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The roles of Cu, Zn and Mn in $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst for methanol decomposition

S.T. Yong, K. Hidajat, S. Kawi *

Department of Chemical and Biomolecular Engineering, National University of Singapore, Block E5, Engineering Drive 4, Singapore 119260

Abstract

$Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst has been studied for methanol decomposition by in situ infrared (IR) spectroscopy analysis and micro reactor study. Methoxy species is formed by dissociative adsorption of methanol which subsequently converts into formate species via step-wise dehydrogenation process. The activities of surface intermediates on reduced CuO, ZnO and Mn_2O_3 catalysts are strongly affected by the ease of hydrogen desorption from the site, the strength of C–H bonding and the availability of oxygen. A synergism between Cu and MnO whereby the Cu serves as a sink for reverse hydrogen atoms spillover from MnO has been proposed. The micro reactor analysis correlates well with the IR results.
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Keywords: Spinel-lattice catalyst; Methanol decomposition; In situ infrared; Synergism

1. Introduction

Autothermal partial oxidative steam reforming of methanol has attracted much interest recently. Prior to further research on this reaction system, the understanding of reaction mechanism for methanol decomposition is essential. This is because methanol decomposition (Eq. (1)) serves as the basis of the former reaction system and hence the intermediates formed from the methanol decomposition would attribute to the overall mechanism of the autothermal reaction system.

$$CH_3OH \rightarrow 2H_2 + CO \qquad \Delta H^\circ_{298} = +128\,\text{kJ mol}^{-1} \tag{1}$$

The most common catalysts used for methanol decomposition include Cu due to its versatile properties. Although the mechanism of methanol decomposition on Cu has been widely studied, the effect of the interactions of supports and promoters with Cu may complicate the overall mechanism. The roles of supports and promoters in the reaction mechanism remain controversial. Some authors [1] proposed that the spillover of hydrogen from Cu restores the OH groups on the metal oxide, which react with methoxy and subsequently result in formate and carbonate formation. In contrast, another research group [2] proposed that the reverse spillover of hydrogen from metal oxide to Cu promotes the dehydrogenation process of methanol decomposition on the metal oxide. On the other hand, Manzoli et al. [3] suggested that the perturbation of oxygen vacancy equilibria between Cu and the metal oxide enhances the catalytic activity on the metal oxide. However, in general, it has been commonly accepted that the active site for the formation of formate and its decomposition occurs on the metal oxide which comprises of the majority of the catalysts [1–3].

We have previously identified $Cu_{0.5}Zn_{0.5}Mn_2O_4$ as the best catalyst among a series of spinel-lattice catalysts tested for the autothermal partial oxidative steam reforming of methanol [4]. Moreover, this catalyst also shows higher durability than the commonly used $Cu/ZnO/Al_2O_3$ catalyst. The good catalytic performance on the $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst hence prompted us to study the interactions of MnO with Cu and ZnO in the spinel-lattice and investigate the chemical natures of these mixed elements for the reaction mechanism of methanol decomposition.

In the present paper, Cu, ZnO and MnO catalysts, and $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst are tested for the methanol decomposition via in situ IR analysis in conjunction with micro reactor studies. Our objective is to develop a comprehensive reaction mechanism for the methanol decomposition on $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst and to identify the synergism occurring in the catalyst.

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* Corresponding author. Fax: +65 6779 1936.
E-mail address: chekawis@nus.edu.sg (S. Kawi).

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2. Experimental

2.1. Catalysts preparation

CuO/SiO_2, ZnO/SiO_2, Mn_2O_3/SiO_2 and $Cu_{0.5}Zn_{0.5}Mn_2O_4/SiO_2$ catalysts used for the IR studies were prepared by wet impregnation method. Nitrate salts of copper, zinc and manganese were dissolved in deionized water followed by immersing the silica in this solution overnight. The impregnated silica was dried at room temperature (RT) and calcined in air at 500 °C for 10 h. The metal contents of CuO/SiO_2, ZnO/SiO_2 and Mn_2O_3/SiO_2 catalysts were 2.5, 2.9 and 9.3 wt%. The total metal content of $Cu_{0.5}Zn_{0.5}Mn_2O_4/SiO_2$ was 13.7 wt% with Cu:Zn:Mn weight ratio of 2.5:2.7:8.5. These metal compositions were determined by inductively coupled plasma (ICP) using Perkin-Elmer PE2400. SiO_2 (Cab-O-Sil M5 200 $m^2\,g^{-1}$) was used to dilute the catalysts to permit the transmittance of IR beam.

The pure unsupported CuO, ZnO, Mn_2O_3 catalysts and the $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst used for the micro reactor kinetic studies were prepared by coprecipitation method and calcined at 500 °C for 10 h.

2.2. In situ infrared spectroscopy analysis

The sample was outgassed from RT up to 400 °C in O_2, then cooled down to RT in the same atmosphere and subsequently outgassed prior to the H_2 gas reduction treatment. CuO/SiO_2, ZnO/SiO_2 and $Cu_{0.5}Zn_{0.5}Mn_2O_4/SiO_2$ catalysts were reduced at 310 °C, while the Mn_2O_3/SiO_2 catalyst was reduced at 400 °C. These reduction temperatures were determined in our previous study [4]. The first reduction of Mn_2O_3 to Mn_3O_4 could be achieved at similar temperature as those required for the reduction of CuO into Cu metal. However, higher temperature is required for the further reduction of Mn_3O_4 to MnO. After H_2 reduction, the catalysts were cooled down to RT under outgassing. Methanol was purified by a series of freeze–thaw cycles to remove dissolved gases. Adsorption process involved the exposure of the reduced catalyst to 1 vol% methanol in Ar flowing at 60 cm^3/min for 30 min and then purging in He flowing at 60 cm^3/min for 30 min at RT, 130, 200 and 300 °C. Spectra were collected using Nicolet Magna 750 after He purge. Each spectrum was referred to the spectrum of the reduced catalyst collected at the same temperature in flowing He.

2.3. Micro reactor analysis

Catalytic activity experiments were performed at atmospheric pressure in a packed-bed micro reactor consisting of a quartz tube and a coaxially centered thermocouple with its tip located in the middle of the bed. 100 mg of catalyst was used for each reaction experiment. 0.027 cm^3/min of methanol was fed by means of a Shimadzu LC-10AT micro pump. 43 cm^3/min of He was used as the carrier gas. Prior to reaction, the catalysts were pre-reduced in H_2 gas at the same temperatures set for IR analysis. The system was then purged with He for 30 min to remove any residual H_2 before the reaction was started.

3. Results and discussion

3.1. IR analysis

3.1.1. Methanol adsorption and decomposition on CuO/SiO_2 catalyst

Fig. 1 shows the infrared spectra of Cu/SiO_2 catalyst after it has been subjected to methanol exposure and outgassed at different temperatures. At RT (Fig. 1, curve a), bands develop at 1464 and 1443 cm^{-1} in the 1600–1300 cm^{-1} region of the spectrum. The band at 1443 cm^{-1} is the characteristic band for CH_3O–Cu due to CH_3 bending vibration [5,6].

It is generally accepted that dissociative adsorption of methanol on Cu is only viable when Cu is partially oxidized into Cu^+ [7]. The oxygen atoms attached on Cu creates adsorption sites for the dissociative adsorption of methanol by forming hydrogen bond with the proton from the hydroxyl end of CH_3O–H. According to studies on methanol adsorption on

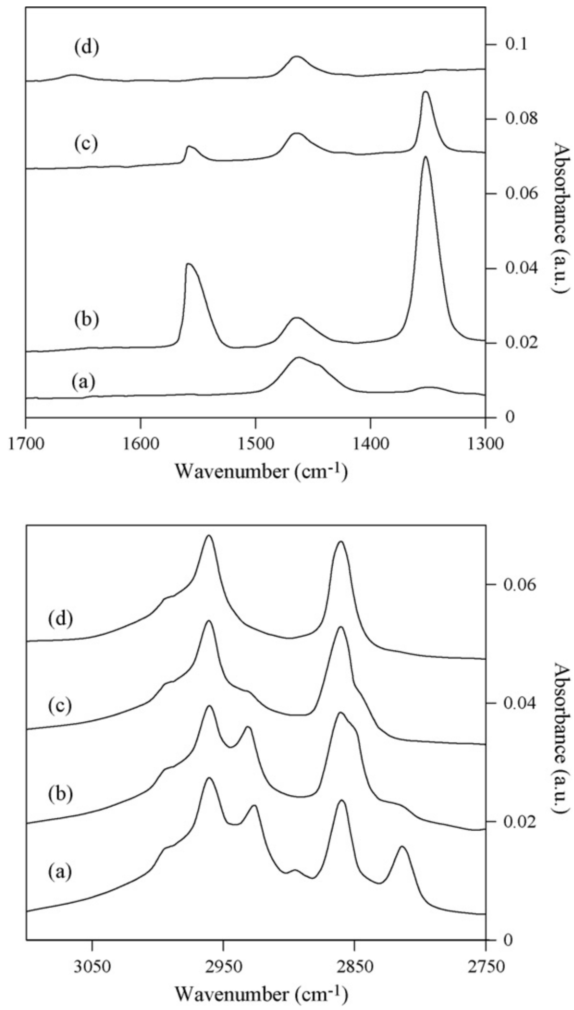


Fig. 1. Surface species evolution during thermal treatment of methanol adsorption on CuO/SiO_2. (a) RT; (b) 130 °C; (c) 200 °C; (d) 300 °C.

clean Cu (1 1 0) and clean polycrystalline Cu surface at RT, no significant reaction occurred even after methanol exposure of several hundred langmuir monolayer [8]. In contrast, the adsorption of methoxy is greatly enhanced by the presence of oxygen in the feed gas which can partially oxidize Cu^0 into Cu^+. In our previous study [4], we have shown that the maximum reduction temperature for CuO into Cu metal is about 310 °C. Despite prolonged H_2 gas reduction at 310 °C, some oxygen atoms may still attach on Cu. This is because continuous flow of non-dehydrated or wet methanol is available for the reaction and the moisture in the feed could act as a source for oxygen as the dissociation of water into hydrogen and adsorbed oxygen can occur at temperature as low as 73 °C on reduced polycrystalline Cu [9]. Another source of oxygen could be the residual oxygen on Cu due to the incomplete H_2 reduction prior to catalytic reaction. According to previous study on methanol decomposition over $Cu/ZnAl_2O_4$ [10], a small but finite amount of oxygen remains on the surface of Cu despite H_2 gas reduction at temperature as high as 350 °C.

The stronger band centered at 1464 cm^{-1} is attributed to the adsorption of methoxy on silica due to the bending mode of CH_3O–Si [2,11]. According to literature [12], the formation of methoxy groups on pure silica which is subjected to methanol exposure at RT occurs if the silica has previously been heated in vacuum or in an inert atmosphere above 350 °C to produce strained Si–O–Si bonds. Another possible route for the formation of CH_3O–Si groups is the spillover of the methoxy species from the Cu site on to silica. This route cannot be excluded as the methoxy groups could be mobile over the catalyst surface.

Correspondingly, the spectrum of C–H stretching region (3100–2650 cm^{-1}) is also presented in Fig. 1. The bands at 2995, 2961 and 2862 cm^{-1} can be assigned to CH_3O–Si [2,11] while the bands at 2928, 2895 and 2814 cm^{-1} can be assigned to CH_3O–Cu [2,13]. A weak band is observed at 1352 cm^{-1}, which can be ascribed to traces of bidentate formate adsorbed on copper as COOH–Cu species (Table 1).

Upon heating at 130 °C (Fig. 1, curve b), all the mentioned features ascribed to CH_3O–Cu reduce drastically in intensity, indicating the fast consumption of methoxy groups. This disappearance of CH_3O–Cu coincides with the steep increase in intensity of the band at 1352 cm^{-1} due to COOH–Cu [11]. This band is accompanied by a new feature at 1559 cm^{-1} which is also ascribed to COOH–Cu [11]. Correspondingly in the C–H stretching region, the bands at 2932 and 2850 cm^{-1} assigned to the same mode of formate species can be observed.

Table 1
List of observed IR bands and their assignments

Wavenumber (cm^{-1})	Assignment
1443, 2814, 2895, 2928	CH_3O–Cu
1470, 2818, 2913, 2936	CH_3O–Zn
1435, 2813, 2923	CH_3O–Mn
1464, 2862, 2961, 2995	CH_3O–Si
1352, 1559, 2850, 2932	COOH–Cu
1364, 1577, 2870	COOH–Zn
1367, 1574, 2818, 2856, 2926	COOH–Mn
1659	CH_3COOH–Cu
1352, 1503	CO_3–Mn

It is widely accepted that the formate species is formed from the dehydrogenation of methoxy species via formaldehyde [15]. Formaldehyde species is not detected in our present study which could be due to its rapid oxidation into formate species. Wachs and Madix [7] proposed that this fast oxidation of formaldehyde into formate proceeds via dioxymethylene species. According to literature [16], dioxymethylene seems to be very unstable even at room temperature and it can only be clearly detected by specially designed experiments, for example by the direct adsorption of formaldehyde and HREELS analysis.

Upon further heating to 200 °C (Fig. 1, curve c), CH_3O–Cu is consumed completely as noted by the total disappearance of the bands at 2928, 2895, 2814 and 1443 cm^{-1}. Meanwhile, the characteristic features previously mentioned for COOH–Cu decrease in intensities too. With further heating to 300 °C (Fig. 1, curve d), these features disappear completely, indicating the total decomposition of formate over the reduced CuO catalyst. A very weak band at 1659 cm^{-1} ascribed to methyl formate [2] appears at this reaction temperature. According to literature [2], the methyl formate formed over Cu catalyst at high temperature is attributed to the reaction between formaldehyde and formate species, which is subsequently transformed into methyl formate via polyoxymethylene. However, as similarly observed by Millar and Rochester [14], the polyoxymethylene surface species is not observed in the present study, probably due to the low thermal stability of this species.

3.1.2. Methanol adsorption and decomposition on ZnO/SiO_2 and Mn_2O_3/SiO_2 catalysts

Figs. 2 and 3 show the IR spectra of surface species evolving on reduced ZnO/SiO_2 and Mn_2O_3/SiO_2 catalysts after they have been exposed to methanol under thermal treatment. Methanol adsorption and desorption on ZnO at RT (Fig. 2, curve a) results in the appearance of a band at 1470 cm^{-1} due to the formation of chemisorbed CH_3O on ZnO (CH_3O–Zn), which corresponds to the bands at 2936, 2913 (shoulder) and 2818 cm^{-1} in the CH stretching region [17]. On the other hand, the band due to CH_3O–Mn (Fig. 3, curve a) can be observed at 1435 cm^{-1}, which also corresponds to the bands at 2923 and 2813 cm^{-1} in the CH stretching region [18].

During H_2 gas reduction process, negligible ZnO could be reduced to Zn metal and ZnO was mainly hydroxylated (polar) due to the H_2 gas reduction prior to the catalytic reaction. Meanwhile, Mn_2O_3 could be reduced to MnO upon H_2 gas reduction at about 400 °C according to our previous study [4]. Hydroxylated surface could be formed on MnO too. Unlike Cu catalyst, the availability of oxygen is not compulsory for the dissociative adsorption of methanol on the surface of these hydroxylated metal oxides. The formation of methoxy on ZnO is due to the formation of hydrogen bond between the hydroxyl groups on Zn and the proton from the hydroxyl end of CH_3O–H. However, not all of the methoxy groups adsorbed on MnO are formed from the same route as the hydroxylated ZnO. This

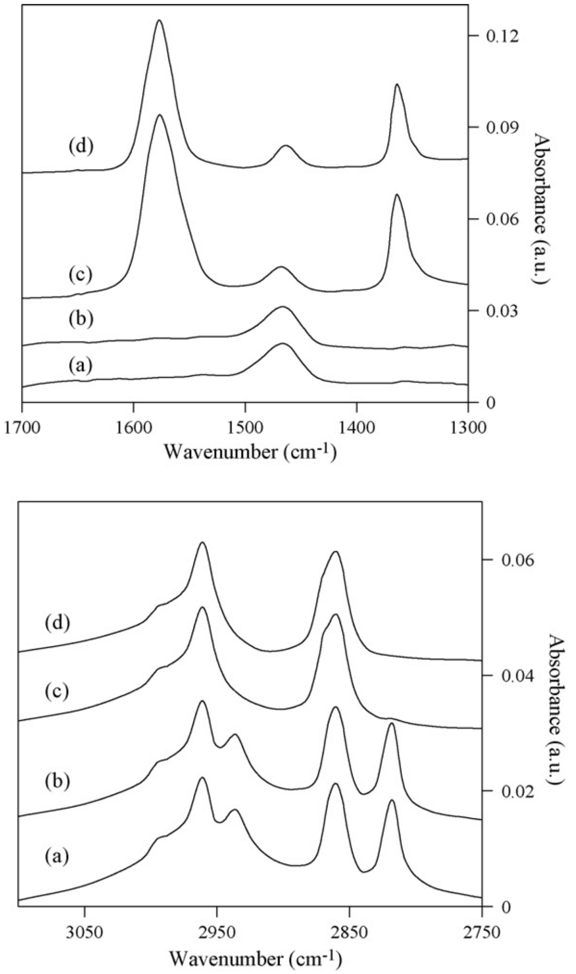


Fig. 2. Surface species evolution during thermal treatment of methanol adsorption on ZnO/SiO_2. (a) RT; (b) 130 °C; (c) 200 °C; (d) 300 °C.

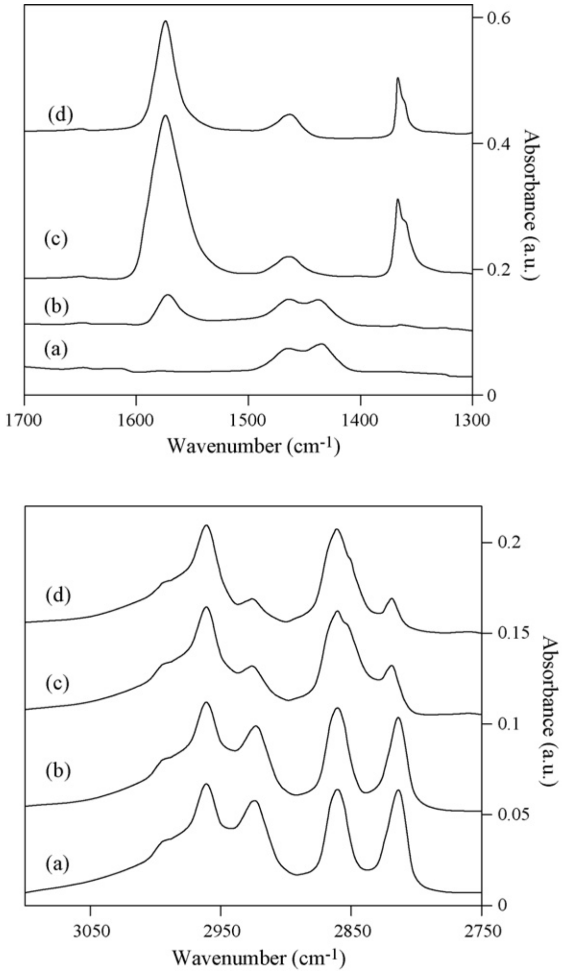


Fig. 3. Surface species evolution during thermal treatment of methanol adsorption on Mn_2O_3/SiO_2. (a) RT; (b) 130 °C; (c) 200 °C; (d) 300 °C.

is because oxygen vacancies were formed during the H_2 gas reduction over Mn_2O_3. Upon exposure to methanol at high temperature, the oxygen atoms from wet methanol would replenish these oxygen vacancies. Therefore, a part of the methoxy groups adsorbed on MnO could be attributed to the hydrogen bond formed between the oxygen on Mn and the proton from the hydroxyl end of CH_3O–H, i.e. the same route as that on Cu. The interactions of oxygen vacancies with the elements present in the catalyst can be studied in more detail with in situ time-resolved X-ray diffraction and X-ray absorption [19].

Upon heating at 130 °C, the features of CH_3O–Zn remain unchanged and no new band is observed (Fig. 2, curve b). On the other hand, the features of CH_3O–Mn slightly decreasing in intensity (Fig. 3, curve b) coincide with the appearance of a new band at 1574 cm^{-1} which is ascribed to COOH–Mn [18]. The route of formation of formate from methoxy on MnO is most possibly the same as that on Cu, i.e. the dehydrogenation of methoxy via formaldehyde and dioxymethylene.

The order of methoxy decomposition of all catalysts is as follows: Cu > MnO > ZnO. Three reasons could be proposed for this order of rate of methanol decomposition into formate species on Cu, ZnO and MnO catalysts. First, the step-wise dehydrogenation of methanol into formate is enhanced on Cu as compared to that on metal oxide due to the ability of continuous associative desorption of hydrogen atoms on Cu site itself. In contrast, such elimination of hydrogen atoms is very difficult on metal oxides [20]. Therefore, the methoxy decomposition on Cu catalyst is more facile than the other two catalysts.

The second factor affecting the order of methoxy reactivity could be the ease of partial oxidation. Alongside with the step-wise dehydrogenation of methoxy into formate, oxygen is required for the partial oxidation of formaldehyde into dioxymethylene which is the precursor of formate. Among all the three catalysts, Cu/SiO_2 catalyst most readily supplies O atoms for this partial oxidation process, due to the direct adsorption of oxygen on Cu upon exposure of the catalyst to wet methanol in the feed stream. For the case of metal oxide catalysts, oxygen can also be supplied indirectly from the hydroxylated surface due to H_2 gas reduction. However, extra energy is required to break the highly polar O–H bond prior to the partial oxidation reaction. Therefore, the formation of formate on reduced metal oxides is slower than that on reduced Cu catalyst. Due to the insertion of some oxygen atoms at the oxygen vacancies on MnO sites as mentioned earlier, the partial oxidation on MnO could be slightly easier than that on ZnO, but still more difficult than that on Cu. This reason correlates well with the order of methoxy decomposition observed for these three catalysts in the present study.

Third, the difference in C–H bond strength of the adsorbed methoxy groups may also contribute to the difference in methoxy reactivity on MnO and ZnO. The C–H stretching vibration frequencies of the methoxy on Mn are about 5–13 cm^{-1} lower than those on ZnO. The C–H bond of methoxy on MnO is thus weaker than that on ZnO; hence the dissociation of C–H bond is easier, facilitating the step-wise dehydrogenation of methoxy on MnO. Therefore, methoxy on Mn is converted more easily into formate. In contrast, the C–H bond of CH_3O–Zn is strong enough not to be oxidized immediately to formate at 130 °C. Therefore, the order of methoxy species dehydrogenating into formate could also be monitored by the bond strength of methoxy groups adsorbed on the catalyst surface. Similarly, the influence of bond strength on the activity of intermediate species has also been emphasized for water gas shift reaction [21].

It is worth mentioning that this stability of CH_3O–Zn from the dissociation of C–H bond could be viewed as an advantage in the methanol synthesis reaction, i.e. the opposite of methanol decomposition reaction. In methanol synthesis from CO_2, CO and H_2 over Cu–ZnO binary or tertiary catalysts, CH_3O–Zn has been reported as a key or more stable intermediate as compared to CH_3O–Cu [22,23]. This methoxy species adsorbed on Zn was capable of being further hydrogenated into methanol, i.e. the desired final product.

Upon further heating to 200 °C (Fig. 2, curve c), features due to the adsorption of formate species on Zn appear at 1577, 1364 and 2870 (shoulder) cm^{-1} [3]. The bands at 1577 and 1364 cm^{-1} are due to the asymmetric and symmetric O–C–O stretching of bidentate formate adsorbed on ZnO (COOH–Zn), respectively [3]. The formation of COOH–Zn is accompanied by intense disappearance of the bands due to CH_3O–Zn. Dioxymethylene seems to be an essential intermediate for the methanol decomposition reaction on metal oxides as it has been observed over a number of different metal oxides such as ZrO_2, TiO_2, ThO_2 [24] and Cr_2O_3 [25]. Therefore, the COOH–Zn species could be formed from the oxidation of methoxy via dioxymethylene, which is the same as that proposed for MnO.

For the thermal treatment at 200 °C on MnO (Fig. 3, curve c), the band at 1574 cm^{-1} grows drastically in parallel with the new bands at 2926, 2856, 2818 and 1367 cm^{-1}. These bands can be ascribed to b-COOH–Mn [18]. Similar to the assignment for ZnO, the bands at 1574 and 1367 cm^{-1} are specifically assigned to the asymmetric and symmetric O–C–O stretching of the adsorbed bidentate formate species, respectively [18].

The features due to COOH–Mn start to disappear upon further heating to 300 °C (Fig. 3, curve d). By comparing the intensities of these bands with those recorded at 200 °C, about a quarter of the bidentate formate has been decomposed. In contrast, the features due to COOH–Zn remain almost unchanged (Fig. 2, curve d), indicating the high thermal stability of this species adsorbed on Zn surface. During the decomposition of formate, the breakage of hydrogen bond from the COO–H proceeds. The ease of formate decomposition follows this order: Cu > MnO > ZnO. This result confirms the strong influence of the ease of hydrogen elimination and the C–H bond strength of formate on the reactivity of this surface species in methanol decomposition reaction.

This trend of formate decomposition is similar to that reported in literatures, where the formate decomposition initiates at about 127 °C [13], 277 °C [26] and 250–300 °C [18] on Cu, ZnO and Mn_3O_4 catalysts, respectively. By comparing the results obtained in the present study with hydroxylated metal oxides, with those in literature without hydroxylation, a decrease in the activity of methanol decomposition could be observed over the former catalysts. The high activity generally observed over non-hydroxylated catalysts may be attributed to the more oxygen readily available for the partial oxidation into formate. Furthermore, the hydrogen atoms produced on the non-hydroxylated catalysts could be eliminated rapidly by the association with the hydroxyl groups (which were formed during methanol dissociative adsorption) on the metal surface which subsequently desorbed as water. This alternative route of the elimination of hydrogen atoms hence facilitates the step-wise dehydrogenation of methanol. Although the rate of methanol decomposition on non-hydroxylated metal oxides maybe faster than that of hydroxylated, the hydrogen atoms may be risked to be produced as water instead of hydrogen gas. Hence, the adsorptive behavior and the catalytic action are affected by the amount of surface hydroxyl groups. Therefore, the hydroxylation treatment should be carefully monitored in order to obtain the desired rate of methanol decomposition and the H_2 production.

3.1.3. Methanol adsorption and decomposition on $Cu_{0.5}Zn_{0.5}Mn_2O_4/SiO_2$ catalyst

Fig. 4 shows the IR spectra characterizing the surface species evolving on $Cu_{0.5}Zn_{0.5}Mn_2O_4/SiO_2$ upon exposure to methanol under thermal treatment. In parallel with the CH_3O–Mn observed at 2925, 2816 and 1433 cm^{-1} [18], the formation of COOH–Mn also initiates at RT (Fig. 4, curve a) as depicted by the band at 1578 cm^{-1} [18]. Upon heating to 130 °C (Fig. 4, curve b), the later band increases gradually alongside with the appearance of the bands at 2930, 2852 and 1370 cm^{-1} also ascribed to COOH–Mn [18]. At 200 °C (Fig. 4, cure c), the intensities of the bands due to COOH–Mn are more than twice of that observed at 130 °C, coinciding with the total vanishing of the bands due to CH_3O–Mn. Upon further heating to 300 °C (Fig. 4, curve d), all the bands previously assigned to COOH–Mn disappear, indicating the total decomposition of formate species on the catalyst surface.

The complete decomposition of methoxy on $Cu_{0.5}Zn_{0.5}Mn_2O_4/SiO_2$ is achieved at much lower temperature than those on Mn_2O/SiO_2. Meanwhile, the temperatures required for formation and decomposition of formate on $Cu_{0.5}Zn_{0.5}Mn_2O_4/SiO_2$ also reduce greatly as compared with those on MnO/SiO_2. Therefore, there must be some kind of synergism present in $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalyst.

According to literature [27], the dissociative adsorption of H_2 molecule is more difficult on metal surface as compared to

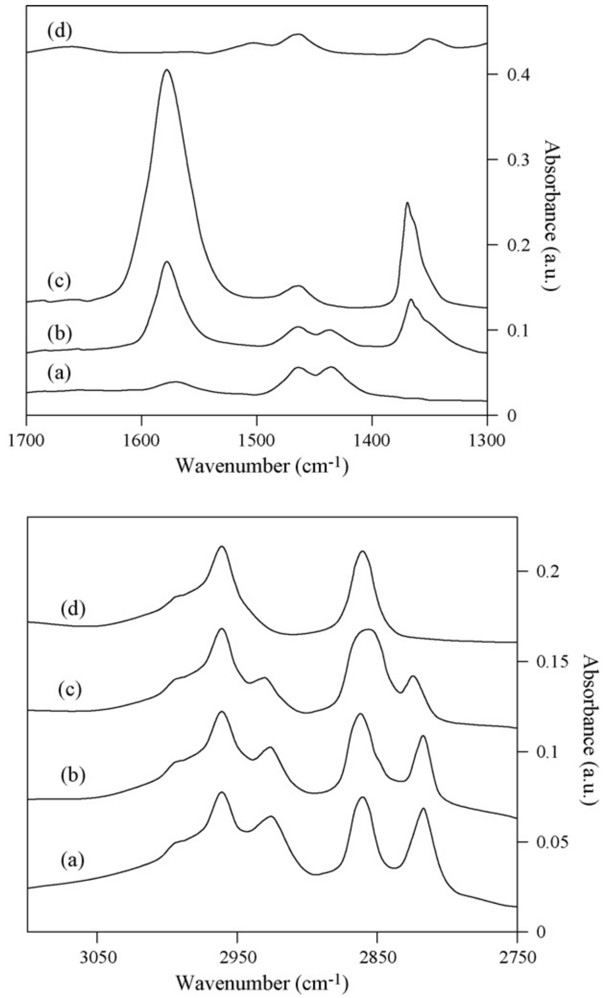


Fig. 4. Surface species evolution during thermal treatment of methanol adsorption on $Cu_{0.5}Zn_{0.5}Mn_2O_4/SiO_2$. (a) RT; (b) 130 °C; (c) 200 °C; (d) 300 °C.

most oxides where the dissociation of H_2 readily occurs. Therefore in the present study, it is reasonable to assume that the reverse process, i.e. the associative desorption of H atoms, may be more difficult on MnO as compared to that on Cu. Furthermore, Treviño et al. [20] proposed that the high energy required for the migration of H atoms was the possible rate determining step in the methanol synthesis on pure metal oxide. Applying these concepts to the adsorption of methanol on pure MnO catalyst, the hydrogen production from the step-wise dehydrogenation of methanol could be strongly hindered when all the intermediate reactions occur on the same sites. The sequential intermediate reactions would occur less readily due to the competitive adsorption of hydrogen atoms on the same sites. Furthermore, the hydroxyl groups on the Mn site required for the partial oxidation of formaldehyde into dioxymethylene may be depleted due to the reaction with these hydrogen atoms on the surface. Therefore, very low activity of methanol decomposition is observed on the MnO catalyst as compared to that on the $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst.

However, the addition of Cu into the MnO catalyst would greatly enhance the catalytic activity of methanol decomposition as evidenced by the faster decomposition of methoxy and formate groups on the reduced $Cu_{.5}Zn_{0.5}Mn_2O_4$ catalyst. Hence, a synergism between Cu and MnO is proposed: Cu acts as a sink for the hydrogen atoms produced during the step-wise dehydrogenation process of methanol on MnO. Such synergism between metal and metal oxide has also been suggested recently on Pd–Ga_2O_3 catalyst despite the difference in the intermediate reactions for methanol decomposition [16]. In methanol synthesis reaction, similar synergism has been proposed to occur between the metal and metal oxide [28]. However, the reverse spillover of hydrogen atoms from the metal to the intermediates located on the metal oxide has been suggested.

The same synergism is also expected to occur between Cu and ZnO in the $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst. However, the synergism effect is obscured by those on MnO which comprises of the major composition of the catalyst. Additionally, in a much lower extent, some methanol is also decomposed on the Cu site of the $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst.

It is worth to note that the hydrogen atoms spillover between the metal and metal oxide only occurs upon successful solid dissolution of metal and the metal oxide into each other in order to provide the interfacial surface required for the migration of hydrogen atoms from one side to another. One essential rule is that the sizes of the metal and metal oxide atoms must be of compatible magnitude for the formation of solid dissolution [3]. In contrast, no such stringent requirement is required for the spinel-lattice catalyst. This is because the Cu and metal oxides are readily dispersed in a controlled dimension whereby the Cu and metal oxide are atomically close to each other in the reduced spinel-lattice, which is the precursor of hydrotalcite-lattice.

As shown in Fig. 4, a weak broad band centered at $1662\ cm^{-1}$ ascribed to adsorbed methyl formate can be observed at 300 °C [2]. This methyl formate could be produced directly on the MnO site, as this species is commonly observed on metal oxides including TiO_2 and HfO_2 [29]. However, the contribution from Cu cannot be excluded as a similar peak is also observed over Cu/SiO_2 catalyst (Fig. 1). It has been suggested that methyl formate was produced from the reaction between formaldehyde and methoxy [30].

Other weak bands due to the surface carbonate on Mn can also be observed at $\sim$1503 and $1352\ cm^{-1}$ upon heating at 300 °C. These characteristic bands are very small relative to the bands ascribed to COOH–Mn. This observation suggests that formate decomposes mainly into gaseous products such as CO_2 and CO. This proposal is further substantiated by the absence of these surface carbonate species on pure MnO where the formate decomposition is very slow at the same temperature. The formation of surface carbonate on the ZnO of $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalyst is relatively difficult due to the lack of labile surface oxygen for the oxidation of CO_2, unlike MnO with oxygen vacancy where the oxygen could be inserted from the wet methanol. The availability of oxygen hence explains the formation of surface carbonate on non-hydroxylated ZnO [31] but not on hydroxylated ZnO [3].

3.2. Micro reactor analysis

In order to verify the roles of all the elements present in $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst on the methanol decomposition reaction, comparisons of the catalytic performance of the reduced CuO, ZnO, Mn_2O_3 and $Cu_{0.5}Zn_{0.5}Mn_2O_4$ spinel-lattice catalyst have also been carried out via micro reactor kinetic analysis.

Fig. 5 shows the methanol conversion and H_2 concentration in the outlet gas stream of methanol decomposition reaction for all the reduced catalysts. In general, the conversions of methanol on CuO and $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalysts initiate earlier than that on ZnO and Mn_2O_3 catalysts. This observation is consistent with the IR results whereby the formate species on both CuO and $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalysts decomposes at much lower temperature than those on ZnO and Mn_2O_3 catalysts. The high methanol conversion observed for $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalysts over ZnO and Mn_2O_3 catalysts verifies the proposed synergism in the ternary catalyst.

Upon heating above 225 °C, the conversion of methanol on $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalyst increases drastically. In contrast, methanol conversion on CuO catalyst decreases monotonously and vanishes at 325 °C. The decrease in the activity of CuO catalyst at higher reaction temperature is due to the thermal deactivation caused by Cu agglomeration since copper has a low Hüttig temperature [32] as reflected by its relatively low melting point. Such deactivation problem is not encountered by $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalyst. In fact, $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalyst still performs very well at temperature as high as 350 °C. This high stability of $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalyst is attributed to the spinel-lattice where after reduction, MnO and ZnO are located atomically close to the Cu atoms, hence hindering the copper agglomeration.

Fig. 5 also shows the hydrogen concentration in the exit gas stream. This result is very useful for the methanol decomposition system since hydrogen production cannot be detected in the IR analysis. It is clear that the trend of hydrogen concentration follows closely as those observed for methanol conversion. Therefore, H_2 is confirmed to be one of the primary products of methanol decomposition reaction. Throughout the entire range of reaction temperature studied, the trends of H_2 concentration for all catalysts are consistent with the trends of disappearance of formate observed for all catalysts via IR analysis, except for CuO catalyst that suffers thermal deactivation in the micro reactor. Therefore, the results clearly show that H_2 is produced from the decomposition of formate species. However, the contribution of the decomposition of methyl formate on hydrogen production at high reaction temperature cannot be excluded for $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalyst.

Fig. 6 shows the selectivities of CO and CO_2 as functions of reaction temperature for all catalysts. It is clear that CO dominates over CO_2 after methanol decomposition reaction has been initiated. According to Eq. (1), CO is the main by-product from the dehydrogenation of methanol. There are a few possible

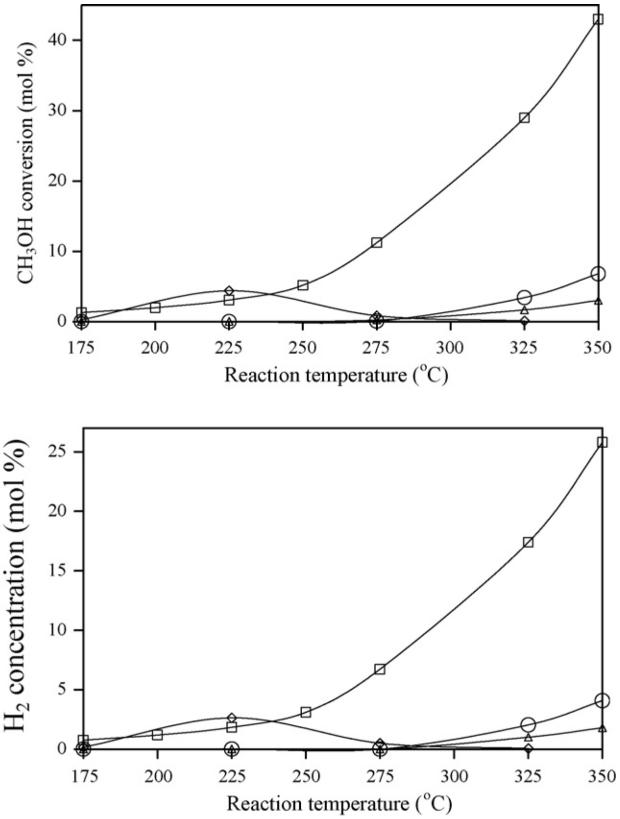


Fig. 5. Methanol conversion and H_2 concentration in the outlet gas stream (excluding He carrier gas) as functions of reaction temperature. (□) $Cu_{0.5}Zn_{0.5}Mn_2O_4$; (◇) CuO; (△) ZnO; (○) Mn_2O_3 catalysts.

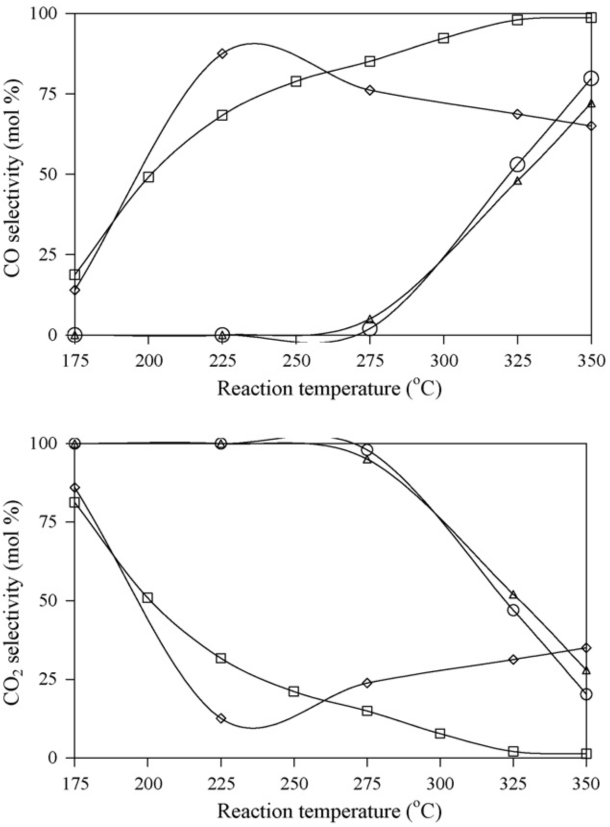
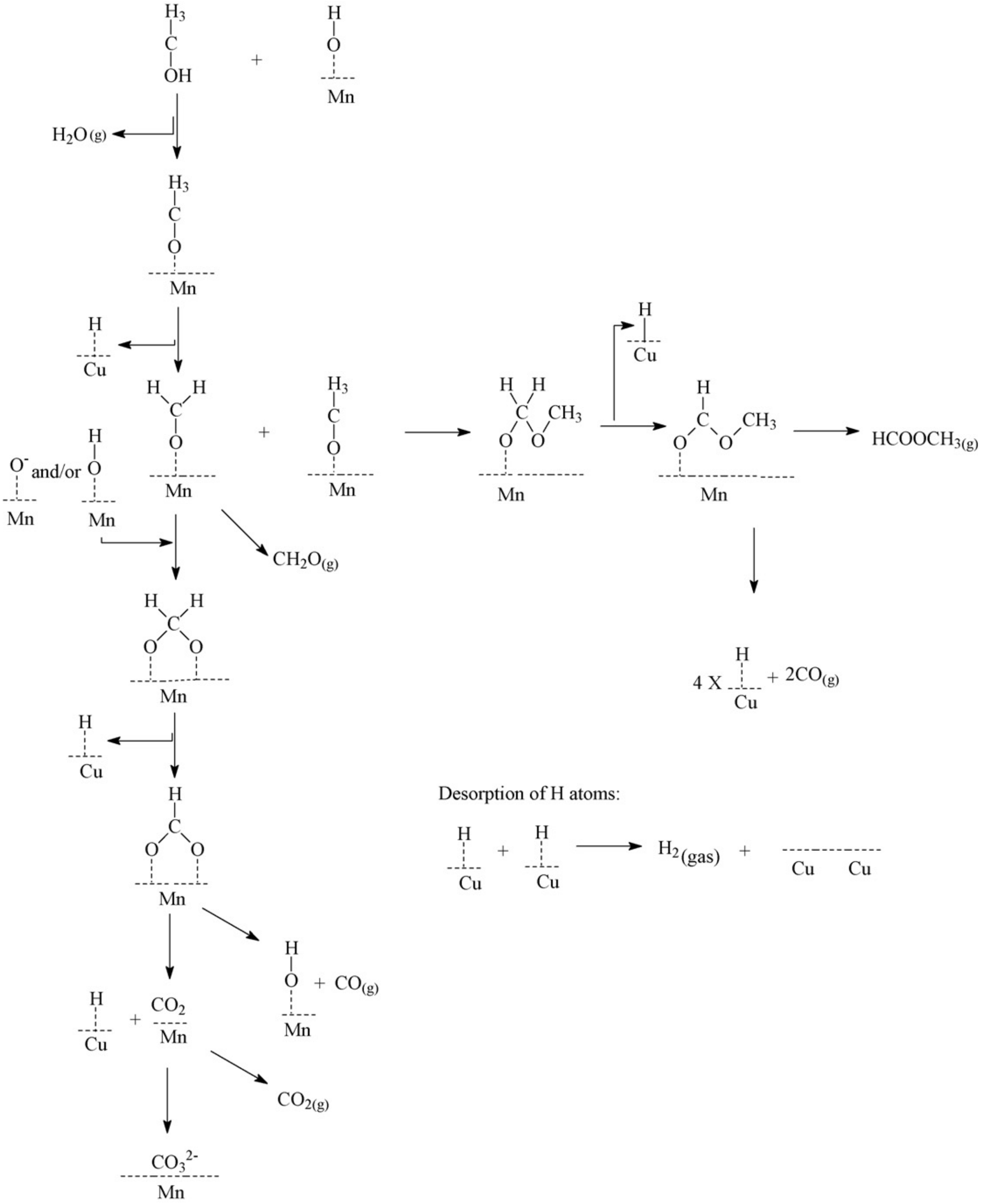


Fig. 6. Selectivities of CO and CO_2 as functions of reaction temperature. (□) $Cu_{0.5}Zn_{0.5}Mn_2O_4$; (◇) CuO; (△) ZnO; (○) Mn_2O_3 catalysts.

pathways for the formation of CO over CuO catalyst, one of those is the formation via the dissociation of CO_2 (precursor of formate) as observed by Clarke et al. [33]. However, according to literature [2], this is a minor source for CO formation. This is because it has been reported that only about 20% of CO_2 could be transformed into CO and O on Cu/SiO_2. In contrast, the concentration of CO obtained is much larger than that of CO_2. Since Minachev et al. [34] reported that CO_2 and H_2 are the only products when formate decomposes over copper surfaces, so the CO present in our reaction system cannot be produced from the formate species. However, it is known that CO can be produced from the decomposition of methyl formate [34]. Moreover in our present study, adsorbed methyl formate has been observed in the IR spectrum (Fig. 1). Therefore, in agreement with literature [2], the decomposition of methyl formate is proposed to contribute to the formation of CO on CuO catalyst.

The higher CO selectivity than that of CO_2 on CuO catalyst could be due to the very weak adsorption of CO on Cu^0 as suggested by Turco et al. [35]. Although the partial oxidation of Cu^0 into Cu^+ is required for the dissociative adsorption of methanol at the beginning of methanol decomposition, the oxidation state of copper with methoxy groups adsorbed would resume to Cu^0 after the elimination of water. Thus, the intermediate reactions on copper proceeding from this step to the decomposition of methyl formate into CO and H_2 mostly occur on Cu^0. Due to the very weak interaction of CO with Cu^0



Scheme 1. Proposed reaction mechanism for methanol decomposition on the predominant active site of $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalyst.

[35], CO could be desorbed easily into the outlet gas stream, hence explaining the much higher selectivity of CO than CO_2 on CuO catalyst as shown in Fig. 6.

For the cases of ZnO and Mn_2O_3 catalysts, both CO and CO_2 can be produced from the decomposition of formate species, as generally observed on metal oxides [29]. The much higher concentration of CO than CO_2 on these two metal oxide catalysts may be due to the lacking of oxygen for the partial oxidation of CO into CO_2. For the methanol decomposition reaction, Bowker et al. [27] reported about 10-fold higher CO concentration compared to that of CO_2 on hydroxylated ZnO; while Roberts and Griffin [26] reported four-fold higher CO_2 concentration compared to that of CO on non-hydroxylated ZnO. Since more oxygen is available on non-hydroxylated ZnO surface, the CO produced from formate decomposition could be partially oxidized into CO_2 more readily. These literatures support our proposal of the influence of oxygen availability on CO and CO_2 selectivities for these reduced ZnO and Mn_2O_3 catalysts. The contribution of CO from the decomposition of methyl formate should not be excluded for the case of Mn_2O_3 catalyst. Furthermore, the oxygen source on Mn_2O_3 is competitively used for the oxidation of CO_2 into surface carbonate as observed in Fig. 4.

Liquid products such as formaldehyde, methyl formate and dimethyl ether have been reported as the minor liquid by-products from methanol decomposition. The formation of the former two species is supported in our present study. These intermediates, apart from reacting to produce hydrogen, may also convert into vapor phase due to equilibrium reactions. According to Choi and Stenger [36], who reported methanol decomposition on commercial $Cu/ZnO/Al_2O_3$, methyl formate was the major undesired by-product (apart from CO) although this species only comprised up to 7 mol% of the total product concentration. Dimethyl ether was formed to a lower extent (about 1.5 mol%) and only at high reaction temperature. It is generally accepted that the formation of dimethyl ether is due to the dehydration of methanol [14,28]. Methane is not detected in our present study. This is not surprising as according to literature [28], reaction temperature of as high as 400 °C is required for the formation of methane via the hydrogenation of dimethyl ether.

4. Conclusion

The reaction mechanism for the decomposition of methanol on the predominant sites of $Cu_{0.5}Zn_{0.5}Mn_2O_4$ catalyst has been proposed and presented in Scheme 1. The order of reactivity of both methoxy and formate species on pure metal and metal oxides is as follows: Cu > MnO > ZnO. The factors affecting this order include the ease of hydrogen desorption from the active site, the availability of oxygen for the partial oxidation of formaldehyde and the strength of C–H stretching bond. The predominant active sites for the production of H atoms are located on Mn sites. Activity is promoted by the synergism between Cu and Mn, whereby Cu acts as a sink for H atoms produced from Mn site. The successful removal of H atoms by associative desorption on Cu enhances the methanol decomposition on Mn.

References

[1] D. Bianchi, T. Chafik, M. Khalfallah, S.J. Teichner, Appl. Catal. A 123 (1995) 89.

[2] I.A. Fisher, A.T. Bell, J. Catal. 184 (1999) 357.

[3] M. Manzoli, A. Chiorino, F. Boccuzzi, Appl. Catal. B: Environ. 57 (2005) 201.

[4] S.T. Yong, K. Hidajat, S. Kawi, Appl. Catal. B: Environ., submitted for publication.

[5] B.A. Sexton, Surf. Sci. 88 (1979) 319.

[6] B.A. Sexton, Surf. Sci. 155 (1985) 366.

[7] I.E. Wachs, R.J. Madix, J. Catal. 53 (1978) 208.

[8] A.F. Carley, A.W. Owens, M.K. Rajumon, M.W. Roberts, Catal. Lett. 37 (1996) 79.

[9] G.C. Chinchen, M.S. Spencer, K.C. Waugh, D.A. Whan, J. Chem. Soc., Faraday Trans. 1 (83) (1987) 2193.

[10] M. Bowker, R.A. Hadden, H. Houghton, J.N.K. Hyland, K.C. Waugh, J. Catal. 109 (1988) 263.

[11] E.A. Wovchko, J.C. Camp, J.A. Glass, J.T. Yates, Langmuir 11 (1995) 2792.

[12] E. Borrello, A. Zecchina, C. Morterra, J. Phys. Chem. 71 (1967) 2938.

[13] D.B. Clarke, D.K. Lee, M.J. Sandoval, A.T. Bell, J. Catal. 150 (1994) 81.

[14] G.J. Millar, C.H. Rochester, Chem. Soc. Faraday Trans. 87 (1991) 2795.

[15] C. Barnes, P. Pudney, Q. Guo, M. Bowker, Faraday Trans. 86 (1990) 2693.

[16] S.E. Collins, M.A. Baltanás, A.L. Bonivardi, Appl. Catal. A: Gen. 295 (2005) 126.

[17] C. Chauvin, J. Saussey, J.C. Lavalley, H. Idriss, J.P. Hindermann, A. Kiennemann, P. Chaumette, P. Courty, J. Catal. 121 (1990) 56.

[18] E. Finocchio, G. Busca, Catal. Today 70 (2001) 213.

[19] X. Wang, J.A. Rodriguez, J.C. Hanson, D. Gamarra, A. Martínez-Arias, M. Fernández-García, J. Phys. Chem. B 110 (2006) 428.

[20] H. Treviño, T. Hyeon, W.M.H. Sachtler, J. Catal. 170 (1997) 236.

[21] P. Liu, J.A. Rodriguez, J. Phys. Chem. B 110 (2006) 19418.

[22] H.Y. Chen, L. Chen, J. Lin, K.L. Tan, J. Phys. Chem. B 102 (1998) 1994.

[23] H.Y. Chen, S.P. Lau, L. Chen, J. Jin, C.H.A. Huan, K.L. Tan, J.S. Pan, Appl. Surf. Sci. 152 (1999) 193.

[24] G. Busca, A.S. Elmi, P. Forzatti, J. Phys. Chem. 91 (1987) 5263.

[25] M.W. Wensch, C.M. Byrd, D.F. Cox, Catal. Today 85 (2003) 279.

[26] D.L. Roberts, G.L. Griffin, J. Catal. 95 (1985) 617.

[27] M. Bowker, H. Houghton, K.C. Waugh, J. Chem. Soc., Faraday Trans. 1 (77) (1981) 3023.

[28] R. Burch, R.J. Chappel, S.E. Golunski, Catal. Lett. 1 (1988) 439.

[29] A.M. Hussein, N. Sheppard, M.I. Zaki, R.B. Fahim, J. Chem. Soc. Faraday Trans. 87 (1991) 2655.

[30] R. Zhang, Y. Sun, S. Peng, Fuel 81 (2002) 1619.

[31] T. Morimoto, K. Morishige, J. Phys. Chem. 79 (1975) 1573.

[32] M.S. Spencer, Nature 323 (1986) 685.

[33] D.B. Clarke, I. Suzuki, A.T. Bell, J. Catal. 142 (1993) 27.

[34] K.M. Minachev, K.P. Kotyaev, G.I. Lin, A.Y. Rpzovskki, Catal. Lett. 3 (1989) 229.

[35] M. Turco, G. Bagnasco, U. Costantino, F. Marmottini, T. Montanari, G. Ramis, G. Busca, J. Catal. 228 (2004) 43.

[36] Y. Choi, H.G. Stenger, Appl. Catal. B: Environ. 38 (2002) 259.