In Situ Spectroscopic and Computational Studies on a MnO₂−CuO Catalyst for Use in Volatile Organic Compound Decomposition

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ABSTRACT: In situ near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and density functional theory calculations were conducted to demonstrate the decomposition mechanism of propylene glycol methyl ether acetate (PGMEA) on a MnO₂−CuO catalyst. The catalytic activity of MnO₂−CuO was higher than that of MnO₂ at low temperatures, although the pore properties of MnO₂ were similar to those of MnO₂−CuO. In addition, whereas the chemical state of MnO₂ remained constant following PGMEA dosing at 150 °C, MnO₂−CuO was reduced under identical conditions, as confirmed by in situ NEXAFS spectroscopy. These results indicate that the presence of Cu in the MnO₂−CuO catalyst enables the release of oxygen at lower temperatures. More specifically, the released oxygen originated from the Mn−O−Cu moiety on the top layer of the MnO₂−CuO structure, as confirmed by calculation of the oxygen release energies in various oxygen positions of MnO₂−CuO. Furthermore, the spectral changes in the in situ NEXAFS spectrum of MnO₂−CuO following the catalytic reaction at 150 °C corresponded well with those of the simulated NEXAFS spectrum following oxygen release from Mn−O−Cu. Finally, after the completion of the catalytic reaction, the quantities of lactone and ether functionalities in PGMEA decreased, whereas the formation of C==C bonds was observed.

INTRODUCTION

The volatile organic compounds (VOCs) released from industrial processes in factories and during fossil fuel burning are air pollutants with the potential to harm both human health and the environment. For example, propylene glycol methyl ether acetate (PGMEA) is used in the manufacture of semiconductors and displays, and it can be detected in air. It is therefore necessary to develop techniques to remove VOCs such as PGMEA from the air. For this purpose, metal oxide catalysts have drawn significant attention to date due to their low costs compared to noble metal catalysts. In recent years, catalytic activities have dramatically increased at low temperatures through the use of hybrid metal oxides, thereby indicating that these materials have the potential for application in industrial VOC removal.

Among the various hybrid metal oxides examined to date, Mn−Cu oxides have received particular attention for removing VOCs. For example, Lamb et al. reported the excellent activity of CuMn₂O₄ in the oxidation of CO at low temperatures. Since then, the superior activity of Mn−Cu oxides in VOC removal has also been reported. For example, Morales et al. reported that Mn−Cu oxides successfully catalyzed the oxidation of ethanol, with complete conversion being achieved at 200 °C. Interestingly, the presence of 14 wt % Cu decreased the crystallinity of the Mn oxides, thereby increasing the catalytic activity. In addition, the poorly-crystalline structure of Mn−Cu oxides increased the number of oxygen vacancies. Furthermore, Njagi et al. reported that Mn−Cu oxides prepared via a redox method removed all of the CO at the ambient temperature. These catalysts also exhibit a high catalytic activity in the oxidation of propane, toluene, and chlorobenzene, and such high catalytic activities can be ascribed to the presence of Cu²⁺ + Mn⁴⁺ ⇌ Cu⁺ + Mn⁵⁺ redox cycle, which results in the electron transfer between the Mn and Cu cations. As the crystalline phase has an enrichment of Cu⁺ and Mn⁴⁺ on the surface, the redox cycle appears to be activated to a greater extent in the amorphous phase than in the crystalline phase.

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To date, three models have been proposed for the mechanism of VOC oxidation over Mn-based oxides, namely, the Mars–van Krevelen (MVK) model, the Langmuir–Hinshelwood model, and the Eley–Rideal model. For example, Li et al. studied the intrinsic kinetics of the catalytic combustion of ethylene in a CO₂ stream over Mn–Cu oxide catalysts and showed that the MVK model was consistent with the intrinsic kinetic experimental data. In addition, Sun et al. studied the mechanism of oxidation of toluene over KMn₈O₁₆·nH₂O. In the absence of atmospheric oxygen (MVK model), C₆H₅−CH₂ is bonded to the surface oxygen species in KMn₈O₁₆·nH₂O and toluene is decomposed. The introduced oxygen vacancy on the surface is supplied from the bulk oxygen.

However, the detailed mechanism involving oxygen release from the hybrid metal oxide and the structural changes taking place in the VOCs during this transformation remain unclear. It is therefore expected that an improved understanding of these mechanisms will lead to the optimization of the structures of Mn–Cu oxides to enhance the catalytic activity. Thus, we herein report the use of in situ surface analysis to examine the mechanism of the catalytic reaction. More specifically, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy will be carried out in an ultrahigh-vacuum system, as atmospheric oxygen can be immediately introduced into the Mn–Cu oxides following the release of oxygen. We will also compare the catalytic activities of MnO₂ and MnO₂–CuO catalysts in the reaction with PGMEA using in situ NEXAFS experiments. In addition, the position of the oxygen released from MnO₂–CuO will be estimated by calculating the energies for oxygen release in various positions of MnO₂–CuO and comparing the obtained and simulated NEXAFS spectra. Structural changes of the decomposed VOCs on the MnO₂–CuO catalyst will also be revealed.

RESULTS AND DISCUSSION
Examination of the morphologies of the MnO₂ and MnO₂–CuO catalysts by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed the presence of aggregates consisting of numerous nanostructured particles measuring approximately 10 nm (Figure 1a–d). In addition, the electron diffraction patterns of the TEM image take the form of broad halos (Figure 1c,d), indicating that these catalysts contain an amorphous phase. Furthermore, in the powder X-ray diffraction (PXRD) pattern of MnO₂ (Figure 1e)
three peaks at 2θ = 20, 37, and 66° were observed. More specifically, the peak at 2θ = 20° originated from the glass holder, whereas the broad peaks at 2θ = 37° and 66° originated from the MnO₂ spacing in an octahedral arrangement, thereby indicating the presence of an amorphous MnO₂ phase.²⁰ Although it has been reported that highly-crystalline MnO₂ forms through calcination of the precipitated MnO₂ above 400 °C, calculation of the MnO₂ and MnO₂−CuO catalysts was carried out at 200 °C, as the amorphous and porous MnO₂ exhibits a high catalytic activity in the decomposition of VOCs.¹⁻²⁻³⁻²¹ In this case, the Mn/Cu ratio was estimated to be 25.5:6.3 from the X-ray photoelectron spectroscopy (XPS) results (Figure S1, Supporting Information (SI)), and so no peaks originating from CuO were detected due to the low Cu content (Figure 1e). Although the crystal phases of MnO₂ and MnO₂−CuO were not estimated from the PXRD patterns, the Raman spectra of both MnO₂ and MnO₂−CuO contain a peak at 647 cm⁻¹, which corresponds to β-MnO₂ (Figure 1f).²⁴ In the case of MnO₂−CuO, no CuO peak was detected at 626 cm⁻¹,²⁵ which is consistent with the PXRD result. In addition, to estimate the dispersion state of Cu in Mn₄, energy-dispersive spectrometry was conducted for bulk analysis, and the Mn/Cu ratio was calculated to be 24.6:5.9, which is similar to the value obtained using XPS, thereby indicating that CuO is dispersed homogeneously in MnO₂.

### Table 1. Pore Properties of MnO₂ and MnO₂−CuO

| pore property | MnO₂ | MnO₂−CuO |
|--------------|------|---------|
| BET surface area (m² g⁻¹) | 398 | 388 |
| pore volume (cm³ g⁻¹) | 0.33 | 0.35 |
| pore diameter (nm) | 3.34 | 3.65 |

Teller (BET) surface areas, pore volumes, and pore diameters. The large BET surface areas (388−398 m² g⁻¹), pore volumes (0.33−0.35 cm³ g⁻¹), and pore diameters (3.34−3.65 nm) of these samples originate from their amorphous structures (Figure 1a−e), which contain both micropores (Table 1) and mesopores (Figure S2, SI). In addition, as the pore properties of these two samples are comparable, these properties can be ignored when addressing the different catalytic reactivities of the two samples later in the discussion.

The oxygen release performance of each catalyst was then estimated by measuring the temperature-programmed reduction (TPR) (Figure 2a,b), as this is an important factor in the decomposition of VOCs. The reduction process was initiated at 118 and 91 °C for MnO₂ and MnO₂−CuO, respectively, and major reduction peaks were observed at 253 and 202 °C for the MnO₂ and MnO₂−CuO catalysts, respectively. In addition, the peak at 285 °C observed for MnO₂ could be attributed to the bulk MnO₂ species, whereas the peak at 253 °C originated from the surface MnO₂. Similarly, the peaks at 247 and 284 °C in the MnO₂−CuO sample could be attributed to the surface and the bulk, respectively, thereby indicating that any MnO₂ interacting with the Cu species could be reduced at lower temperatures than pure MnO₂. A similar result has been reported previously for the CuO−NiO samples.²⁶ These results indicate that MnO₂−CuO releases oxygen at lower temperatures than does MnO₂. In addition, Figure 2c shows the catalytic activities for the oxidation of PGMEA over MnO₂ and MnO₂−CuO, where it is clear that MnO₂−CuO exhibited a higher activity than MnO₂. More specifically, the T₉₀ values for MnO₂ and MnO₂−CuO were 202 and 171 °C, respectively, where T₉₀ is the temperature at which 90% PGMEA conversion is achieved.

To determine the surface chemical states of MnO₂ and MnO₂−CuO before reaction with PGMEA, XPS analysis was carried out (Figure 3). As shown in Figure 3a, the Mn 2p spectrum of the synthesized MnO₂ exhibits a separation of 11.8 eV between the Mn 2p₁/₂ and Mn 2p₃/₂ peaks, indicating that the oxidation state is Mn⁴⁺ (Figure 3a).²⁷ In addition, the Mn 2p spectrum (Figure 3a) of the synthesized MnO₂−CuO sample exhibits a separation of 11.5 eV, which suggests that the average oxidation states of Mn in MnO₂ and MnO₂−CuO are different. Furthermore, the Cu 2p spectrum (Figure 3b) of MnO₂−CuO exhibits a separation of 19.8 eV between the Cu 2p₁/₂ and Cu 2p₃/₂ peaks. In addition to the presence of two satellite peaks at 962.6 and 944.4 eV, these results confirm that the oxidation state is Cu²⁺.²⁸ A more detailed estimation of the oxidation state of Cu was conducted by the calculation of the peak area ratio between the Cu satellite peak and the Cu 2p₁/₂ peak (Figure S3, SI).

The oxidation states of Mn in the synthesized MnO₂ and MnO₂−CuO samples were then estimated from the Mn 2p and Mn 3s spectra in detail. The peak maximum in the Mn 2p₁/₂ spectrum of MnO₂ (642.9 eV) shifted to 642.6 eV in the spectrum of MnO₂−CuO (Figure 3a). In addition, the full width at half-maximum of the peak in the Mn 2p₁/₂ spectrum of MnO₂ (2.42 eV) was smaller than that of the MnO₂−CuO sample (2.72 eV) (Figure 3a). These results indicate that small quantities of Mn⁷⁺ and Mn³⁺ exist in MnO₂−CuO. In addition, the presence of reduced Mn in MnO₂−CuO was confirmed by the Mn 3s spectrum upon consideration of the separation between the two main peaks. More specifically, a separation of 4.8 eV for MnO₂ (Figure 3c) indicates an oxidation state of Mn⁴⁺,²⁹ whereas a 5.2 eV separation for MnO₂−CuO indicates the reduction of Mn,²⁹ which proceeds due to a decrease in the number of oxygen atoms in Mn−O in the presence of Cu²⁺.³⁰

Thus, to estimate the variation in MnO₂ and MnO₂−CuO chemical states following the reaction with PGMEA, in situ NEXAFS experiments were conducted. Figure 4a shows the obtained in situ NEXAFS Mn L₃-edge spectra of MnO₂ and MnO₂−CuO prior to the reaction, where five peaks originating from Mn²⁺, Mn³⁺, and Mn⁴⁺ can be clearly distinguished,²⁰ thereby confirming a complex multiplet electronic structure containing Mn²⁺, Mn³⁺, and Mn⁴⁺. In addition, the observation that MnO₂−CuO was reduced to a greater extent than MnO₂ (Figure 4a) corresponded with the XPS result (Figure 3a,c). Furthermore, Figure 4b shows the obtained Mn L₃-edge spectra of MnO₂ before and after the reaction with PGMEA at 150 °C for 30 min, and it is apparent that no change in the chemical state of Mn in MnO₂ was observed. However, following the reaction of MnO₂−CuO with PGMEA at 150 °C (Figure 4c), reduction was confirmed, which corresponds with the results from the catalytic activity experiments (Figure 2c).

Figure 4d shows the obtained O K-edge spectra for MnO₂−CuO before and after reaction with PGMEA at 150 °C for 30 min. The peaks observed between 530 and 535 eV correspond to the transition from O 1s to the mixing bands of O 2p and Mn 3d.³¹ The peaks originating from CuO were not assigned due to the small quantity of CuO present in the sample. As shown, prior to the reaction, three peaks were observed, i.e., a₁, a₂, and a₃, which originate from the transition from O 1s to e⁻, t₂g−down, and e⁻−down, respectively (Figure 4d). However, after the reaction with PGMEA, only two peaks
(i.e., b1 and b2) were observed, with b1 corresponding to the transition to $t_{2g}$-down and $e_g$-down peaks. These changes can be explained using a schematic diagram of the Mn$^{4+}$ and Mn$^{3+}$ energy levels, such as that shown in Figure 4e. For example, the $e_g$-up level was unoccupied in the Mn$^{4+}$ energy level, but the $e_g$-up level was occupied by a single electron in the Mn$^{3+}$ energy level. This occupation therefore decreases the probability of a transition from O 1s to $e_g$-up, whereas the probability of a transition from O 1s to $t_{2g}$-down and $e_g$-down was increased. Thus, the intensity of peak a1 was greater than that of peak b1, whereas the intensity of peak b2 was greater than that of peaks a2 and a3 due to reaction with PGMEA. These results indicate that a partial change in the chemical state from Mn$^{4+}$ to Mn$^{3+}$ occurred during the reaction with PGMEA. We also estimated the change in state of Mn at 250°C (Figure S4, SI) and found that both MnO$_2$ and MnO$_2$$^{-}$CuO were reduced, with the degree of reduction increasing with increasing reaction time.

The position of oxygen release from MnO$_2$–CuO during the reaction with PGMEA at 150°C was then estimated by calculating the energies required for oxygen release from the various positions of the MnO$_2$–CuO structure (Figure 5a). For the model structure of MnO$_2$–CuO, approximately 20% of Mn in $\beta$-MnO$_2$ is replaced by Cu (Figure 5a), as indicated by the Mn/Cu ratio of 25.5:6.3 estimated from the XPS results (Figure S1, SI). The three types of oxygen atom bonded to two neighboring Mn or Cu atoms were labeled as O(2)-A, O(2)-B, and O(2)-C vacancies, whereas the two types of oxygen atom bonded to three neighboring Mn or Cu atoms were labeled as O(3)-A and O(3)-B vacancies. The obtained energies were as follows: O(2)-A (0.23 eV), O(2)-B (1.14 eV), O(2)-C (1.07 eV), O(3)-A (2.43 eV), and O(3)-B (1.01 eV). In addition, the energy required for oxygen release from MnO$_2$ was calculated to be 1.04 eV, which indicates that oxygen bonded to Cu (i.e., Mn=O–Cu), which is an O(2)-A vacancy in the top layer of MnO$_2$–CuO, is the energetically most favorable site for oxygen release (0.23 eV).

To clarify the structures of these materials, their spectra were simulated computationally. Thus, the simulated spectra shown in Figure 5 were obtained before and after the introduction of an O(2)-A vacancy into the structure of MnO$_2$–CuO (Figure 5a). The photon energy of the simulated spectra was calibrated based on the peak value of the experimental measurement. Unlike the experimental results, the simulated spectra exhibited sharper peaks due to the crystalline structures (Figure 5b,c). However, in the simulated Mn L$_3$-edge spectra (Figure 5b), the differences observed were similar to those of the experimentally obtained spectra (Figure 4c), in which the intensities of the peaks originating from Mn$^{3+}$ and Mn$^{4+}$ decreased upon the introduction of an O(2)-A vacancy. Similarly, the simulated O K-edge spectra (Figure 5c) exhibited spectral changes similar to those obtained experimentally (Figure 4d), confirming that the position of oxygen release was indeed Mn=O–Cu. Calculations of the NEXAFS spectra were also performed for two less stable models containing oxygen vacancies at the O(2)-B and O(2)-C positions (Figure S5). As indicated, the Mn L-edge and O K-edge NEXAFS spectra differed slightly depending on the
position of oxygen defect formation. Thus, in combination with the above results, it is expected that oxygen defects will occur mainly at the O(2)-A position, and that oxygen will participate in the reaction as indicated in our proposed mechanism.

Finally, the mechanism for PGMEA decomposition on MnO$_2$ at 150 °C was estimated by in situ C K-edge NEXAFS experiments. Figure 6a shows the structure of PGMEA, which contains two different oxygen-containing functional groups, namely, lactone and ether groups, which contain no C=C bonds. Figure 6b,c shows the in situ C K-edge NEXAFS spectra obtained for MnO$_2$ and MnO$_2$–CuO following the reaction with PGMEA at 150 °C for 5 and 30 min. In these spectra, the signals at 285 and 292 eV correspond to the C=C π* and C–C π* functionalities, whereas the peak at 288 eV can be attributed to C=O π* and C–O π*. As the MnO$_2$ and MnO$_2$–CuO catalysts were prepared using KMnO$_4$ precursor, two peaks at 298 and 300 eV originating from the potassium L$_3$ and L$_2$ edges were present. In the spectra obtained for the MnO$_2$ catalysts reacted with PGMEA at 150 °C for 5 and 30 min (Figure 6b), no changes were observed upon increasing the reaction time, thereby indicating that PGMEA adsorption had no effect on its structure. A similar tendency was observed for the Mn$_{1-x}$O$_x$–CuO catalyst, the PGMEA structure was altered upon increasing the reaction time (Figure 6b). More specifically, in the spectra shown in Figure 6b, the intensities of the peaks originating from C=O π* and C–O π* decrease, whereas that of the peak corresponding to C=C π* increase. These results indicate that PGMEA was decomposed by the oxygen of the MnO$_2$–CuO catalyst, resulting in the breakdown of lactone and ether functional groups and the formation of C=C bonds.

### CONCLUSIONS

To investigate the effect of Cu addition to a MnO$_2$ catalyst on the decomposition of propylene glycol methyl ether acetate (PGMEA), MnO$_2$ (398 m$^2$ g$^{-1}$) and MnO$_2$–CuO (388 m$^2$ g$^{-1}$) catalysts with similar specific surface areas were synthesized and the catalytic process was investigated. We found that the catalytic activity of MnO$_2$–CuO was higher than that of MnO$_2$ where the $T_{90}$ values for MnO$_2$ and MnO$_2$–CuO were 202 and 171 °C, respectively. These results corresponded with the calculated results for the oxygen release energy for both MnO$_2$ (1.04 eV) and MnO$_2$–CuO (0.23 eV). Calculations also confirmed that oxygen is released from the Mn–O–Cu position on the top layer of the MnO$_2$–CuO structure. Furthermore, the obtained in situ near-edge X-ray absorption fine structure (NEXAFS) spectra indicated that the chemical state of the Mn present in MnO$_2$ was not altered following PGMEA dosing at 150 °C, whereas the Mn present in MnO$_2$–CuO did react with PGMEA. The spectral changes observed in the obtained NEXAFS spectrum of MnO$_2$–CuO correlated well with the simulated NEXAFS spectrum following oxygen release from the Mn–O–Cu site. Finally, the reaction of MnO$_2$–CuO with PGMEA promoted the decomposition of the lactone and ether functional groups in PGMEA, whereas the formation of C=C bonds was observed. This improved understanding of the decomposition mechanism should lead to the optimization of the structures of Mn–Cu oxides to ultimately enhance the catalytic activity.

### EXPERIMENTAL SECTION

**Catalysts.** MnO$_2$ with a specific surface area of 398 m$^2$ g$^{-1}$ (Table 1) was synthesized from a mixture of aqueous solutions of KMnO$_4$ (≥99.0%, Samchun Chemical Co., Ltd.) and...
Mn(CH₃COO)₂·4H₂O (≥99.9%, Junsei Chemical Co., Ltd.). More specifically, an aqueous solution of KMnO₄ was added slowly to an aqueous solution of Mn(CH₃COO)₂·4H₂O in a 2:3 molar ratio. The precipitation of MnO₂ then took place according to the reaction outlined in eq 1

\[
2\text{KMnO}_4(s) + 3\text{Mn(CH}_3\text{COO)}_2(s) + 2\text{H}_2\text{O(l)} \\
\rightarrow 5\text{MnO}_2(s) + 2\text{CH}_3\text{COOK(s)} + 4\text{CH}_3\text{COOH(l)}
\]  

After stirring the solution for 3 h at 25 °C, the suspension was filtered and the precipitate washed with ultrapure water until a neutral pH was achieved. The obtained product was then dried at 80 °C for 24 h prior to calcination at 200 °C for 24 h.

MnO₂−CuO with a specific surface area of 388 m² g⁻¹ (Table 1) was synthesized by the addition of an aqueous solution of Cu(CH₃COO)₂·H₂O (≥99.0%, Junsei Chemical Co., Ltd.) to an aqueous solution of the previously prepared MnO₂ in a Mn/Cu molar ratio of 4:1. Precipitation, filtration, washing, drying, and calcination of the MnO₂−CuO catalyst were carried out according to the above procedure for MnO₂.

**Catalytic Activity Measurements.** The catalytic activities of the prepared MnO₂ and MnO₂−CuO catalysts were evaluated in the total oxidation of PGMEA in a fixed-bed flow reactor at atmospheric pressure. The catalytic powders were pressed, crushed, and sieved to a size of 18−20 mesh (0.84−1.00 mm), and PGMEA vapor was fed into the reactor by adding a mixture of PGMEA (200 ppm) and O₂ gas at a total flow rate of 2500 cm³ min⁻¹. The gas hourly space velocity was set at 10 000 h⁻¹, and the PGMEA conversion was estimated using a gas chromatograph equipped with a flame ionization detector (Agilent 6890N, Agilent Technologies Co., Ltd.).

**Characterization.** The pore properties of the catalysts were measured by N₂ adsorption at −196 °C (TriStar II 3020, Micromeritics Instrument Corp.). Prior to the measurements, each catalyst was outgassed at 150 °C for 2 h. The morphologies of the catalyst samples were observed by scanning electron microscopy (SEM; S4800, Hitachi Ltd.) and transmission electron microscopy (TEM; Titan G2 80-200, FEI). For the TEM observations, each catalyst was observed at an acceleration voltage of 300 kV. The crystalline structures of the catalysts were analyzed by powder X-ray diffraction (PXRD; SmartLab, Rigaku Co.) with Cu Kα radiation (λ = 0.1542 nm) and by Raman spectroscopy (NRS 3200, JASCO Co.) with a 532 nm laser. The reduction temperatures of the catalysts were then determined by temperature-programmed reduction (TPR) measurements between 25 and 900 °C at a heating rate of 5 °C min⁻¹. A mixture of H₂/N₂ (1:9) was introduced over the catalyst sample in a quartz tube at a rate of 10 cm³ min⁻¹ and at ambient pressure. The quantity of H₂ consumed in the reduction of the sample was monitored using a thermal...
conductivity detector. The surface chemical states were characterized by X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi, Thermo Fisher Scientific Inc.). XPS analysis was conducted using an Al Kα X-ray gun at 10 mA and 15 kV and with a pass energy of 10 eV. The flood gun was used as a charge neutralizer. The C 1s peaks (285 eV) of the catalyst XPS

Figure 5. (a) Representation of the MnO₂−CuO structure. Twenty percent of Mn in β-MnO₂ is replaced by Cu. (b) Simulated Mn L₃-edge spectra of MnO₂−CuO and MnO₂−CuO (O(2)-A vacancy). (c) Simulated O K-edge spectra of MnO₂−CuO and MnO₂−CuO (O(2)-A vacancy). The spectra of MnO₂−CuO were obtained using the structure shown in (a). The spectra of MnO₂−CuO (O(2)-A vacancy) were obtained after introducing an O(2)-A vacancy into the structure shown in (a).

Figure 6. (a) Structure of PGMEA. (b) C K-edge spectra of MnO₂ after reaction with PGMEA at 150 °C for 5 and 30 min. (c) C K-edge spectra of MnO₂−CuO after reaction with PGMEA at 150 °C for 5 and 30 min.
spectra were used for calibrating the binding energy values. All of the maximum intensities of the Mn 2p spectra were adjusted to 1.0, and the intensities of the other spectra were normalized.

Changes in the surface chemical states after reaction with PGMEA were subsequently analyzed by in situ NEXAFS at the 8A2 undulator beamline of the Pohang Light Source in the Pohang Accelerator Laboratory, Korea. The partial electron yield detection mode was used for the NEXAFS spectra by recording the sample current normalized to a signal current measured simultaneously using a gold mesh in an ultrahigh vacuum (UHV). A P-polarized synchrotron photon beam (≈85%) with an energy of 630–665 eV for the Mn L-edge spectra, 520–565 eV for the O K-edge spectra, and 270–320 eV for the C K-edge spectra was employed. In addition, the probing depth was ≈50 Å for surface-sensitive measurements and the spectral energy resolution (ΔE) was 0.1 eV. All of the NEXAFS experiments were carried out in a UHV chamber, which was connected to a preparation chamber with a gas-dosing system. The NEXAFS spectra of the MnO2 and MnO2−CuO samples were measured before and after dosing with gaseous PGMEA. Each catalyst was loaded in the preparation chamber and heated at 200 °C for 30 min to remove any surface impurities. The samples were then cooled to room temperature and the NEXAFS spectra recorded. To estimate the changes in the surface chemical states after reaction with PGMEA, the samples were first heated at 150 °C for 30 min, then exposed to gaseous PGMEA for either 5 or 30 min, and the NEXAFS spectra were recorded. The pressure of the chamber was increased from 2.0 × 10−8 to 9 × 10−6 Torr during PGMEA dosing. The maximum intensities of all of the peaks in the Mn L-edge spectra originating from Mn2+ were adjusted equally, and the intensities of the other spectra were normalized.

Computational Approach. To assign the spectral features of our NEXAFS experiments, we calculated the theoretical NEXAFS spectra using the plane-wave density functional theory code CASTEP of the Materials Studio 8.0 software suite. The surface structures of the MnO2-based catalysts, namely, MnO2 and MnO2−CuO, were taken from the (110) surface. Their surface structures and energies were then determined using the generalized gradient approximation functional of PBESol with a plane wave cutoff of 500 eV. A 6 × 6 × 9 k-point mesh in the Brillouin zone was applied for appropriate scaling of the supercells.

Theoretical calculations of the NEXAFS spectra employ a “core−hole” pseudopotential, which is generated by removing half an electron from the 1s state of an atom during pseudopotential generation.34−37 In the CASTEP calculation process, ultrasoft pseudopotentials were generated on the fly when performing core−hole calculations.38,39 However, a pseudopotential code is not appropriate to describe the core-excited state, as the wavefunctions of the valence and conduction bands can only be described as pseudowave functions rather than all-electron wavefunctions in the general plane-wave pseudopotential code. Hence, a projector-augmented wave reconstruction is used in the CASTEP process to reduce the pseudopotential error, although little deviation from the spectra generated using an all-electron code was observed.35

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