Roles of ZnO in Cu/Core–Shell Al–MCM-41 for NO Reduction by Selective Catalytic Reduction with NH₃: The Effects of Metal Loading and Cu/ZnO Ratio

Thidarat Imyen,† Wanwisa Limphirat,§ Günther Rupprechter,‖ and Paisan Kongkachuichay*†∥

1Department of Chemical Engineering, Faculty of Engineering and 2Research Network of NANOTEC-KU on NanoCatalysts and NanoMaterials Sustainable Energy and Environment, Kasetsart University, Bangkok 10900, Thailand
3Synchrotron Light Research Institute, Nakhon Ratchasima 30000, Thailand
4Institute of Materials Chemistry, Technische Universität Wien, Getreidemarkt 9/1060, Vienna 1060, Austria

ABSTRACT: Cu−ZnO/Al−MCM-41 catalysts were studied for NO₃ reduction. The total metal loading was varied as 3, 5, and 7 wt %, whereas the Cu-to-ZnO ratio was fixed at 1:1. Too high metal loading led to lower reducibility of Cu²⁺, as CuO and ZnO covers on the catalyst surface could partially block pores and hinder gas molecules to access the Cu²⁺ ions. Subsequently, Cu loading was fixed at 2.5 wt %, whereas ZnO content was varied as 0, 2.5, and 3.5 wt %. The results demonstrated that 2.5Cu−2.5ZnO/MCM-41 exhibits the best catalytic activity, as it gave the average NO conversion of 87%.

1. INTRODUCTION

Copper-based zeolites have been extensively investigated for selective catalytic reduction of NO by ammonia (NH₃-SCR) due to their good activity over a wide temperature range and high selectivity toward N₂.⁰ Although Cu/ZSM-5 was discovered as an active catalyst for NO reduction,¹ the main drawback of Cu/ZSM-5 is the lack of stability and durability.² However, it has been found that Cu/Al−MCM-41 shows similar activity to that of Cu/ZSM-5 but exhibits better thermal stability due to its mesoporous structure. It was reported in our previous work³ that Al−MCM-41 with the core−shell structure, in which the core part is mesoporous silica and the shell part is aluminosilicate, enhances the catalytic activity for NO reduction. With the presence of aluminosilicate shell, specific active sites of Cu are created surrounding the outer surface, leading to better accessibility of the copper active sites. Moreover, a better accessibility of these copper sites is helpful for the transformation of Cu²⁺ to Cu⁺, which is beneficial for NO reduction.

The oxidation state of copper plays an important role in NO reduction. It has been suggested that Cu⁺ is the key active species for NO reduction,⁴ and the transition between Cu²⁺ and Cu⁺ species taking place under SCR reaction was found to be the key factor in this reaction.¹ The nature of Cu can be modified by a promoter and different metal loadings. Our previous work⁵ reported that the introduction of Zn in the form of ZnO can improve the catalytic performance of Cu/core−shell Al−MCM-41, as it provides surface oxygen for nitrite and nitrate formation and also promotes the number of Cu⁺. However, the effects of ZnO content on the nature of Cu have not been studied yet. Therefore, in this work, the effects of metal loading and Cu-to-ZnO ratio on the nature of copper and thus the catalytic performance of Cu−ZnO/Al−MCM-41 were investigated.

2. RESULTS AND DISCUSSION

2.1. Morphology of Prepared Catalysts. Transmission electron microscopy (TEM) images of Cu−ZnO/Al−MCM-41 catalysts with different metal contents shown in Figure 1 illustrate the core−shell structure of mesoporous silica−aluminosilicate composites. The shell thickness is in the range of 10−20 nm. During metal loading, loaded metals are expected to be mainly at the aluminosilicate shell and the TEM images demonstrate that the core−shell structure is still preserved after the introduction of metals onto the support. On the other hand, the surface morphology of the catalyst was observed by SEM. As shown in Figures S1a, S2a, and S3a, the images exhibit the agglomeration of spherical particles having size around 100 nm, which is a typical feature of mesoporous materials.⁶ Furthermore, energy-dispersive system (EDS) mapping shows that both Cu and Zn are well-distributed on the surface of Al−MCM-41 support (see Supporting Information).
Figures S1b, S2b, and S3b). It can be seen that with increasing metal loading, the metals are more plentiful on the surface of the catalyst; however, the metals are still well-distributed.

2.2. Crystal Structures. The X-ray diffraction (XRD) patterns of Cu–ZnO/Al–MCM-41 catalysts with different metal loadings are presented in Figure 2. The peaks at 2θ of 35.5, 38.8, and 44.5° are attributed to CuO phase, whereas the diffraction peaks at 2θ of 36.0 and 38.1° are assigned to ZnO phase. There is no sign of mixed Cu–Zn oxide formation in the prepared catalysts. As shown in Figure 2, the intensity of the diffraction peaks is rather weak, implying that Cu and Zn species in these catalysts have very small crystallite size. However, by using impregnation to increase metal contents in the catalysts, both Cu and Zn crystallite sizes become bigger, as indicated by the higher intensity of the diffraction peaks.

2.3. Textural Properties. The Brunauer–Emmett–Teller (BET) surface area, average pore diameter, and pore volume of the prepared catalysts are summarized in Table 1. It can be seen that BET surface area of Cu–ZnO/Al–MCM-41 catalysts decreased with increasing metal contents. This is because CuO and ZnO species formed on the surface of the catalysts could
Table 1. Textural Properties and Metal Contents of Cu–ZnO/Al–MCM-41 Catalysts with Different Metal Loadings

| sample       | Cu content (wt %) | Zn content (wt %) | BET area (m²/g) | pore diameter (nm) | pore volume (cm³/g) |
|--------------|------------------|------------------|-----------------|-------------------|-------------------|
| 1.5Cu–1.5ZnO| 1.41             | 1.54             | 1093            | 4.65              | 1.27              |
| 2.5Cu–2.5ZnO| 2.09             | 2.52             | 1076            | 4.31              | 1.19              |
| 3.5Cu–3.5ZnO| 3.20             | 3.58             | 983             | 5.63              | 1.38              |

partially block pores of the catalyst, resulting in the decrease of pore diameter, pore volume, and surface area. However, for 3.5Cu–3.5ZnO sample, the pore diameter and pore volume increased whereas BET surface area decreased. These results suggest that the pore structure might be altered because of high metal loading. Consequently, the order of pore structure was lower, causing larger pores.14

2.4. Oxidation State of Copper and Zinc. 2.4.1. X-ray Absorption Spectroscopy (XAS). XAS was used to study the oxidation state of copper in Cu–ZnO/Al–MCM-41 catalysts. For the evaluation, the XAS spectra of catalysts are shown along with those of standard compounds as references (Cu foil, Cu₂O, and CuO). As shown in Figure 3, the spectrum of each fresh catalyst is close to that of CuO standard, as it exhibits the main peak at around 1.5 Å corresponds to the first shell of Cu²⁺ at six oxygen neighbors (Cu–O), and the peak at 2.5 Å is attributed to Cu–O bonds in CuO–Cu edge-shared octahedral, whereas the weak feature at 3 Å refers to the Cu²⁺ to other Cu²⁺ atoms. However, the peak intensity of CuO standard (see Figure S3a) is in the oxidation state of Cu²⁺.15 This result indicates that copper in the fresh catalysts is in the oxidation state of Cu²⁺.

Structural information can be obtained by using EXAFS. In agreement with XANES results, the EXAFS spectrum of each catalyst is quite similar to that of CuO standard (see Figure S3b), confirming that Cu–ZnO/Al–MCM-41 catalysts consist of CuO particles. Three features at around 1.5, 2.5, and 3.0 Å are observed for CuO standard compound. The main peak at 1.5 Å corresponds to the first shell of Cu²⁺ at six oxygen neighbors (Cu–O), and the peak at 2.5 Å is attributed to Cu–O bonds in CuO–Cu edge-shared octahedral, whereas the weak feature at 3 Å refers to the Cu²⁺ to other Cu²⁺ atoms. However, the peak intensity of Cu–ZnO/Al–MCM-41 catalysts is less than that of CuO standard, probably due to smaller CuO crystallites. Moreover, the weak feature at 3.0 Å is absent for Cu–ZnO/Al–MCM-41 catalysts. This could be caused by the diluted content of CuO species in the catalysts compared to that of pure CuO, making the scattering of the farther Cu–Cu shell difficult to be detected.16 The results of the first-shell analysis of Cu K-edge k²-weighted EXAFS spectra of different Cu–ZnO/Al–MCM-41 catalysts are shown in Figure S4 and Table S2. All samples have a Cu–O bond distance ca. 1.93 Å with a coordination number ca. 3.0 (Table S2), in agreement with previous works reported elsewhere.15,17 However, slightly lower Cu–O bond distance of all samples compared to that of CuO standard (typically 1.96 Å) could be due to the fact that these Cu–ZnO/Al–MCM-41 catalysts are not composed of only CuO species in the system.

2.4.2. H₂ Temperature-Programmed Reduction (H₂ TPR). The reducibility of the prepared catalysts was studied by H₂ TPR technique. As shown in Figure 4, each H₂ TPR profile was deconvoluted into subpeaks, corresponding to different reduction processes. The first reduction peak at a lower temperature is likely attributed to a one-step reduction of CuO located on the external surface of the catalysts to Cu⁰. Meanwhile, the second reduction peak at around 270–310 °C can be assigned to nanosized CuO located deeper in the pore structure of the catalysts.20 During the catalyst preparation, some part of the copper precursor (i.e., Cu(NO₃)₂) was confined by the capillary effect inside the channels of the catalyst, resulting in the formation of small crystalline CuO species in pores.21 The presence of both external surface CuO and nanosized CuO crystals in the Cu-containing catalysts was also found in the previous works.8,9,10

Generally, Cu²⁺ ions at the exchange sites are reduced to Cu⁰ via a two-step reduction process.16 Hence, the reduction peaks at around 380–480 °C are attributed to the reduction of Cu²⁺ to Cu⁺ ions whereas the reduction peaks at around 570–640 °C correspond to the reduction of Cu⁺ to Cu⁰. The results reveal that there are multiple copper species existing in the catalysts. In addition, it can be seen that the fraction of CuO species (both external and nanosized CuO species) increased with increasing metal loading, a fact which is confirmed by X-ray photoelectron spectroscopy (XPS) results (see Section 2.4.3). It should be noted that in this work, the Cu loading of the catalysts was increased by using the impregnation method.

Figure 3. Cu K-edge XANES (a) and Fourier-transformed (k²-weighted) Cu K-edge extended X-ray absorption fine structure (EXAFS) (b) spectra of 1.5Cu–1.5ZnO, 2.5Cu–2.5ZnO, and 3.5Cu–3.5ZnO compared to that of standard Cu foil, Cu₂O, and CuO.
in which copper predominately exists as CuO species. In addition, with higher metal loading, it is more difficult for a copper precursor to infiltrate deeper in the channels of the catalysts and occupy the exchange sites, leading to the formation of more CuO species on the surface of the catalyst. Interestingly, the reduction temperatures for the two-step reduction of Cu²⁺ are observed to increase with increasing metal content, suggesting that it is more difficult to reduce copper ions. With higher metal loading, copper ions at the exchange sites were hindered by CuO and ZnO covering on the surface of the catalyst, resulting in a lower accessibility of these copper ions to H₂ molecules and a lower reducibility.

Furthermore, reduction at a very high temperature (700–750 °C) is observed for all Cu–ZnO/Al–MCM-41 catalysts (Figure 1). Some previous works suggested that Cu⁺ could be reduced to Cu⁰ at very high temperature (>700 °C). On the other hand, the reduction of Zn species can also take place at high temperature. However, this reduction at very high temperature is absent for the Cu/Al–MCM-41 catalyst (see Figure 8). Therefore, the peak at around 700–750 °C can be assigned to the reduction of ZnO species. The reduction peak of ZnO species is much smaller than that of CuO species, confirming the low reducibility of ZnO species.

### 2.4.3. XPS

As shown in Figure 5, all Cu 2p regions show two main peaks centered at around 933 and 953 eV, assigned to 2P₁/₂ and 2P₃/₂ transition of Cu²⁺, respectively. Each of the Cu 2p peaks was deconvoluted into two doublets (A and B components) by XPSPEAK 4.1 software, as shown in Figure 5 and Table 2. The Cu 2P₃/₂ transition exhibits two peaks at the binding energy (BE) around 933 eV (A) and 935 eV (B), whereas the Cu 2P₁/₂ transition shows two peaks at the binding energy around 953 eV (A) and 955 eV (B). The component with lower binding energy (A) is assigned to CuO species. Meanwhile, the component with higher binding energy (B) likely corresponds to isolated Cu²⁺ ions.

The XPS results confirm that both CuO species and isolated Cu²⁺ ions coexist in Cu–ZnO/Al–MCM-41 catalysts; however, copper species in these catalysts are mostly presented

![Figure 4. H₂ TPR profiles of (a) 1.5Cu–1.5ZnO, (b) 2.5Cu–2.5ZnO, and (c) 3.5Cu–3.5ZnO.](image)

![Figure 5. Cu 2p (left) and Zn 2p (right) XPS spectra of (a) 1.5Cu–1.5ZnO, (b) 2.5Cu–2.5ZnO, and (c) 3.5Cu–3.5ZnO.](image)

| Sample     | Component A BE (eV) % | Component B BE (eV) % |
|------------|----------------------|----------------------|
| 1.5Cu–1.5ZnO | 933.70 67.13          | 935.09 32.87          |
|            | 953.09 68.84          | 955.80 31.16          |
| 2.5Cu–2.5ZnO | 933.64 81.36          | 935.45 18.64          |
|            | 953.60 78.81          | 955.90 21.19          |
| 3.5Cu–3.5ZnO | 933.64 85.93          | 935.95 14.07          |
|            | 953.50 79.90          | 956.40 20.10          |

Table 2. Binding Energy (BE) and Percentage of the Different Copper Species Identified in the Cu 2p Region of Cu–ZnO/Al–MCM-41 Catalyst with Different Total Metal Contents
in the form of CuO. As shown in Table 2, the contribution of CuO species increased with increasing metal content, a fact which is in agreement with H2 TPR results.

Meanwhile, the Zn 2p XPS spectra of Cu−ZnO/Al−MCM-41 catalysts with different metal loadings are also depicted in Figure 5. By fitting the Zn 2p XPS spectra, only one component is observed at 1023 eV for Zn 2P3/2 transition and 1046 eV for Zn 2P1/2 transition and assigned to ZnO species.24 The absence of Zn2+ ions at the exchange sites of the catalysts in this work can be explained by the fact that Zn was loaded onto the catalysts by the impregnation method only. By using this method, the majority of Zn species was formed as ZnO, as reported in our previous work.18

2.5. NH3-SCR Activity Test. All three Cu−ZnO/Al−MCM-41 catalysts were tested for their NH3-SCR activity in terms of NO conversion, N2 selectivity, N2O selectivity, and NO2 selectivity, as shown in Figure 6. The results show that N2 is the main product of NH3-SCR over these catalysts, as the N2 selectivity of all catalysts is close to 100%. Only trace amounts of N2O and NO2 were detected. The average NO conversion of Cu/Al−MCM-41 and Cu−ZnO/Al−MCM-41 catalysts for NH3-SCR at 300 °C for 3 h is shown in Table 3.

The results demonstrate that 2.5Cu−2.5ZnO/Al−MCM-41 catalyst exhibits the highest activity compared to that of others, as it gave the average NO conversion for 3 h of 87%. As the total metal content was increased from 3 to 5 wt %, more active sites were available and thus the NH3-SCR activity was improved. However, too much metal loading could negatively affect the catalytic performance, as shown by the lowest NH3-SCR activity of 3.5Cu−3.5ZnO/Al−MCM-41. For 3.5Cu−3.5ZnO/Al−MCM-41 catalyst, the BET surface area significantly decreased, whereas the average pore diameter increased compared to that of other catalysts (see Table 1), which are likely due to the partial destruction of the structure and pore blockage upon the metal introduction.

In addition, the previous work1 stated that the most active copper species for NO reduction is isolated Cu2+ ions at the

![Figure 6. Catalytic performance for NH3-SCR of NO on 1.5Cu−1.5ZnO, 2.5Cu−2.5ZnO, and 3.5Cu−3.5ZnO at 300 °C for 3 h: (a) NO conversion, (b) N2 selectivity, (c) NO2 selectivity, and (d) N2O selectivity.](image-url)

| catalyst                      | NO conversion (%) |
|-------------------------------|-------------------|
| 1.5Cu−1.5ZnO/Al−MCM-41       | 80                |
| 2.5Cu−2.5ZnO/Al−MCM-41       | 87                |
| 2.5Cu−Al−MCM-41              | 76                |
| 2.5Cu−3.5ZnO/Al−MCM-41       | 72                |
| 3.5Cu−3.5ZnO/Al−MCM-41       | 73                |

Table 3. Average NO Conversion of Different Cu−ZnO/Al−MCM-41 Catalysts for SCR of NO with at 300 °C for 3 h
exchange sites. As indicated by XPS results, 3.5Cu−3.5ZnO/Al−MCM-41 shows the lowest contribution of isolated Cu$^{2+}$ ions. Moreover, the isolated Cu$^{2+}$ ions in 3.5Cu−3.5ZnO/Al−MCM-41 catalyst have the lowest accessibility for gas molecules and are reduced to Cu$^+$ with difficulty, as shown in H$_2$-TPR profile.

### 2.6. Effects of ZnO Content.

As discussed in our previous work, the introduction of ZnO can improve NH$_3$-SCR activity by giving more active sites for NH$_3$ adsorption and nitrite/nitrate formation and promoting a number of Cu$^+$ ions in the system. To investigate the effects of ZnO content on the chemical state of Cu and the NH$_3$-SCR activity, another set of Cu−ZnO/Al−MCM-41 catalysts were studied, in which Cu loading was fixed at 2.5 wt % whereas Zn loading was varied as 0, 2.5, and 3.5 wt %, corresponding to Cu-to-ZnO ratios of 1:0, 1:1, and 1:1.4, respectively. Although it is demonstrated that the presence of ZnO can enhance the catalytic performance for NO reduction of Cu/Al−MCM-41 (see Figure 7 and Table 3), too high ZnO content in Cu−ZnO/Al−MCM-41 catalyst can result in lower NO conversion. It can be seen that 2.5Cu−3.5ZnO/Al−MCM-41 shows lower catalytic activity than that of 2.5Cu−2.5ZnO/Al−MCM-41 (Figure 4), as it yielded lower NO conversion for the entire reaction time, with an average NO conversion for 3 h of 72%.

The H$_2$ TPR results shown in Figure 8 demonstrate that the reduction peaks referring to the two-step reduction of isolated Cu ions at the exchange sites are shifted to higher temperature with increasing ZnO content, confirming that ZnO incorporation in these catalysts impedes the reduction of copper ions. It was reported that zinc is reduced with difficulty and might hinder Cu ions (both Cu$^{2+}$ and Cu$^+$) from being reduced. The introduction of ZnO can stabilize Cu$^+$ species and hinder the reduction of Cu$^+$ to Cu$^0$ during the pretreatment via the interaction between ZnO and Cu$^+$, a fact which is beneficial for NO reduction, as Cu$^+$ ions are the active species for this reaction. However, too strong interactions between ZnO and Cu species can make the reduction of Cu$^{2+}$ to Cu$^+$ much more difficult, leading to lower Cu reducibility and a number of Cu$^+$ species in the system. Moreover, the XPS results show that the Cu 2p binding energy of 2.5Cu−3.5ZnO/Al−MCM-41 slightly shifts to lower energy (see Figure 9). This can be explained by the increase of electron cloud density around Cu ions caused by the electron donation from ZnO promoter, which can decrease the reducibility of Cu. Therefore, on the basis of the experimental results in this study, Cu−ZnO/Al−MCM-41 catalyst with a total metal content of 5 wt % and Cu-
NH₃-SCR activity was improved with increasing metal loading by using impregnation method. The contribution of CuO species increased with hindering gas molecules from accessing the Cu²⁺ ions. Too high metal loading can result in lower BET surface area and lower reducibility of Cu²⁺ ions, as CuO and ZnO covers on the surface of the catalyst can partially block pores and hinder gas molecules from accessing the Cu²⁺ ions. Even though it was demonstrated that the presence of ZnO can enhance the NH₃-SCR activity of the catalyst, too high ZnO content can give negative effects. Too strong interactions between Cu and ZnO impede the reduction of Cu²⁺ to Cu⁺, leading to lower Cu reducibility and lower number of Cu⁺ species in the system. Hence, on the basis of the experimental results in this study, Cu–ZnO/Al–MCM-41 catalyst with a total metal content of 5 wt % and Cu-to-Zn ratio of 1:1 exhibits the best catalytic performance for NH₃-SCR.

4. EXPERIMENTAL SECTION

4.1. Preparation of Catalysts. A core–shell structured Al–MCM-41 was synthesized via the method reported by Chamnankid et al. (2012), in which cetyl trimethylammonium bromide (CTAB: 98%, APS Ajax Finechem) was used as a structural directing agent whereas tetraethyl orthosilicate (TEOS: 98%, Sigma-Aldrich) and aluminum nitrate (Al(NO₃)₃·9H₂O: 98%, QREC) were used as silica and alumina sources, respectively. The molar gel composition was 1SiO₂:0.2CTAB:100H₂O, whereas the Al₂O₃/SiO₂ ratio was fixed at 0.1. TEOS was first added to a mixture of Al(NO₃)₃ and CTAB at 40 °C. After stirring for 1 h, the pH of the mixed solution was adjusted to 6.5 by adding 1 M sodium hydroxide (NaOH: 98%, Carlo Erba). Next, the mixture was stirred for another 5 h before being transferred to a Teflon-lined autoclave for hydrothermal treatment at 100 °C for 24 h. The obtained product was filtered and washed with distilled water, dried at 80 °C overnight, and calcined at 600 °C for 5 h.

For metal loading, the Cu-to-ZnO molar ratio was fixed at 1:1. The method for Cu and Zn loading was modified from our previous work. Copper loading was performed by the combined method: substitution, followed by ion exchange, and incipient wetness impregnation, whereas Zn loading was conducted by incipient wetness impregnation only.

First, copper (0.5 wt %) was incorporated into the core–shell Al–MCM-41 except that copper nitrate (Cu(NO₃)₂·3H₂O: 99.5%, Loba Chemie) was added into the mixture of Al(NO₃)₃ and CTAB before adding TEOS. Then, the resultant product was further suspended in 0.1 M of Cu(NO₃)₂ solution to perform ion exchange at 40 °C for 10 h. The product was then filtered and rinsed with deionized water, dried overnight at 100 °C, and calcined at 400 °C for 5 h. Last, the obtained product was impregnated with a mixture of copper nitrate and zinc nitrate (Zn(NO₃)₂·6H₂O: 98%, Loba Chemie) solution with different concentrations and then calcined in air at 400 °C for 5 h. It should be noted that for the substitution and ion exchange steps, Cu loading was identical for all catalysts. On the other hand, the metal loading was varied for the incipient wetness impregnation step. The nomenclature and the metal content of the obtained catalysts are shown in Table S1.

4.2. Catalysts Characterization. The metal content in the obtained catalysts was measured by inductively coupled plasma optical emission spectroscopy (Agilent 700-ES series).

The core–shell structure of the sample was confirmed by a transmission electron microscope (TEM, JEOL JEM-3100 (HR)) operated with an acceleration of 300 kV. Sample preparation entailed suspension of the sample in ethanol, followed by evaporation of ethanol on a copper grid coated with a carbon film. Additionally, the morphology and the metal dispersion of the catalysts were examined by using a field-emission scanning electron microscope (JEOL JSM-7600F)
The textural properties of the catalysts were obtained from nitrogen adsorption–desorption isotherm measurement by using a Quantachrome Autosorb-1C instrument. Prior to the measurement, the samples were degassed at 200 °C for 12 h. The adsorption isotherms were measured at −196 °C and 10−3 < P/P0 < 1.0. The specific surface area was estimated by the BET method using P/P0 values between 0.05 and 0.30. The pore size distribution was obtained using desorption branch of the Barrett–Joyner–Halenda method. The total pore volume was estimated from adsorption data at P/P0 of 0.99.

X-ray diffraction (XRD) analysis was conducted using a Philips X’Pert diffractometer with Cu Kα radiation (40 kV and 30 mA). The XRD patterns were collected with a step size of 0.02° in the 2θ range from 10 to 50°.

X-ray photoelectron spectroscopy (XPS) experiments were conducted in an AXIS Ultra DLD spectrometer. All recorded spectra were decomposed by using XPSPeak 4.1 software. The peak shape was set as p-type, in which an area ratio of 2P3/2 to 2P1/2 was fixed at 2:1.

X-ray adsorption spectroscopy (XAS) experiments were done at beamline 2.2: time-resolved absorption spectroscopy (Bonn-SUT-SLRI) of the Synchrotron Light Research Institute (SLRI), Thailand. The electron storage ring was used at energy of 1.2 GeV (beam current: 80–150 mA). The energy was selected with a Si(220) crystal monochromator for collecting the Cu K-edge in transmission mode. The obtained data was processed by using ATHENA and ARTEMIS software. For the first-shell analysis of Cu K-edge EXAFS spectra, the normalized data was k-weighted and the analysis was performed in a k-range of 2–9 Å and R-range of 1.2–2.2.

Temperature-programmed reduction with hydrogen (H2-TPR) was performed in a tubular reactor (Inconel-600, OD 3/8 in.). The catalyst (0.25 g) blended with quartz sand (1 g) was heated from 30 to 900 °C with a ramping rate of 5 °C/min under a flow of 9.6% H2/Ar (15 mL/min). The H2 consumption was detected by a Shimadzu gas chromatograph (GC-2014) equipped with a thermal conductivity detector (TCD). All H2-TPR profiles were deconvoluted by OriginPro 8.5 software with a Gaussian peak function.

### 4.3. Catalyst Activity Measurement

NH3-SCR activity test was conducted in a fixed-bed tube reactor (a 3/8 in. diameter) using a 0.2 g sample mixed with 0.8 g of quartz sand. The sample was pretreated by reduction with H2 at 350 °C for 2 h. The gas flow rate and gas hourly space velocity were controlled at 30 mL/min and 1300 h−1, respectively. For all experiments, the feed gas contained 500 ppm NO, 500 ppm NH3, 3% O2, and He as the balance. The NH3-SCR activity of the catalysts was tested at atmospheric pressure and 300 °C for 3 h. The outlet gaseous composition was determined by gas chromatograph (Shimadzu, GC-14A TCD detector) equipped with two columns: Unibeads C column for detecting N2 and O2 and Porapak-Q column for detecting NO, NO2, and N2O. Consequently, NO conversion (XNO) was calculated from following equation

\[
X_{NO} \; (\%) = \left( \frac{[NO]_{\text{inlet}} - [NO]_{\text{outlet}}}{[NO]_{\text{inlet}}} \right) \times 100 \tag{1}
\]

The N2, NO2, and N2O selectivity were calculated from their detected amounts divided by the amount of NO consumed.

### ACKNOWLEDGMENTS

This work was supported by the Thailand Research Fund (TRF) through the Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0139/2556 for T.I.) and partially supported by the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand through its program of Research Network NANOTEC (RNN) (for P.K.). G.R. acknowledges the Austrian Science Fund (FWF) (DK+ Solids4Fun W1243).

### REFERENCES

1. (1) Wang, L.; Li, W.; Qi, G.; Weng, D. Location and nature of Cu species in Cu/SAPO-34 for selective catalytic reduction of NO with NH3. J. Catal. 2012, 289, 21–29.

2. (2) Iwamoto, M.; Furukawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S.-I.; Kagawa, S. Copper(II) ion-exchanged ZSM-5 zeolites as highly active catalysts for direct and continuous decomposition of nitrogen monoxide. J. Chem. Soc., Chem. Commun. 1986, 16, 1272–1273.

3. (3) Sultana, A.; Nanba, T.; Haneda, M.; Hamada, H. SCR of NOx with NH3 over Cu/NaZSM-5 and Cu/HZSM-5 in the presence of decane. Catal. Commun. 2009, 10, 1859–1863.

4. (4) Wan, Y.; Ma, J.; Wang, Z.; Zhou, W.; Kaliaguine, S. On the mechanism of selective catalytic reduction of NO by propylene over Cu-Al-MCM-41. Catal. Today, 2005, 59, 235–242.

5. (5) Chamnankid, B.; Samanpratan, R.; Kongkachuichay, P. Effect of core-shell structure and chitosan addition on catalytic activities of copper-containing silica/alumino-silicate composites in deNOx reaction by H2. J. Nanosci. Nanotechnol. 2012, 12, 9325–9332.

6. (6) Sultana, A.; Nanba, T.; Haneda, M.; Sasaki, M.; Hamada, H. Influence of co-cations on the formation of Cu+ species in Cu/ZSM-5 and its effect on selective catalytic reduction of NO, with NH3. Appl. Catal., B 2010, 101, 61–67.

7. (7) Intana, T.; Föttinger, K.; Rupprecht, G.; Kongkachuichay, P. Physicochemical properties of Cu loaded onto core-shell Al-MCM-41: Effect of loading methods. Colloids Surf., A 2015, 467, 157–165.

8. (8) Imyen, T.; Yigit, N.; Poo-Arporn, Y.; Föttinger, K.; Rupprecht, G.; Kongkachuichay, P. Promotional effects of Zn doping on Cu/ core-shell Al-MCM-41 for selective catalytic reduction of NO with NH3. J. Nanosci. Nanotechnol. 2019, 19, 743–757.

9. (9) Yan, B.; Li, Y.; Zhou, B. Covalently bonding assembly and photophysical properties of luminescent molecular hybrids Eu-TTA-
Si and Eu-TTASi-MCM-41 by modified thenoyltrifluoroacetone. *Microporous Mesoporous Mater.* 2009, 120, 317–324.

(10) Balaraju, M.; Rekha, V.; Sai Prasad, P. S.; Prasad, R. B. N.; Lingaiah, N. Selective hydrogenolysis of glycerol to 1, 2 propanediol over Cu–ZnO catalysts. *Catal. Lett.* 2008, 126, 119–124.

(11) Guo, X.; Mao, D.; Lu, G.; Wang, S.; Wu, G. Glycine-nitrate combustion synthesis of CuO–ZnO–ZrO2 catalysts for methanol synthesis from CO2 hydrogenation. *J. Catal.* 2010, 271, 178–185.

(12) Vijayakumar, S.; Vaseeharan, B.; MalaiKozhundan, B.; Divya, M.; Abhinaya, M.; Gobi, N.; Bhattacharyya, A.; Balashanmugam, N.; Surmitha, D.; Murugan, K.; Benelli, G. Ecotoxicity of *Musa paradisiaca* leaf extract-coated ZnO nanoparticles to the freshwater microcrustacean *Ceriodaphnia cornuta*. *Limnologica* 2017, 67, 1–6.

(13) Siwawut, J.; Namkhang, P.; Kongkachuichay, P. Co-metal catalysts on SiO2–TiO2 for methanol production from CO2-Effect of preparation methods. *Chem. Eng. Technol.* 2015, 38, 2153–2160.

(14) Ling, Y.; Long, M.; Hu, P.; Chen, Y.; Huang, J. Magnetically separable core–shell structural γ-Fe2O3@Cu/Al-MCM-41 nano-composite and its performance in heterogeneous Fenton catalysis. *J. Hazard. Mater.* 2014, 264, 195–202.

(15) Deka, U.; Lezcano-Gonzalez, I.; Warrender, S. J.; Lorena Picone, A.; Wright, P. A.; Weckhuysen, B. M.; Beale, A. M. Changing active sites in Cu-CHA catalysts: deNOx selectivity as a function of the preparation method. *Microporous Mesoporous Mater.* 2013, 166, 144–152.

(16) Shishido, T.; Yamamoto, M.; Li, D.; Tian, Y.; Morioka, H.; Honda, M.; Sano, T.; Takehira, K. Water-gas shift reaction over Cu/ZnO and Cu/ZnO/Al2O3 catalysts prepared by homogeneous precipitation. *Appl. Catal., A* 2006, 303, 62–71.

(17) Korhonen, S. T.; Fickel, D. W.; Lobo, R. F.; Weckhuysen, B. M.; Beale, A. M. Isolated Cu2+ ions: active sites for selective catalytic reduction of NO. *Chem. Commun.* 2011, 47, 800–802.

(18) Imyen, T.; Yigit, N.; Dittanet, P.; Barrabés, N.; Föttinger, K.; Rupprecht, G.; Kongkachuichay, P. Characterization of Cu-Zn/core-shell Al-MCM-41 as a promising catalyst for selective catalytic reduction of NO with NH3: Effect of Zn promoter. *Ind. Eng. Chem. Res.* 2016, 55, 13050–13061.

(19) Xue, J.; Wang, X.; Qi, G.; Wang, J.; Shen, M.; Li, W. Characterization of copper species over Cu/SAPO-34 in selective catalytic reduction of NOx with ammonia: Relationships between active Cu sites and de-NOx performance at low temperature. *J. Catal.* 2013, 297, 56–64.

(20) Liang, M.; Kang, W.; Xie, K. Comparison of reduction of Fe3O4, ZnO and ZnFe2O4 by TPR technique. *J. Nat. Gas Chem.* 2009, 18, 110–113.

(21) Zhou, J.; Xia, Q.-H.; Shen, S.-C.; Kawi, S.; Hidajat, K. Catalytic oxidation of pyridine on the supported copper catalysts in the presence of excess oxygen. *J. Catal.* 2004, 225, 128–137.

(22) Pereda-Ayo, B.; De La Torre, U.; Illán-Gómez, M. J.; Bueno-López, A.; González-Velasco, J. R. Role of the different copper species on the activity of Cu/zeolite catalysts for SCR of NOx with NH3. *Appl. Catal., B* 2014, 147, 420–428.

(23) Moreno-Tost, R.; Santamaría-González, J.; Rodríguez-Castellón, E.; Jiménez-López, A.; Autié, M. A.; González, E.; Glacial, M. C.; De las Pozas, C. *Appl. Catal., B* 2004, 50, 279–288.

(24) Niu, X.; Gao, J.; Miao, Q.; Dong, M.; Wang, G.; Fan, W.; Qin, Z.; Wang, J. Influence of preparation method on the performance of Zn-containing HZSM-5 catalysts in methanol-to-aromatics. *Microporous Mesoporous Mater.* 2014, 197, 252–261.

(25) Tseng, H.-H.; Lin, H.-Y.; Kuo, Y.-F.; Su, Y.-T. Synthesis, characterization, and promoter effect of Cu-Zn/γ-Al2O3 catalysts on NO reduction with CO. *Chem. Eng. J.* 2010, 160, 13–19.