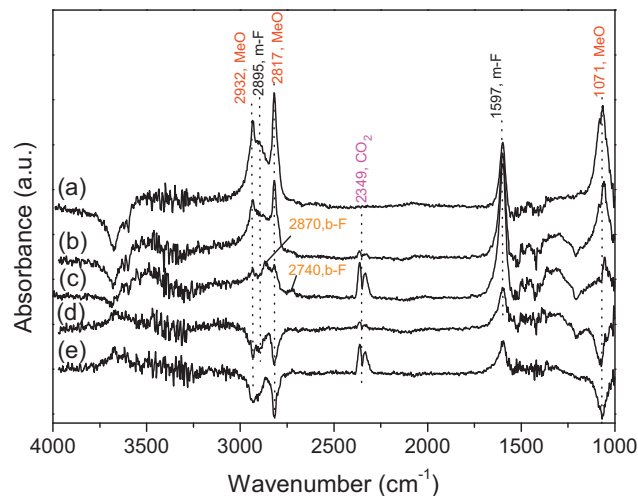


Fig. 4. DRIFTS spectra of (a) MeOH adsorption at 393 K over the calcined Cu/ZnO and the subsequent stepwise TPD to (b) 433 and (c) 473 K. The difference spectra include (d) 433–393 K and (e) 473–433 K. MeO: methoxy, m-F: monodentate formate, b-F: bidentate formate.

2739 cm^{-1} indicate the presence of b-F [30,40]. The small bands appearing at 3050, 1441, 1263 cm^{-1} might be due to methyl formate (MF) [30]. The increasing temperature converted MeO from MeOH adsorption on ZnO to formate species.

Fig. 4 shows the DRIFTS spectra and the difference spectra of MeOH adsorption at 393 K and subsequent sTPD over the calcined Cu/ZnO. Surface MeO and m-F were found after MeOH adsorption at 393 K. When the temperature increased stepwise to 433 K and 473 K, the intensity of the methoxy bands decreased. In the meantime, bands of CO_2 (2349 cm^{-1}) and the $\nu_{(\text{OCO})}$ (1597 cm^{-1}) of m-F increased, as shown in the difference spectra of Fig. 4(d) and (e). At 473 K, the bands attributable to b-F (2870 and 2740 cm^{-1}) became visible (Fig. 4(c)), but its intensity did not increase with increasing temperature as indicated by the difference spectrum. This suggests that b-F formed at a relatively low concentration during MeOH adsorption at 393 K and its concentration did not change during sTPD. The formation of CO_2 over the calcined Cu/ZnO catalyst suggests that it contained active oxygen for the reaction.

Fig. 5 shows the DRIFTS spectra of the methanol adsorption and the following sTPD over the partially reduced (450 K-reduced)

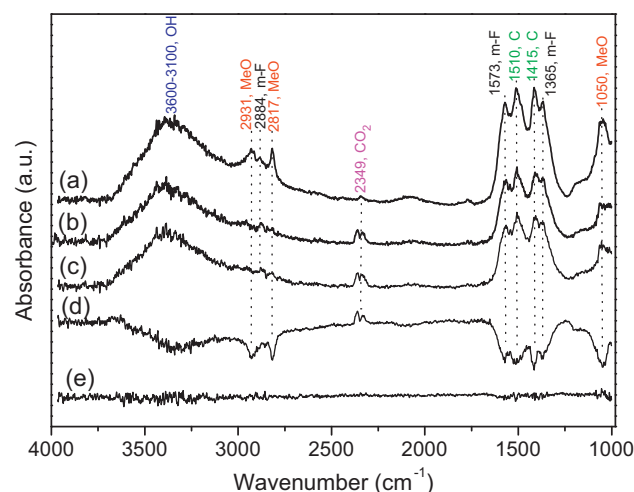


Fig. 5. DRIFTS spectra of (a) MeOH adsorption at 393 K over the 450 K-reduced Cu/ZnO and the subsequent stepwise TPD to (b) 433 and (c) 473 K. The difference spectra include (d) 433–393 K and (e) 473–433 K. MeO: methoxy, m-F: monodentate formate, C: carbonate.

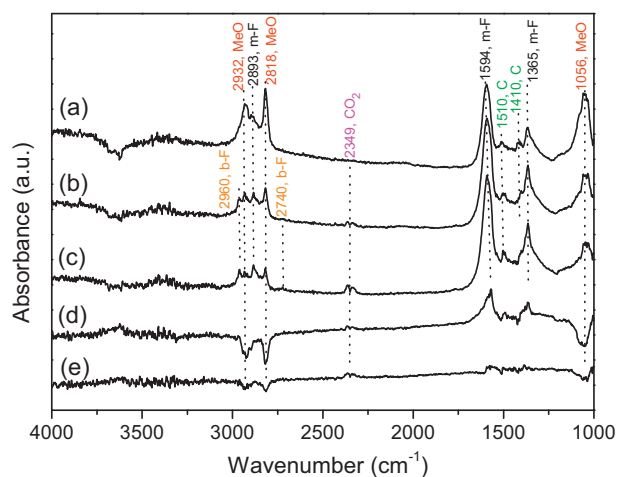


Fig. 6. DRIFTS spectra of (a) MeOH adsorption at 393 K over the 493 K-reduced Cu/ZnO and the subsequent stepwise TPD to (b) 433 and (c) 473 K. The difference spectra include (d) 433–393 K and (e) 473–433 K. MeO: methoxy, m-F: monodentate formate, C: carbonate, b-F: bidentate formate.

Table 1

The reduction degrees^a of Cu/ZnO after different treatments.

Conditions	Calcination	H ₂ , 450 K	H ₂ , 493 K	H ₂ , 523 K
After pretreatment	0	57	75	100
After MeOH adsorption and a following sTPD to 473 K	7	66	79	100

^a The reduction degrees were based on the hydrogen consumption calculated from TPR results, normalized by the hydrogen consumption of the calcined Cu/ZnO sample.

Cu/ZnO. Intense bands of hydroxyl and water (3600–3100 and 1700–1250 cm⁻¹) appeared after MeOH adsorption, while MeO, m-F, CO₂, and carbonates also appeared at 393 K. In comparison, the temperature at which CO₂ started to form was lower over the partially reduced Cu/ZnO than over the completely oxidized Cu/ZnO (Fig. 4). This implies that the oxygen within the partially reduced Cu/ZnO was more active than that in the calcined Cu/ZnO. The formation of hydroxyl and water can also be explained by the reaction between the oxygen and the hydrogen released by MeOH dehydrogenation. Increasing the temperature to 433 K caused the formation of more CO₂ at the expense of MeO, m-F, C, and some water. The difference spectrum in Fig. 5(e) shows that no further change occurred from 433 to 473 K. The MeO might have been exhausted at 433 K, as suggested by the very low absorbance of MeO.

Fig. 6 shows the DRIFTS spectra of MeOH adsorption at 393 K and the following sTPD to 473 K over the 493 K-reduced Cu/ZnO. TPR analysis (Table 1, will be discussed later) shows that the 493 K-reduced catalyst was almost completely reduced. At 393 K, the spectrum (Fig. 6(a)) showed the presence of MeO, m-F, and carbonates. Unlike that of the 450 K-reduced Cu/ZnO, no H₂O formed and the intensity of carbonates was much lower which suggests that the 493 K-reduced catalyst contained less active oxygen. When the temperature increased to 433 and to 473 K, surface MeO decreased while CO₂ increased. At 433 and 473 K, the absorbances of b-F (at 2960 and 2740 cm⁻¹) became visible in Fig. 6(b) and (c), but the difference spectra suggest that b-F was a spectator species.

3.4. Effect of methanol adsorption temperature

Fig. 7 shows the DRIFTS spectra of the methanol adsorption at 473 K over the 523 K-reduced Cu/ZnO and the 473 K-reduced ZnO.

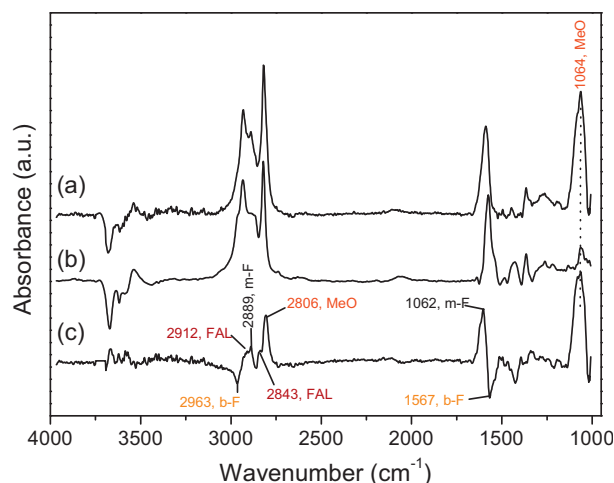


Fig. 7. DRIFTS spectra of the MeOH adsorption at 473 K over (a) the 523 K-reduced Cu/ZnO, (b) the 473 K-reduced ZnO, and (c): the difference spectrum of (a) minus (b). MeO: methoxy, m-F: monodentate formate, b-F: bidentate formate, FAL: formaldehyde.

The spectrum over ZnO (Fig. 7(b)) is almost the same as that over the non-reduced ZnO (Fig. 3(c)), which is the spectrum of sTPD to 473 K after MeOH adsorption at 393 K. Neither the hydrogen treatment at 473 K nor the methanol adsorption temperature caused significant differences in the DRIFTS over ZnO at 473 K. This suggests that the adsorbed species over ZnO changed due to thermodynamic stability.

The methanol adsorption at 473 K over the 523 K-reduced Cu/ZnO catalyst had a similar spectrum as that over ZnO. This suggests that the absorbances were originated mainly from adspecies on ZnO surface. However, bands attributable to formaldehyde (FAL) [36,44] appeared in the difference spectrum, Fig. 7(c), wherein negatives peaks indicate less b-F over the completely reduced Cu/ZnO. The sequential dehydrogenation of MeOH, MeOH → MeO → FAL → formyl → CO, is suggested by a comprehensive DFT calculation over Cu(110) [45]. Our previous work [27] also indicates that an H-abstraction sequence of MeOH → MeO → FAL → formyl → CO occurs over Cu/ZnO when active oxygen is eliminated by co-feeding hydrogen with MeOH. The presence of FAL over the completely reduced Cu/ZnO (Fig. 7(c)) is consistent with that MeOH underwent dehydrogenation in the absence of oxygen for further reaction.

3.5. Degree of reduction of differently pretreated Cu/ZnO

The degree of reduction of a catalyst can be used as a quantitative index of lattice oxygen. Table 1 shows the reduction degrees of the Cu/ZnO with different pretreatments, based on the hydrogen consumption of TPR analyses. The reduction degree increased, as expected, with increasing hydrogen reduction temperature. The procedures used in DRIFTS analysis were carried out exactly the same prior to TPR experiments, including the MeOH adsorption and a following sTPD. The in situ MeOH treatment (i.e., adsorption and sTPD) also increased the reduction degrees of differently pretreated Cu/ZnO catalysts. This indicates that the lattice oxygen related with Cu was consumed during the in situ methanol treatment and that the lattice oxygen was active under the conditions used in this study. This agrees with our previous results that there are more oxygen contents in the products than in the feed during methanol conversion on the calcined and partially reduced Cu/ZnO catalysts [28].

4. Discussion

Based on the TPR of the calcined Cu/ZnO (Table 1), the 523 K-reduced catalyst was completely reduced, while the 493 K-reduced catalyst was slightly less than completely reduced. The most significant difference in the DRIFTS of these two (Figs. 6(a) and 7(a)) was in CO₂ formation, which appeared in the 493 K-reduced but not in the 523 K-reduced Cu/ZnO. This suggests that the slightly oxidized Cu state in the 493 K-reduced Cu/ZnO caused the formation of CO₂, since the experiments in this study were controlled with a limited supply of oxygen in feed using dry MeOH and dry gases. The slight increase in surface hydroxyl (Fig. 6(d)) during MeOH sTPD to 473 K over the 493 K-reduced Cu/ZnO also suggests the presence of a small amount of active oxygen.

The 450 K-reduced Cu/ZnO showed intense surface hydroxyl bands, and CO₂ formation appeared upon MeOH adsorption at 393 K. The lattice oxygen must be the source of oxygen for the formation of surface hydroxyl and CO₂. These results suggest similar hydroxyl and CO₂ formation over the calcined Cu/ZnO because it contains a large amount of lattice oxygen; however, this did not occur as shown in Fig. 4. A negligible amount of hydroxyl and CO₂ formed during MeOH adsorption at 393 K over the calcined Cu/ZnO, and they were produced only at higher temperatures in the following sTPD. This implies that reduced Cu surface is necessary for the formation of hydroxyl and CO₂ at 393 K. This is the catalytic effect of reduced Cu. The partially reduced Cu/ZnO contained reduced Cu surface and a supply of lattice oxygen for oxidation reaction, and therefore the formation of CO₂ and hydroxyl was the most obvious in this study. Previous studies report the formation of water and CO₂ during MeOH adsorption over oxygen-precovered Cu surfaces [41,46]. For example, Singnurkar et al. [46] reported the formation of H₂O during MeOH adsorption on 0.25 monolayer O-precovered Cu(1 1 0) at 180 K. The surface oxygen over reduced Cu appears to be more active than the lattice oxygen reported in this study. This study provides the first infrared evidence of the participation of lattice oxygen of Cu to interact with MeOH.

On oxygen-free Cu surfaces, MeOH adsorption leads to MeO. Thereafter, a sequential dehydrogenation to FAL, formyl, and CO occurs during MeOH decomposition. Comprehensive DFT calculations [45] and experiments involving model systems [47] and real catalysts [27] revealed such a sequential dehydrogenation mechanism. MeO to FAL is the rate determining step in this MeOH sequential dehydrogenation. [27,45,47]. In this study, FAL appeared over the completely reduced Cu/ZnO (Fig. 7) but no CO₂ formed. Over the other incompletely reduced Cu/ZnO (Figs. 4–6), no FAL appeared but CO₂ formed. This suggests that active oxygen can react readily with either MeO or FAL leading to CO₂ evolution. A η^2 -formaldehyde species was proposed as the intermediate leading to CO₂, when FAL interacts with OH over an oxygen-precovered Cu(1 1 0) surface [46]. Based on DFT calculations, Bo et al. [48] reported that the reaction of FAL with O_{ad} over Cu(1 0 0) is thermodynamically more favorable than the reaction with OH_{ad}, and that formate is an intermediate to the formation of CO₂. These results clearly demonstrate that surface O and OH can react with FAL to form CO₂ over a Cu surface. The results of this study imply that lattice oxygen in the partially reduced Cu/ZnO catalyst migrates to the surface and participates in the adsorption of MeOH and subsequent surface reaction.

The support surface of Cu catalysts provides additional sites for MeOH adsorption. The MeOH adsorption over ZnO also results in MeO and formate. The adsorbed MeOH gives away one H to become MeO, probably due to the hydrogen adsorption capability of ZnO surface [49]. However, neither FAL nor CO₂ appeared on ZnO in this study, although previous research reports FAL from MeOH adsorption over polar ZnO surface [50]. The absence of CO₂ formation agrees with the negligible MeOH decomposition activity over ZnO,

indicating that the hydroxyl groups on ZnO cannot be a source of active oxygen for CO₂ formation. Formate was present on ZnO due to the interaction of MeO with surface hydroxyls or lattice oxygen, as indicated by the formation of more formates at the expense of MeO during sTPD (Fig. 3).

The adspecies over ZnO can migrate to the metal-support interface and become converted with the help of Cu, provided the migration of adspecies is thermally driven. From the sTPD over differently pretreated Cu/ZnO, DRIFTS analyses indicate that MeO decreased as the temperature increased, which in turn increased the formates and CO₂. The increase in formates is at least partially due to MeO conversion on ZnO surface. Over the partially reduced Cu/ZnO, carbonates and water were formed upon MeOH adsorption at 393 K. These species decreased together with MeO and m-F as the temperature increases, while CO₂ was formed. This implies that the surface carbonates and m-F may decompose or the m-F on ZnO may migrate to the Cu–ZnO interface to form CO₂. After heating to 473 K, the lower intensity of MeO band over partially reduced Cu/ZnO (Figs. 5(c) and 6(c)) compared to that over ZnO (Figs. 3(c) and 7(b)) suggests the migration of adspecies on ZnO to the Cu–ZnO interface for reaction. However, Fig. 6 suggests that b-F is just a spectator species, which may be due to its low migration mobility.

The formation of CO₂ and waters (hydroxyls) occurs at a lower temperature over the partially reduced Cu/ZnO than that over the calcined Cu/ZnO. This is consistent with previous results about methanol decomposition, for example, methanol conversions at 423 K were 0, 1.1, and 5.2% on the calcined, the 450 K-reduced and the 493 K-reduced Cu/ZnO catalysts, respectively [28]. This indicates that the transformation rate of adspecies increases with the increase in reduction degree of the Cu/ZnO catalyst. This suggests that the reduced Cu surface catalyzed the reaction between the adspecies and the oxygen migrated from lattice. The most likely morphology in the partially reduced Cu/ZnO should be Cu particles with a reduced Cu surface and a CuO_x core. The interaction of O (or OH) with adspecies from MeOH adsorption over Cu surfaces proceeds readily at temperatures below 120 K [41]. Under the conditions of this study, the mobility of lattice oxygen is obviously sufficient for supplying O to the surface. Over Cu surface, O and OH take part in the MeOH adsorption and reaction, as indicated in the MeOH sTPD over the partially reduced Cu/ZnO. The migration of adspecies over ZnO to the Cu–ZnO interface may contribute to the formation of CO₂ over the Cu surface. For the calcined Cu/ZnO, the reaction can occur only after part of the oxidized Cu surface is activated and reduced by the H from MeOH dehydrogenation (to MeO and m-F). The lattice oxygen can then participate in the reaction. This can be confirmed by the enhancement of reduction degree of the calcined and partially reduced Cu/ZnO after *in situ* methanol treatment as shown in Table 1.

5. Conclusions

1. Over ZnO surface, MeOH adsorption resulted in methoxy and monodentate-formate adspecies. Increasing the temperature caused the transformation of methoxy to formate. No further reaction occurred on ZnO. However, adspecies migrated to the Cu–ZnO interface and became oxidized when active oxygen was present.
2. Over the calcined Cu/ZnO, methoxy, and formate formed upon MeOH adsorption. Increasing the temperature caused the conversion of methoxy to formate and CO₂. The lattice oxygen participated in the oxidation of adspecies only after thermal activation.
3. Over the partially reduced Cu/ZnO, MeOH adsorption at 393 K resulted in water and CO₂ formation in addition to methoxy,

formate, and carbonates. The higher oxidation activity of lattice oxygen suggests a catalytic effect of reduced Cu.

4. Over the completely reduced Cu/ZnO, the sequential dehydrogenation of MeOH appeared in MeOH adsorption and sTPD. In the absence of lattice oxygen, no CO₂ formation appeared.

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