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Hydrothermal stability of CuZSM5 catalyst in reducing NO by NH$_3$ for the urea selective catalytic reduction process

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Abstract

To confirm the hydrothermal stability of CuZSM5 for urea selective catalytic reduction (SCR), NO removal activity over a series of the catalyst containing various amounts of copper, ranging from 1 to 5 wt%, was examined before and after hydrothermal treatment under a simulated feed gas stream containing 10% water at a temperature range of 600–800 °C. The degree of catalyst aging varies with respect to the copper content of the catalyst and the aging temperature. The optimal copper content seems to be about 4 wt% (nearly 125% in terms of ion-exchange level) from the standpoint of catalyst aging. The catalysts before and after aging were characterized by XRD, ^{27}Al-MAS-NMR, BET, XAFS, and ESR to gain insight into the sintering mechanism of CuZSM5 for the urea SCR process. A slight alteration of the catalyst structure was observed by XRD and BET analysis on catalyst aging. The copper ions on the surface of CuZSM5 catalysts on aging remained as either isolated Cu^{2+} and/or an oxide form of copper, as confirmed by EXAFS. However, ESR spectra of the catalysts clearly revealed four distinct local structures of Cu^{2+} species in the framework of ZSM5 in the form of a square pyramidal site, a square planar site, and two unresolved distorted sites. Migration of Cu^{2+} ions from the square pyramidal and/or the square planar sites of the isolated cupric ions to the two unresolved sites occurs during hydrothermal treatment. This causes an alteration of the population of isolated cupric ions on the square pyramidal and/or planar sites and is responsible for the hydrothermal stability of the CuZSM5 catalyst in the urea SCR process.
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1. Introduction

The selective catalytic reduction (SCR) of NO$_x$ with urea is a recognized well-developed technology to remove NO$_x$ from light- and heavy-duty diesel engines [1,2]. For the actual diesel engine exhaust system, the H$_2$O content generated from the combustion of diesel fuel with a high carbon number is distinctive in the gas stream, and the development of a hot spot in the catalytic converter from the sudden burning of locally collected particulate can be expected. Consequently, achieving

hydrothermal stability of the catalyst is a critical issue in the commercial application of urea SCR technology to the exhaust stream from diesel engines [3].

CuZSM5 is one of the most promising catalysts for the SCR of NO$_x$ by urea at an exhaust temperature of around 150 °C, particularly for light-duty diesel engines [3,4]. For the decomposition of urea, 1 mol of urea is thermally decomposed and then easily hydrolyzed on the catalyst surface to produce 2 mol of ammonia and 1 mol of carbon dioxide, leading to the practically equivalent overall reaction to NH$_3$ SCR of NO [3–7]. Numerous studies have been conducted regarding the nature of Cu on the surface of zeolite, which is generally recognized as an active reaction site for the present reaction system,

and its reaction mechanism through redox chemistry [8–14]. It has been commonly accepted that isolated Cu^{2+} and Cu–O–Cu dimer species on the catalyst surface play key roles in the NH_3 SCR reaction. Mizumoto et al. [12] prepared Cu-Y zeolite containing mainly isolated Cu^{2+} to suggest a Langmuir–Hinshelwood-type reaction mechanism by the reaction between strongly adsorbed NH_3 and weakly adsorbed NO on isolated copper ions over the catalyst surface. Choi et al. also confirmed a similar mechanism by temperature-programmed desorption experiments of NO and NH_3 over Cu-exchanged Mordenite-type zeolite catalyst [13]. Komatsu et al. [14] studied NH_3 SCR for a series of Cu zeolites with varying copper exchange levels and Si/Al ratios and concluded that the active reaction site of the CuZSM5 catalyst for NH_3 SCR is copper dimer formed on the catalyst surface. The active reaction site on the surface of Cu-exchanged zeolite has been also investigated for the decomposition of NO and HC (hydrocarbon) SCR by luminescence, Fourier transform infrared spectroscopy, electron spin resonance (ESR), and X-ray absorption fine structure (XAFS) studies [15–23]. Iwamoto et al. proposed oxygen-bridged binuclear $[Cu–O–Cu]^{2+}$ in CuZSM5 for NO decomposition [15], and Sárkány et al. reported experimental evidence indicating that the complex forms all at once [16]. Ddeček et al. examined the four distinctive sites of Cu ion coordination over various zeolite structures, including MFI, MOR, FER, BEA, and FAU, using a multispectroscopic approach including Cu^+ emission spectra, in situ infrared spectroscopy for Cu^{2+}-adsorbing NO, and ESR of Cu^{2+} [17].

But little literature exists on the inactivation of the active reaction sites for NH_3 SCR, although the hydrothermal stability of zeolite has long been considered a necessary issue to resolve for the commercial application of zeolite-type catalyst to automotive engines from the standpoint of alteration of the active reaction sites, including isolated Cu^{2+}, and Cu^{2+} dimer during the reaction. It has been commonly observed that the deactivation of SCR activity over CuZSM5 catalyst is due mainly to the degradation of zeolite support and/or the formation of Cu-aluminate by dealumination, the decrease in active reaction sites by the transformation of Cu^{2+} to CuO, the redistribution of the reaction sites through the migration of Cu^{2+}, or a combination of these mechanisms [19,20,24–28]. Furthermore, the optimal copper content on the catalyst surface has been little examined from the standpoint of catalyst aging for commercial application.

The purpose of the present study was to optimize the copper content on the surface of ZSM5 catalyst from the standpoint of catalyst aging by evaluating the hydrothermal stability of a series of CuZSM5 catalysts. To accomplish this goal, various complementary spectroscopic techniques were used and their results compared. In particular, XAFS and ESR studies were carried out to investigate the nature of copper ions on the surface of CuZSM5 catalyst, such as the oxidation states of copper and the coordination structure of Cu^{2+} in the framework of zeolite on the catalyst sintering with respect to aging temper-

Table 1
Physicochemical properties of the catalysts employed in the present study

Sample	Cu content (wt%)	Ion exchange level (%)	BET (m^2/g)	Micropore surface area (m^2/g)
CuZSM5-61-fresh	1.95	61	400	377
CuZSM5-61-600				
CuZSM5-61-700			372	331
CuZSM5-61-800			363	321
CuZSM5-92-fresh	2.93	92	387	362
CuZSM5-92-600				
CuZSM5-92-700			357	319
CuZSM5-92-800			321	303
CuZSM5-124-fresh	3.87	124	383	354
CuZSM5-124-600			355	328
CuZSM5-124-700			324	285
CuZSM5-124-800				
CuZSM5-150-fresh	4.73	150	357	323
CuZSM5-150-600			337	301
CuZSM5-150-700			294	260
CuZSM5-150-800			191	182

2. Experimental

2.1. Catalyst preparation

NH_4^+ type ZSM5 (Si/Al ratio = 14), obtained from Tosoh Corp., was used as a parent catalyst for preparing the series of catalysts in the present study. The ZSM5 was exchanged with a 0.01 M $(CH_3CO_2)_2Cu\cdot H_2O$ (Aldrich, 98%) solution to obtain a Cu-based ZSM5 at room temperature for 5 h [3,4]. The room temperature for exchanging copper ions into ZSM5 catalyst was used to avoid the formation of copper oxides on the catalyst surface during the course of the ion exchange [4]. This was followed by drying at 110 °C for 12 h and calcining at 500 °C in air for 5 h. The copper content was controlled by repeating the ion-exchange procedure.

To investigate the hydrothermal stability of CuZSM5, the catalyst samples were sintered under a simulated feed gas stream containing 10% H_2O in air balance with a flow rate of 500 cc/min at 600, 700, and 800 °C for 24 h. Cu-based ZSM5 catalysts containing a various copper loadings with respect to the aging temperatures were obtained and designated as CuZSM5-x-y, where x and y represent the percentage degree of Cu^{2+} ion exchange, and the aging temperature, respectively. Table 1 lists the physicochemical properties of the catalysts prepared in this study.

2.2. Reactor system and experimental procedure

For urea SCR technology, urea is thermally decomposed into one mol of ammonia and one mol of isocyanic acid initially, and the isocyanic acid formed by the thermal decomposition of urea can readily undergo hydrolysis on the catalyst surface to produce another mol of ammonia [7]. Thus, the complete decomposition of 1 mol of urea produces 2 mol of ammonia and 1 mol of carbon dioxide [1,5–7].

This leads to the practically equivalent overall reaction of NO to NH_3 SCR. The identical $deNO_x$ performance of the CuZSM5 catalyst by urea SCR to that by NH_3 SCR was observed under the specific reaction conditions [3]. Therefore, an NH_3 SCR test to confirm the hydrothermal stability of the series of the CuZSM5 catalysts for urea SCR was performed for experimental convenience.

The activity of the CuZSM5 catalysts for NO reduction by NH_3 was examined in a fixed-bed flow reactor, typically containing ca. 1 g of the catalyst was sieved to a mesh size of 20/30 to minimize the mass transfer limitations of the catalyst. Before the evaluation of activity, the catalyst was pretreated in situ with a total flow of 3300 cc/min containing 79% N_2 and 21% O_2 at 500 °C, and then cooled to room temperature. A reaction gas mixture consisting of 500 ppm NO, 500 ppm NH_3, 5% O_2, and 10% H_2O in N_2 balance was fed into the reactor system through Brooks mass flow controllers (model 5850E). A total flow rate of 3300 cc/min (corresponding to GHSV = 100,000 h^{-1}) was mainly used for the catalyst activity testing. The NO concentration was analyzed by an on-line chemiluminescence $NO–NO_x$ analyzer (Thermo Electron, model 42H). The details of the reactor system have been given elsewhere [3,7].

2.3. Catalyst characterization

BET surface areas were measured by Micromeritics ASAP 2010 sorption analyzer with a static volumetric technique, based on the amount of N_2 adsorbed at liquid N_2 temperature. The samples were degassed at 200 °C in vacuum for 5 h before the adsorption measurements. BET surface area and micropore volume were calculated by the t-plot method. The micropore surface area was obtained by subtracting the external surface area from the total surface area.

Powder XRD patterns for the catalysts were observed by using an M18XHF X-ray diffractometer with Ni-filtered Cu-K$_\alpha$ radiation ($\lambda \sim 1.54184$ Å). Data were collected in angles ranging from 5° to 90° with a step size of 0.02° and a step time of 10 s under continuous sample rotation during the scan.

The ^{27}Al magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectra were obtained on a Bruker AVANCE 500 spectrometer at an ^{27}Al frequency of 130.325 MHz in 4-mm rotors at a spinning rate of 10.0 kHz. The spectra were obtained with the acquisition of ca. 10,000 pulse transients, which were reported with a $\pi/4$ rad pulse length of 5.00 µs and a recycle delay of 1.0 s.

Extended X-ray absorption fine structure (EXAFS) spectroscopic measurements were performed with the synchrotron radiation by using the EXAFS facility installed at beamline 3C1 in the Pohang Accelerator Laboratory. The ring was operated at 2.5 GeV with 200 mA electron current and 1% coupling. The spectra were measured with an Si(111) channel-cut monochromator with an energy resolution of $\Delta E/E = 2 \times 10^{-4}$ that remained constant at the Cu K-edge (8979 eV).

The samples spread uniformly between adhesive tapes to obtain an optimal absorption jump. All of the data were recorded in a transmission mode at room temperature, and the intensities

N_2-filled ionization chambers. CuO, Cu_2O, and Cu metal were used as reference compounds.

The data analyses for EXAFS were carried out by a standard procedure. The inherent background in the data was removed by fitting a polynomial to the edge region and then extrapolating through the entire spectrum from which it was subtracted. The resulting spectra, $\mu(E)$, were normalized to an edge jump of unity for comparing the X-ray absorption near-edge structures (XANES) directly. The EXAFS function, $\chi(E)$, was obtained from $\chi(E) = \{\mu(E) - \mu_0(E)\}/\mu_0(E)$ [29]. The resulting EXAFS spectra were k^2-weighted to compensate for the attenuation of EXAFS amplitude at high k and then Fourier transformed in the range of 2.0 Å$^{-1} \leqslant k \leqslant 11.5$ Å^{-1} with a Kaiser–Bessel function of d$k = 1$ Å^{-1}. To determine the structural parameters, nonlinear least squares curve fitting was performed in the range of $R \leqslant \sim 2$ Å corresponding to the distance to the Cu–O in the central-atom phase-corrected Fourier-transformed (FT) spectra, using the UWXAFS and IFEFFIT packages according to the following EXAFS formula [30]:

$$\chi(k) = -S_o^2 \sum_i \frac{N_i}{kR_i^2} F_i(k) \exp\{-2\sigma_i^2 k^2\} \exp\{-2R_i/\lambda(k)\}$$
$$\times \sin\{2kR_i + \phi_i(k)\}, \tag{2}$$

where the backscattering amplitude, $F_i(k)$, the total phase shift, $\phi_i(k)$, and the photoelectron mean free path, $\lambda(k)$, were theoretically calculated for all scattering paths, including multiple ones by a curved wave ab initio EXAFS code FEFF8 [31].

The ESR spectra were obtained at room temperature in the X-band using a JEOL model JES-TE300 spectrometer. The ESR signals of Cu^{2+} were recorded in the field region from 2000 to 4000 G with a sweep time of 10 min. A coaxial quartz cell was placed in the ESR cavity and connected with stainless steel capillaries of the flow system by Teflon ferrules. The samples were heated at 500 °C in pure O_2, evacuated, and sealed off in situ. To provide the maximum accuracy of the ESR signals, the packing height of the ampoule was constant in all cases, with the center of the sample positioned in the middle of the ESR cavity. The ESR signal from DPPH ($g_\parallel = 2.0036$) was used as an internal standard. The Origin and Excel programs for Windows were used for the baseline correction, analysis of the fourfold hyperfine lines, and double-integration of the recorded ESR spectra.

3. Results and discussion

3.1. Effect of aging on NO removal activity

The NO removal activity for a series of CuZSM5 catalysts before and after aging, particularly at 700 °C, where catalyst deactivation is specifically evident, is given in Fig. 1. The figure shows a bell-shaped activity profile with respect to the reaction temperature, typical for NH_3 SCR catalyst maintaining a wide operating temperature window (200–400 °C) containing NO conversion > 90%. In a reaction temperature range higher
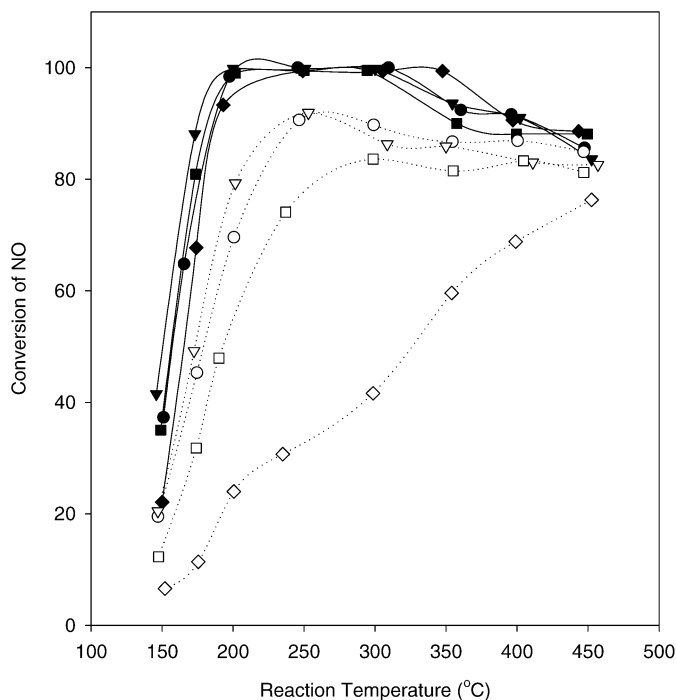
Fig. 1. Activity of a series of CuZSM5 catalysts before and after aging at 700 °C [(◆) CuZSM5-61-fresh, (■) CuZSM5-92-fresh, (▼) CuZSM5-124-fresh, (●) CuZSM5-150-fresh, (◇) CuZSM5-61-700, (□) CuZSM5-92-700, (▽) CuZSM5-124-700, (○) CuZSM5-150-700] for the reduction of NO by NH_3. Feed gas composition is 500 ppm NO, 500 ppm NH_3, 5% O_2, 10% H_2O in N_2 balance.

the oxidation of NH_3 at the high reaction temperature with oxygen leading to a significant decrease in NH_3 selectivity for NO_x reduction as follows [32]:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O. \tag{3}$$
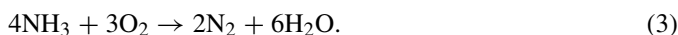
Among the catalysts before and after aging, CuZSM5-124 exhibited the best performance for NO removal activity maintenance, even at a reaction temperature below 200 °C, which is critical for the application of the present urea SCR technology to light-duty diesel engines. However, the activity for underexchanged CuZSM5-61 catalyst aged at 700 °C decreases significantly.

Figs. 2 and 3 illustrate the aging effect of a series of CuZSM5 catalysts with respect to the copper content and the aging temperatures on NO removal activity in a reaction temperature range of 150–450 °C. For the catalysts containing <4% copper loading, NO removal activity increases as the Cu loading increases, regardless of the catalyst aging. However, for a highly overexchanged catalyst such as CuZSM5-150, the activity decrease due to the catalyst sintering is somewhat milder than that for slightly overexchanged catalyst, CuZSM5-124. For an underexchanged catalyst containing low copper content, such as CuZSM5-65, the worst catalyst deactivation can be observed, even for the catalyst aged at 600 °C. However, the cause of the sintering of Cu-based zeolite catalyst for SCR reaction has not yet been systematically examined. It has been simply speculated, probably

ation of the chemical state of copper on the catalyst surface [19,20,24–28].

3.2. Confirming the structure of the catalyst support, ZSM5, by ^{27}Al MAS-NMR and powder XRD

^{27}Al MAS-NMR spectra were examined for the CuZSM5-150 catalyst before and after hydrothermal treatment with the simulated aging gas stream containing 10% water, as shown in Fig. 4. No shoulder due to extra-framework AlO_4 units was detected even for CuZSM5-150-800, except for that assigned to tetrahedral Al species. It may be direct evidence for the maintenance of the catalyst structure without dealumination from the framework of zeolite due to hydrothermal treatment even at 800 °C. Identical NMR results were observed for all of the catalysts before and after aging. However, the intensity of the Al tetrahedral peak decreased, as also shown in Fig. 4, probably due to the paramagnetic field of the Cu ions at their ion-exchange positions in the framework of zeolite structure. This characteristic of the Cu ions also produces an intensified and extended side band of the NMR spectra, which may be originated from the anisotropic dipolar interaction between the electron spin of the Cu ions and the nuclei spin of the Al in the zeolite framework [33].

Fig. 5 shows the typical powder XRD patterns for the series of the catalysts prepared before and after hydrothermal treatment. The relative intensities of X-ray peaks decrease due to the amount of Cu loadings on the catalyst surface and the aging temperature, particularly for underexchanged CuZSM5 catalysts. In addition, a fairly obvious weaker crystallinity for the overexchanged CuZSM5 compared with the underexchanged one is seen. It closely agrees with the decreasing trends of BET and micropore surface areas on the hydrothermal treatment of the catalysts as listed in Table 1. The irreversible decrease of the catalyst surface areas mainly causes a permanent loss of NO removal activity for overexchanged CuZSM5 catalysts aged at the high sintering temperature. It may be also attributed to the simultaneous effects of the combination of high Cu loading and harsh aging conditions on the framework structure of ZSM5-type zeolite catalyst [34]. In addition, a broad XRD peak can be observed at 2θ of ca. 35.5° and 39° in the patterns of CuZSM5-150 catalysts, indicating formation of CuO on the catalyst surface, even for the fresh counterpart catalyst, but basically no CuO peak for the slightly underexchanged CuZSM5 catalyst, regardless of the aging temperatures. This may cause the decrease of NO removal activity of overexchanged CuZSM5 catalyst aged at 800 °C, as mentioned earlier, but catalyst deactivation for underexchanged CuZSM5 catalysts can barely be elucidated. Note that the additional XRD peaks for the formation of CuO and Cu_2O on the catalyst surface of underexchanged CuZSM5 also cannot be identified, as shown in Fig. 5. Also note that formation of the Cu-aluminate related to the octahedral Al of the catalyst was hardly observed on the basis of the ^{27}Al MAS-NMR and XRD results, although we did not conduct a TPR analysis to confirm its formation, as was done by
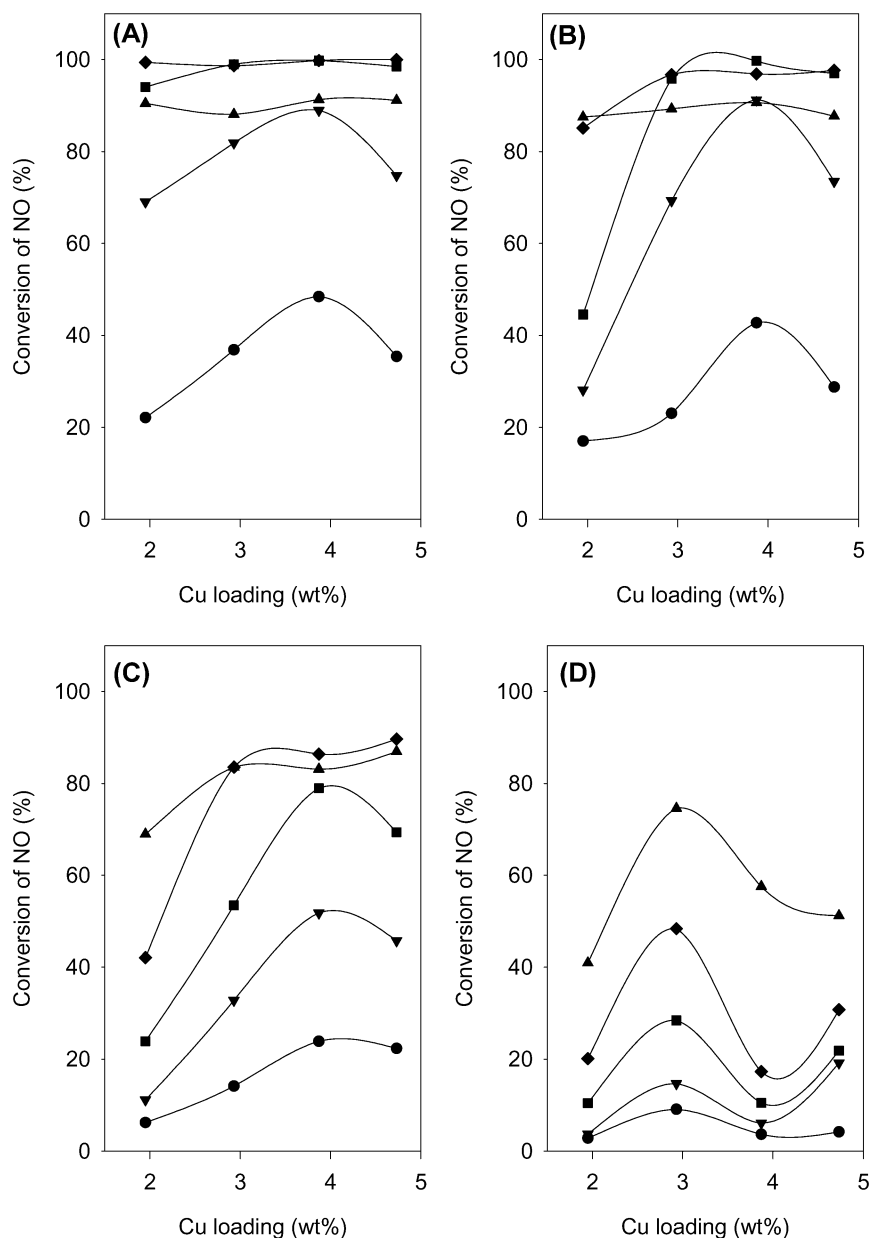
Fig. 2. Effect of Cu loading on the conversion of NO for CuZSM5 catalysts: (A) fresh, (B) aged at 600 °C, (C) aged at 700 °C, and (D) aged at 800 °C. Feed gas composition is 500 ppm NO, 500 ppm NH$_3$, 5% O$_2$, 10% H$_2$O in N$_2$ balance, and SV is 100,000 h^{-1}. [Reaction temperature: (●) 150, (▼) 175, (■) 200, (◆) 300, and (▲) 400 °C.]

3.3. Local structure of copper ions by XAFS

The shape and position of the Cu K-edge XANES provide information on the electronic structure and the local coordination geometry of the absorbing Cu atom [22–24,35–42]. Fig. 6 shows the XANES spectra for CuZSM5 catalysts, which are quite typical for the existence of the distorted octahedral Cu^{2+} on the catalyst surface. The first derivatives of the XANES spectra for the catalyst samples on the hydrothermal treatment are given in Fig. 7; the general patterns are basically identical. In fact, the weak pre-edge peaks (I), corresponding to an electric dipole-forbidden, but quadruply and vibronically allowed 1s → 3d electronic transition and providing direct information

which is the fingerprint of Cu^{2+} species on the catalyst surface [23,36].

The primary absorption peaks (II and III) for all of the catalysts appear at ca. 8986–8988 and 8995–8998 eV, respectively, which are attributed to the charge transfer from the metal ligand to the 3d orbital (ligand-to-metal charge transfer) corresponding to the degree of Cu(3d)–O(2p) bond covalence, and 1s → 4p transition, respectively [23,36]. The shift of peak positions has been also observed at the lower absorption energy. The evolution of the absorption peaks (II and III) in Fig. 7 with respect to the Cu content and the aging condition may be due to the gradual polymerization of Cu^{2+} ions with oxygen ion (O^{2-}) on the catalyst surface. To identify and evaluate the peak posi-

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