

Partial Oxidation Reaction of Methanol on Cu/MnO Thin Films Grown on Ni (100) Surface

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Partial oxidation reaction of methanol has been investigated on Cu/MnO thin films grown on Ni (100) surface in an ultra high vacuum (UHV) system combined with a reaction cell. The partial oxidation reaction of methanol proceeds on the Cu/MnO surfaces with Cu films thicker than 1.5 ML at a lower temperature of 470 K, in consistent with the activity of copper manganese oxide catalysts prepared by co-precipitation method. Post-reaction surface analysis by 2p X-ray photoelectron spectroscopy (XPS) and LMM Auger electron spectroscopy (AES) of Cu and Mn have demonstrated that Cu⁺ species exist as Cu₂O overlayers which are stabilized by MnO underlayers acting as a template during the reaction. It is proposed that partial oxidation reaction of methanol proceeds through surface formate destabilized on the Cu₂O overlayers at lower temperatures. [DOI: 10.1380/ejssnt.2009.898]

Keywords: Alcohol; Thin film; X-ray photoelectron spectroscopy; Copper; Manganese; Catalysis

I. INTRODUCTION

Hydrogen is expected to play a major role in the future as carbon free energy carrier. In recent years, polymer electrolyte fuel cell (PEFC) systems using hydrogen have attracted much attention due to their potential as a clean and silent power source for many applications [1–4]. Hydrogen can be extracted from several sources including natural gas, water, biomass, or other more complex hydrocarbons. In particular, methanol has been recommended as the best source for hydrogen among the liquid fuels with a high energy density. Methanol can be converted to hydrogen over traditional Cu/ZnO-based catalyst by several reactions, including methanol decomposition reaction ($\text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO}$), steam reforming reaction of methanol ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$), partial oxidation reaction of methanol ($\text{CH}_3\text{OH} + 1/2\text{O}_2 \rightarrow 2\text{H}_2 + \text{CO}_2$), and oxidative steam reforming reaction of methanol ($2\text{CH}_3\text{OH} + \text{H}_2\text{O} + 1/2\text{O}_2 \rightarrow 5\text{H}_2 + 2\text{CO}_2$) [5–11]. Huang *et al.* concluded that over the Cu/ZnO catalyst with normally operating around 523 K both of Cu⁰ and Cu⁺ species are essential for hydrogen production via partial oxidation reaction of methanol and the activity of catalyst is dependent on the ratio of Cu⁺/Cu⁰ in the catalyst [5]. On the other hand, some authors have found that the Cu⁰ species in catalysts is an active species for high activity and the Cu⁺ species inhibits the hydrogen production from the partial oxidation reaction of methanol. Although introduction of appropriate amounts of Zn is helpful to stabilize the Cu⁰, the Cu/ZnO catalyst deactivates rapidly after 20 h reaction at 503 K [6, 7]. Compared to Cu/ZnO catalysts, recent studies have reported that Cu/MnO catalysts exhibit even superior activity to the industrial catalyst Cu/ZnO/Al₂O₃ for (ox-

idative) steam reforming reaction of methanol. As an example, a Cu₃₀Mn₇₀ (Cu 30 wt% and Mn 70 wt%) oxide catalyst achieved 99.3% methanol conversion with 96.9% H₂ selectivity at 513 K for steam reforming reaction of methanol [8, 9]. We have also found that Cu-Mn catalysts prepared by co-precipitation method are more active for partial oxidation reaction of methanol as well as steam reforming reaction of methanol in hydrogen production at a low temperature of 473 K. XRD measurements demonstrated that the Cu-Mn catalysts after calcination were composed of a spinel phase of Cu_{1.5}Mn_{1.5}O₄ and reduced to Cu⁰ and MnO in a flowing 50 vol% H₂/He mixture at 673 K for 30 min before the reaction. Moreover, Cu 2p XPS and LMM Auger data revealed mainly the presence of Cu⁰, Cu⁺ and less Cu²⁺ species on the surface of Cu-Mn catalysts [10]. However, the precise oxidation states of copper and the role of MnO in the Cu/MnO catalysts are still not well understood.

Recently, Iwai *et al.* have studied partial oxidation reaction of methanol over Cu and Cu-Zn thin films on Ni(100) single crystal as model Cu/ZnO catalysts. It has been observed that the rate of hydrogen production in a reactor cell reached a maximum at 3 ML Cu film thickness and the addition of 0.25 ML Zn increased the reaction rate independent of Cu film thickness in a range of 1–6 ML at the temperature of 550 K. Post-reaction surface analysis by Cu 2p XPS and LMM Auger showed Cu agglomeration on the Ni substrate and the presence of predominant Cu⁰ species with Cu⁺. It is proposed, accordingly, that the existence ratio of Cu⁰ and Cu⁺ is related to the reactivity [11]. In this study, we have fabricated the Cu/MnO thin films as a model surface of Cu/MnO catalysts, which are derived from Cu-Mn oxides, prepared by co-precipitation method. The reaction between methanol and oxygen on the Cu/MnO thin films has been studied as a function of Cu film thickness at a reaction temperature of 470 K. To compare the difference between the Cu overlayers on Ni(100) substrate and MnO underlayers, the

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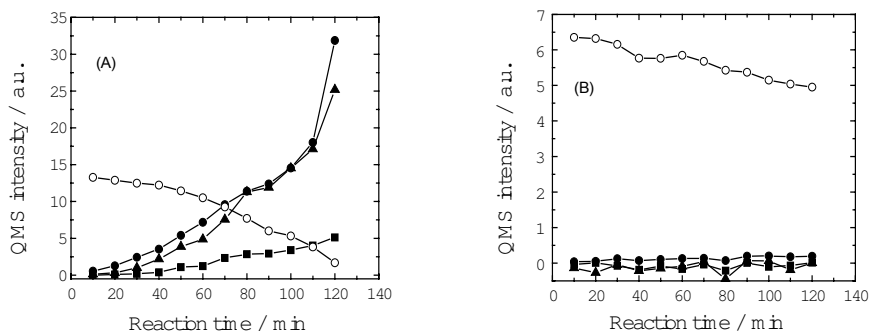


FIG. 1: QMS intensities of major products during CH_3OH and O_2 reaction on: (A) 3 ML Mn, and (B) 3 ML MnO films. (●) H_2 , (▲) CO, (■) CO_2 , (○) O_2 .

precise oxidation states of copper and the role of MnO in the Cu/MnO thin films were analyzed by the XPS and AES.

II. EXPERIMENTAL

The experiments were carried out in an UHV (base pressure $< 4 \times 10^{-8}$ Pa) chamber equipped with facilities for XPS, LEED (Low Energy Electron Diffraction) and QMS (Quadrupole Mass Spectrometry). The Ni(100) single crystal was cooled down to 100 K using liquid nitrogen and heated above 1300 K by passing current through Ta lead wires. Sample temperature was measured by a chromel-alumel thermocouple spot-welded to the side of the crystal. The Ni (100) substrate was cleaned by repeated Ar^+ sputtering and annealing at 1300 K until no impurities were detected by XPS. Cu and Mn were evaporated on the clean Ni surface kept at 300 K independently from a resistively heated alumina tube containing Cu wire (1 mm in diameter, purity $> 99.99\%$) or Mn flake (purity $> 99.99\%$). The growth of Mn films can be fitted to a layer-by-layer mode where the changes of Ni and Mn $2p$ XP signals at a constant evaporation rate show straight-line segments with several breaking points as well as the growth of Cu films on Ni(100) [11]. We define the thickness of Mn films based on these breaking points, although there was no ordered LEED pattern appeared. MnO thin films were then formed by the exposure of evaporated Mn films to oxygen ($P_{\text{O}_2} = 1.33 \times 10^{-6}$ Pa $\times$ 1 min at 300 K, see Fig. 7(a) and (b)). Cu(2)/MnO(4) denotes that Cu films equivalent to 2 ML were sequentially evaporated on 4 ML MnO prepared on Ni(100) substrate. After thin films were prepared, the sample was transferred to a reaction cell of about 0.2 L, so that the sample could be sealed from the main UHV chamber instantly. Reactant gases (oxygen of 99.9% purity and methanol of 99.8% purity) with Ar as a pressure calibration were introduced to the reaction cell via bellows valves from a gas inlet system. Partial pressures of methanol, oxygen and argon were 54, 27 and 27 Pa, respectively. Partial oxidation reaction of methanol was monitored continuously or at 10 min interval with the QMS intensities of respective reactants and products introduced through a variable leak valve between the UHV chamber and the reaction cell, taking the QMS sensitivity toward H_2 , CO, O_2 and CO_2 into account. Before and

after reaction, thin films were characterized by XPS at a detection angle of 43° to sample vertical in photoemission. For a more detailed characterization of topmost surface of thin films, the sample was tilted to collect the photoelectrons at a grazing angle of 68° , keeping the X-ray source and the analyzer at fixed positions. After each experiment, the sample cleaning procedures were repeated until the Mn and/or Cu XP signals were no longer detected.

III. RESULTS AND DISCUSSION

A. Reaction of methanol and oxygen on Mn and MnO films

Prior to Cu/Mn systems, a reaction between methanol and oxygen was studied over two differently prepared Mn and MnO overlayers on Ni(100) substrate. To minimize the influence of Ni as much as possible, the reaction was experimented on the thickness of Mn with 3 ML or more. Figs. 1(A) and (B) compare the partial pressures of H_2 , CO, O_2 and CO_2 in a course of reaction at 470 K. On the metallic Mn films, a certain amount of CO_2 is produced with H_2 and CO during a time of 120 min, as shown in Fig. 1(A). In the initial course of reaction, O_2 consumption rate is slower than those of H_2 and CO production, and CO_2 is hardly produced. This suggests that CO and H_2 were mainly produced from methanol decomposition reaction. In the later course of the reaction, the consumption of O_2 was gradually accelerated and abrupt increase of H_2 and CO formation occurred concomitant with the consumption of oxygen. Lower concentration of CO_2 compared to CO in the reaction products indicates that partial oxidation reaction of methanol proceeds to some extent on Mn thin films in addition to the main reaction of methanol decomposition. In contrast, on the MnO thin films, only oxygen decreased slowly as shown in Fig. 1(B). There is no other change in the gas phase components, clearly indicating that no reaction takes place between methanol and oxygen. From these results, Cu overlayers on MnO films have been intensively studied hereafter as Cu/MnO model surfaces.

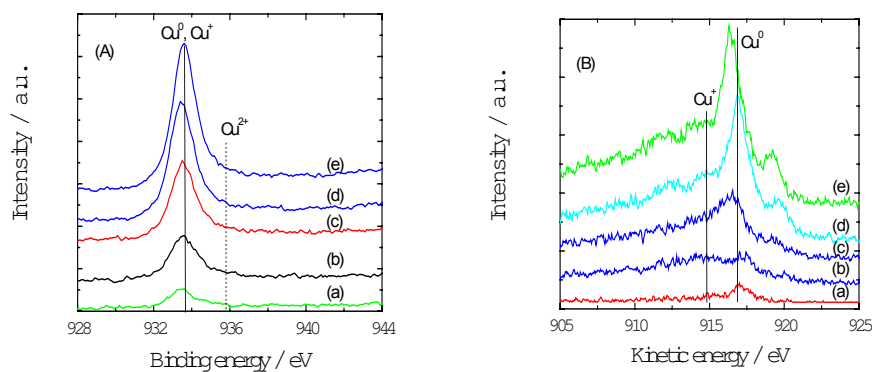


FIG. 2: (A) Cu $2p_{3/2}$ XP and (B) Cu LMM AES spectra for as grown films as a function of Cu film thickness on 4 ML MnO: (a) 0.25 ML, (b) 0.5 ML, (c) 0.75 ML, (d) 1.5 ML, (e) 2.0 ML.

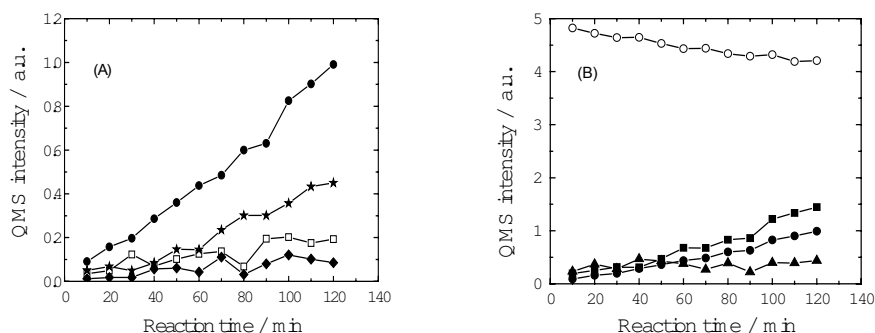


FIG. 3: (A) QMS intensities of H_2 in partial oxidation reaction of methanol on Cu/MnO(4) thin films as a function of Cu film thickness at 470 K: ($\square$) 0 ML, ($\blacklozenge$) 0.75 ML, ($\star$) 1.5 ML, ($\bullet$) 2.0 ML. (B) QMS intensities of H_2 , CO, O_2 and CO_2 in a course of reaction between CH_3OH and O_2 on Cu(2)/MnO(4) films at 470 K: ($\bullet$) H_2 , ($\blacktriangle$) CO, ($\blacksquare$) CO_2 , ($\circ$) O_2 .

B. Catalytic reaction on Cu/MnO films

The electronic states of Cu for Cu/MnO films on Ni(100) have been investigated by the combination of Cu $2p_{3/2}$ XP and Cu LMM Auger spectra for as grown films as a function of Cu film thickness on 4 ML thick MnO in Figs. 2(A) and (B), respectively. The intensities of Cu increased proportionally to the amount of Cu evaporated on MnO films in both figures. All spectra in Fig. 2(A) exhibit a single peak located at the binding energy of 934 eV without any peak due to cupric oxide (Cu^{2+}) at a higher binding energy. The peak of 934 eV can be assigned to either Cu^0 or Cu^+ in the form of metallic copper (Cu^0), cuprous oxide (Cu^+), or both species because the peaks due to Cu^0 and Cu^+ species overlap in the energy level of Cu $2p_{3/2}$ and cannot be resolved by deconvolution [12–14]. These species can, however, be distinguished from the positions of their LMM Auger transition in XP spectra, which are the kinetic energy of 915 eV and 917 eV for Cu^+ and Cu^0 , respectively [13]. A shoulder at 915 eV with a main metallic Cu peak (917 eV) is due to Cu^+ species in Fig. 2(B). For Cu film thickness less than 0.5 ML, the contribution of Cu^+ is more than that of Cu^0 on MnO, but Cu^0 is predominant when Cu thickness exceeds 0.75 ML. With increase in Cu film thickness, the ratio of Cu^+ to Cu^0 gradually decreases. Accordingly, it is most likely concluded that a part of Cu is oxidized and exists as Cu^+ at the interface of MnO and Cu. This

is considered as a model surface of Cu/MnO catalysts, because spinel phases of $Cu_{1.5}Mn_{1.5}O_4$ prepared by coprecipitation method were reduced to Cu^0 and MnO before the reaction conditions for steam reforming reaction and partial oxidation reaction of methanol.

In regards to a change of the electronic states of Cu overlayers, the reaction between methanol and oxygen on Cu/MnO(4) thin films have been studied as a function of Cu film thickness at a reaction temperature of 470 K. As shown in Fig. 3(A), any noticeable hydrogen formation did not take place on Cu(0.75)/MnO(4) films as similar to MnO surface mentioned above. However, H_2 evolution occurred when the amount of Cu deposition was increased to 1.5 ML thickness denoted as Cu(1.5)/MnO(4). Partial pressure of H_2 increased almost linearly with time up to 120 min in a course of reaction. The rate of H_2 production further increased when increasing Cu film thickness to 2 ML. These results indicate that Cu on MnO thin films is active for the reaction between methanol and oxygen at lower temperatures if there is a certain amount of Cu present on the surface. Fig. 3(B) is partial pressures of H_2 , CO, O_2 and CO_2 in the course of reaction between methanol and oxygen on the Cu(2)/MnO(4) films. The partial pressure of O_2 decreased slowly with time up to 120 min. Similar monotonous accumulation of hydrogen molecule was observed on Cu thin films on Ni(100), where H_2 and CO_2 were mainly produced with a small amount of CO, showing that the reaction is apparently independent

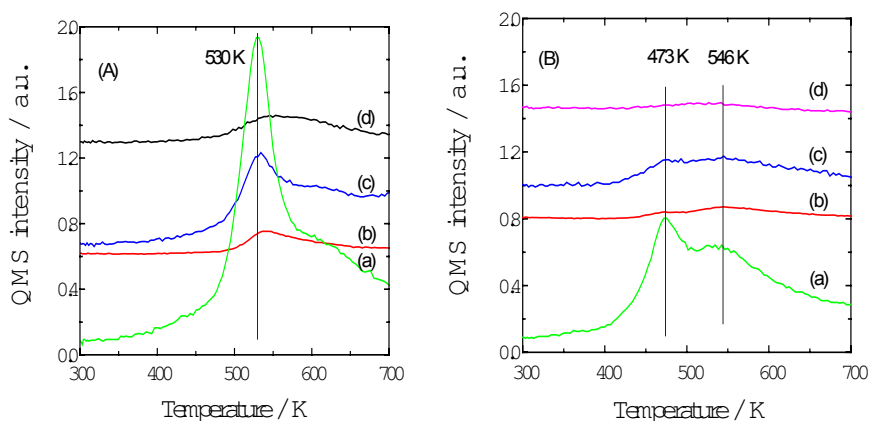


FIG. 4: TPD spectra after partial oxidation reaction of methanol on: (A) 3 ML Cu, and (B) Cu(2)/MnO(4) thin films: (a) CO₂, (b) H₂, (c) CO, (d) CH₂O.

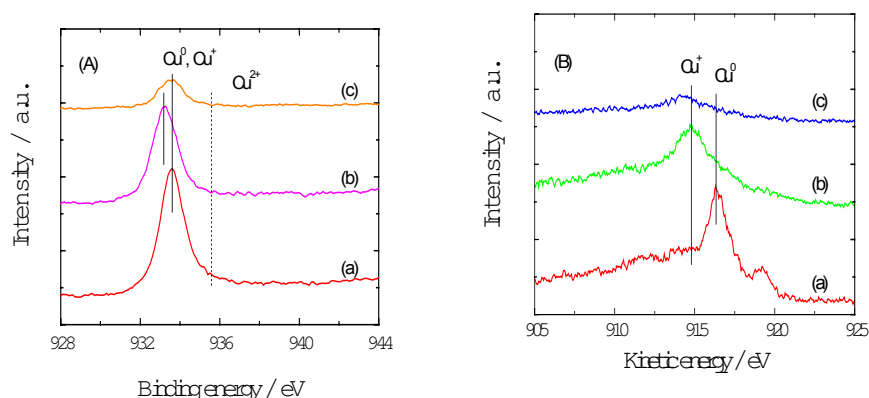


FIG. 5: (A) Cu 2p_{3/2} XP and (B) Cu LMM AES spectra for Cu(2)/MnO(4) films taken in the following conditions: (a) as grown, (b) after reaction, and (c) at grazing angle (68°) after reaction.

of reactant pressures [11]. Thus, addition of Cu 2 ML to MnO thin films greatly suppressed the formation of CO, and dramatically accelerated the rate of CO₂ formation. The low concentration of CO compared to CO₂ in the reaction products indicates partial oxidation reaction of methanol mainly occurs on Cu/MnO thin films, different from on the Mn and MnO surfaces. This result is in good agreement with the fact that Cu/MnO catalysts are more active for partial oxidation reaction of methanol as well as steam reforming reaction of methanol in hydrogen production at a lower temperature of 470 K than industrial catalysts of Cu/ZnO [5, 11]. Iwai *et al.* have studied partial oxidation reaction of methanol on Cu/Ni(100) as a function of Cu film thickness in a range of 1-6 ML at 550 K as model Cu/ZnO surfaces and observed the maximum rate of hydrogen production at 3 ML Cu films [11]. It is to be noted that the rate of partial oxidation reaction of methanol on Cu(2)/MnO(4) at the lower temperature of 470 K approaches one-fifth of the maximum rate on 3 ML Cu films at the higher temperature of 550 K.

To investigate surface species after reaction, 3 ML Cu films on Ni(100) after partial oxidation reaction of methanol was characterized using TPD as displayed in Fig. 4(A). The primary desorbing species was CO₂, which desorbed in a feature spanning from 350 to 700 K with a

largest, narrow peak centered at 530 K. Since CO₂, CO and H₂ desorbed almost simultaneously at nearly 530 K temperature, it is considered that the products of CO₂, CO and H₂ are derived from the decomposition of a common intermediate, surface formate [11, 15]. As shown in Fig. 4(B), Cu(2)/MnO(4) thin films show a similar feature of CO₂, CO, H₂ and CH₂O desorption as Cu 3 ML thin films. However, the intensity of each desorbed species decreased by about half. Compared to 3 ML Cu films on Ni(100), clear distinction in the spectrum is the appearance of two peaks at 473 K and 546 K. The former desorption is observed at the lower temperature than on Cu films, and this formate intermediate is considered to be related to the activity of partial oxidation reaction of methanol on Cu(2)/MnO(4) thin films.

C. XPS characterization of Cu(2)/MnO(4) thin films after reaction

In a recent paper, coexistence of Cu⁰ and Cu⁺ species on the catalyst surface is suggested to influence the formation of active sites on the copper oxide catalysts for methanol reforming reaction [5, 11]. To elucidate the active sites of Cu/MnO catalyst, the electronic states of Cu and Mn on Ni (100) have been investigated by XPS.

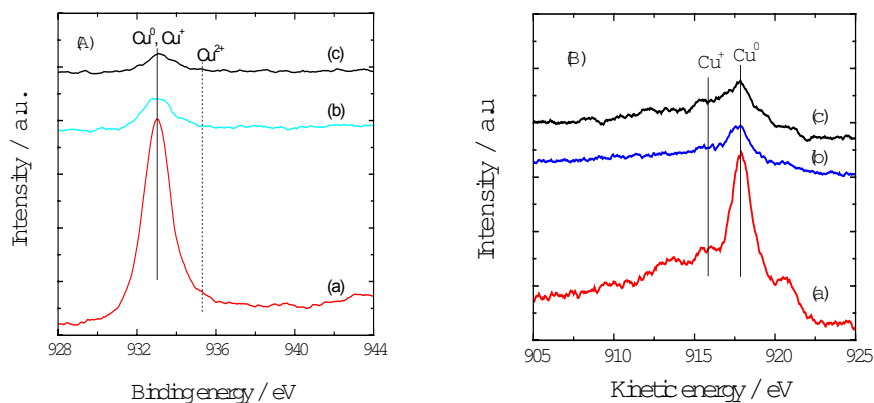


FIG. 6: (A) Cu $2p_{3/2}$ XP and (B) Cu LMM AES spectra for Cu(2)/MnO(4) films taken in the following conditions: (a) as grown, (b) after reaction, and (c) at grazing angle (68°) after reaction.

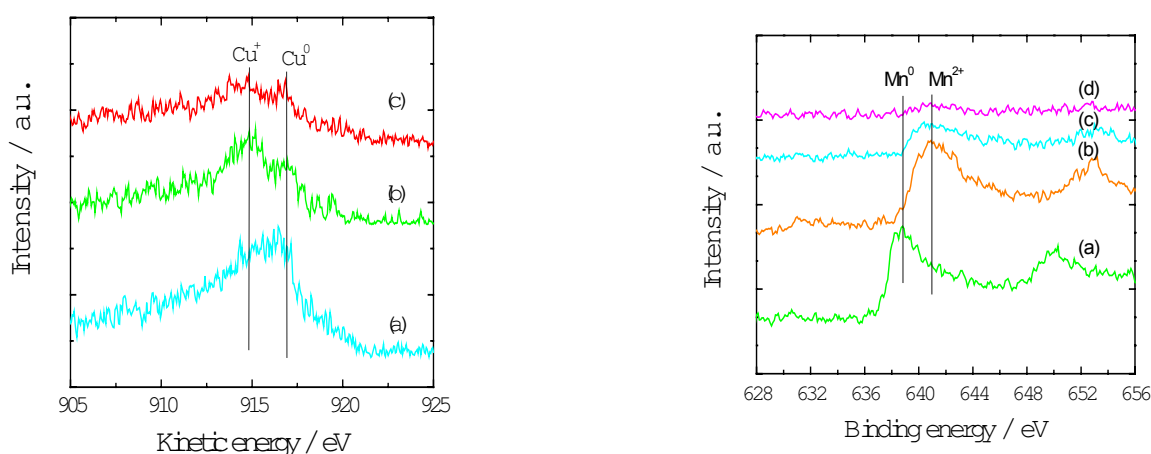


FIG. 7: Cu LMM AES spectra for Cu(0.5)/MnO(4) films taken in the following conditions: (a) as grown, (b) after reaction, and (c) at grazing angle (68°) after reaction.

Typical results for Cu(2)/MnO(4) films are shown by the combination of Cu $2p_{3/2}$, Cu LMM AES and Mn $2p_{3/2}$ XPS in the following conditions: (a) as grown, (b) after reaction, (c) at grazing angle (68°) after reaction.

Cu $2p_{3/2}$ XP spectra in Fig. 5(A) show a single peak located at the binding energy of approximately 934 eV which can be assigned to either Cu^+ or Cu^0 . According to Cu LMM Auger electron spectra as shown in Fig. 5(B), as grown films contained Cu^0 (917 eV) species with almost no Cu^+ (915 eV) species, but most of Cu^0 were converted to Cu^+ after the reaction. It demonstrates that a large part of topmost surface consists of Cu^+ after the reaction. In the reaction of 120 min, the production rates of H_2 and CO_2 are constant as shown in Fig. 3(B). It is most likely that active Cu^+ species was formed on the surface instantly after the introduction of reactant to the reaction cell. Furthermore, the binding energy of the $2p_{3/2}$ level for post reaction is shifted negatively about 0.5 eV toward the lower binding energy side, as compared to those observed from the metallic copper Cu^0 state. Many researchers have been reported the negative binding energy shift in Cu-Mn spinel oxide, and this anomalous chemical shift is interpreted to be due to the tetrahedral Cu^+

FIG. 8: Mn $2p_{3/2}$ XP spectra for Cu(2)/MnO(4) thin films taken in the following conditions: (a) after evaporation of 4ML Mn, (b) after exposure of oxygen to (a), (c) after evaporation of 2 ML Cu on (b), and (d) after reaction on (c).

species in the cubic spinel of Cu-Mn oxide [13, 16–19]. That is, it is expected that such an oxide structure including Cu^+ is formed on the surface of Cu(2)/MnO(4) in post reaction. There is a minor change in the peak intensity between as grown and post reaction films, although the peak intensity decreased when the detection angle was changed. The decrease in Cu intensities after the reaction is supposed to be influenced by the presence of absorbent as demonstrated in TPD above. For comparison with Cu/MnO films, Figs. 6(A) and (B) show Cu $2p_{3/2}$ XP and Cu LMM AES spectra of 3 ML Cu films on Ni(100) for as grown and post reaction films at the temperature of 550 K. There is a very large change of peak intensity between as grown and post reaction films, although no noticeable change in intensity was obtained at both detection angles after the reaction. Therefore, it strongly suggests Cu sintering in a large extent. Since the intensity ratio between both detection angles after the reaction was relatively small for Cu/MnO series, sintering is effectively inhibited. Thus, Figs. 5(A) and (B) indicate that metallic copper is changed into Cu^+ species-rich surface during partial oxidation reaction of methanol, and

Cu still forms a layered structure such as Cu₂O films on MnO template after the reaction. Furthermore, according to the AES for the Cu/Ni(100) films after the reaction, Cu⁰ species exists predominantly as shown in Fig. 6(B). Also, Fig. 7 shows the amount of Cu⁰ on Cu(0.5)/MnO(4) is greater than that on Cu(2)/MnO(4) after the reaction at 470 K. These results indicate that Cu⁺ species is stabilized by MnO under a reaction mixture of oxygen and methanol.

The interpretation above is further supported by Mn 2p_{3/2} XP spectra displayed in Fig. 8. According to the references, Mn 2p_{3/2} XP electronic states are reported as follows: the position of Mn⁰ is 638.8 eV and Mn²⁺ shifted to an approximately 2.1 eV high binding energy of 640.9 eV. Mn³⁺ and Mn⁴⁺ appeared at higher energies of 641.8 eV and 642.3 eV by about 3.0 eV and 3.5 eV shift, respectively [9, 13, 20–24]. In the present study, upon evaporation of 4 ML thick Mn on Ni substrate, Mn metallic electronic state appeared at 639 eV. Exposure the Mn films to oxygen caused a shift to Mn²⁺ (641 eV) electronic state without the intensity loss in consistent with the formation of MnO layers. Successive Cu evaporation equivalent to 2 ML thickness reduced the intensity of Mn²⁺ to one-third which is expected for the attenuation length corresponding to 2 ML thick. After partial oxidation reaction of methanol at 470 K, the peak intensity of Mn 2p_{3/2} was further reduced due to a large amount of adsorbate on the surface. Accordingly, these changes are in good agreement with the formation of Cu₂O overlayers on MnO films.

As mentioned before, we have revealed that Cu/MnO catalysts are active for partial oxidation reaction of

methanol as well as steam reforming reaction of methanol in hydrogen production at a lower temperature of 470 K compared to Cu/ZnO catalysts normally operating around 523 K. As for the latter model surface, we have studied partial oxidation reaction of methanol on Cu/Ni(100) as a function of Cu film thickness in a range of 1–6 ML at 550 K and observed the maximum rate of hydrogen production at 3 ML Cu films which nucleate to form three-dimensional clusters consisting of predominantly Cu⁰, as demonstrated in Fig. 6. In contrast, the activity of Cu(2)/MnO(4) for partial oxidation reaction of methanol at the lower temperature of 470 K is most likely related to the presence of Cu⁺ as Cu₂O overlayers which are stabilized by MnO underlayers acting as a template.

IV. CONCLUSIONS

Cu overlayers on MnO thin films have been fabricated on Ni(100) substrate as a model surface of Cu/MnO catalysts which are derived from Cu-Mn oxides prepared by co-precipitation method. In the reaction of methanol and oxygen, Cu films thicker than 1.5 ML on MnO produced hydrogen with a low concentration of CO compared to CO₂ at the low temperature of 470 K in agreement with Cu/MnO catalysts active for partial oxidation reaction of methanol as well steam reforming reaction of methanol. Post-reaction surface analysis by XPS and AES of Cu and Mn have revealed that Cu metallic films are mainly converted to Cu⁺ during the reaction and Cu₂O overlayers are stabilized by MnO underlayers acting as a template.

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