Catalytic Performances of Cu/MCM-22 Zeolites with Different Cu Loadings in NH₃-SCR

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Abstract: The NH₃-SCR activities and hydrothermal stabilities of five xCu/MCM-22 zeolites with different Cu loadings (x = 2–10 wt%) prepared by incipient wetness impregnation method were systematically investigated. The physicochemical properties of xCu/MCM-22 zeolites were analyzed by XRD, nitrogen physisorption, ICP-AES, SEM, NH₃-TPD, UV-vis, H₂-TPR and XPS experiments. The Cu species existing in xCu/MCM-22 are mainly isolated Cu²⁺, CuOₓ and unreducible copper species. The concentrations of both isolated Cu²⁺ and CuOₓ species in xCu/MCM-22 increase with Cu contents, but the increment of CuOₓ species is more distinct, especially in high Cu loadings (>4 wt%). NH₃-SCR experimental results demonstrated that the activity of xCu/MCM-22 is sensitive to Cu content at low Cu loadings (≤ 4 wt%). When the Cu loading exceeds 4 wt%, the NH₃-SCR activity of xCu/MCM-22 is irrelevant to Cu content due to the severe pore blockage effects caused by aggregated CuOₓ species. Among the five xCu/MCM-22 zeolites, 4Cu/MCM-22 with moderate Cu content has the best NH₃-SCR performance, which displays higher than 80% NOₓ conversions in a wide temperature window (160–430 °C). Furthermore, the hydrothermal aging experiments (xCu/MCM-22 was treated at 750 °C for 10 h under 10% water vapor atmosphere) illustrated that all the xCu/MCM-22 zeolites exhibit high hydrothermal stability in NH₃-SCR reactions.

Keywords: Cu/MCM-22; NH₃-SCR; Cu loading; hydrothermal aging

1. Introduction

The burning of fossil fuels and intense human activities have caused sharp increases in the emissions of CO₂, SO₂ (SO₂ and SO₃) and nitrogen oxides (NOₓ, mainly NO and NO₂) in the atmosphere, which have resulted in a series of environmental problems, such as acid rain, photochemical smog, the greenhouse effect and haze [1–3]. As a very stable gas in the atmosphere with 114 years of half-life, NOₓ has attracted considerable attention in recent years due to its much higher greenhouse gas effect: 298 CO₂ global warming equivalents in 100 years [4]. Selective catalytic reduction of NOₓ by ammonia (NH₃-SCR) is one of the most widely used methods to reduce NOₓ emissions from both industrial off-gases and diesel engine exhausts due to its high efficiency and low cost, as it can use liquid ammonia or urea as the NH₃ source [5,6].

Limited by the narrow temperature window (320–450 °C), insufficient hydrothermal stability and biotoxicity, conventional vanadia catalysts have gradually been replaced by nontoxic metal-based
zeolite catalysts, especially Cu-based zeolites with a wide temperature window (200–500 °C) and high hydrothermal stability in NH$_3$-SCR [4,5], owing to their unique properties such as high surface areas, considerable acidity and well-defined pore systems with stable structure which can sustain up to 800 °C [6,7]. In addition, due to the high redox activity of Cu species, Cu-based zeolites such as Cu/SSZ-13 [7,8], Cu/SAPO-34 [9,10], Cu/LTA [8,11] and Cu/SSZ-39 [12,13] have become the most used catalysts in NH$_3$-SCR, especially in the low temperature range (200–350 °C) [13,14]. Currently, Cu/SSZ-13-based catalysts have been commercially applied in the treatment of diesel engine exhausts in the USA and Europe [5,14,15]. However, the high-temperature stability of Cu/SSZ-13 in NH$_3$-SCR still cannot meet the industrial requirements [16]. According to the literature [17], the NH$_3$-SCR activity of aluminum-rich (Si/Al < 8) Cu/SSZ-13 dramatically decreased after hydrothermal treatment at 750 °C for 12 h in air containing 10% H$_2$O. As the NH$_3$-SCR reactions usually occur in hydrothermal conditions at 200–550 °C with H$_2$O (as one of the products) in the reaction atmosphere, Cu/SSZ-13 with low hydrothermal stability would result in frequent replacement of catalysts in practical applications. Lately, Cu/SAPO-34 with an identical CHA (Chabazite) structure to Cu/SSZ-13 was repeatedly found to be more stable than Cu/SSZ-13 during high-temperature (>700 °C) hydrothermal aging [18], and correspondingly became a better long-term SCR stable catalyst. However, Cu/SAPO-34 was proven to lack durability at low temperatures (<100 °C) in the presence of moisture [19,20]. Due to the destructive effect of H$_2$O on the SAPO-34 framework, H$_2$O in air could destroy Cu/SAPO-34 zeolite even at room temperature [21], which would lead to the loss of activity for Cu/SAPO-34 in NH$_3$-SCR. Therefore, it is of great significance to develop novel Cu-based zeolite catalysts with both high activity and good hydrothermal stability in a wide temperature window.

MCM-22 with MWW topology is a kind of layered zeolite which has three different types of pores: two-dimensional sinusoidal channels with elliptical 10-membered ring cross-sections (0.40 × 0.51 nm), cylindrical supercages (0.71 nm in diameter and 1.82 nm in height) that are accessible through 10-membered ring (0.40 × 0.55 nm) windows and pockets on the external surface (0.71 nm in diameter and 0.70 nm in height) [22,23]. In comparison with SSZ-13 which can only be synthesized within narrow Si/Al ratios (5–50) with costly organotemplates such as N,N,N-trimethyladamantammonium hydroxide (TMAdaOH) [24], MCM-22 zeolites are synthesized in a wider composition range (Si/Al ratios of 10–200) with much lower costs [23,25]. As a result, MCM-22 zeolites are used as catalysts for the liquid-phase alkylation of benzene to cumene and ethylbenzene and as a good cracking zeolite additive for the fluid catalytic cracking (FCC) process in the petrochemical industry [26,27].

Corma and co-workers [28] found that Cu/MCM-22 zeolites were active catalysts with relatively high hydrothermal stability in selective catalytic reduction of NO with propane. Rutkowska and co-workers [29] found that Cu/MCM-22 zeolites could reach about 75% NO conversion with >90% N$_2$ selectivity at only 180 °C in NH$_3$-SCR. In addition, Cu/MCM-22 zeolites could still maintain 100% NO conversion and >90% N$_2$ selectivity at 250–450 °C after hydrothermal aging in air with H$_2$O at 550 °C for 3 h, which indicated that they were potential catalysts in NH$_3$-SCR with good hydrothermal stability. Palella and co-workers [30] compared the decomposition of NO and N$_2$O over Cu/MCM-22 and Cu/ZSM-5 zeolites, and revealed that Cu/MCM-22 displayed higher hydrothermal stability than Cu/ZSM-5. Lately, our group [22] found that the one-pot synthesized Fe/MCM-22 zeolite showed excellent activity in a wide temperature range (200–500 °C) in NH$_3$-SCR. The above research results concerning the MCM-22 zeolites proved that Cu-based MCM-22 zeolites should be potential catalysts in NH$_3$-SCR. However, detailed investigations about Cu/MCM-22 zeolites in NH$_3$-SCR are still lacking.

According to previous studies [31], the main active sites of Cu-based zeolites in NH$_3$-SCR reactions are isolated Cu$^{2+}$ species or its hydrated form [Cu(OH)]$^+$. Highly aggregated Cu$^+$ species show much lower activity than isolated Cu$^{2+}$ species in NH$_3$-SCR; besides, they will inevitably catalyze the ammonia oxidation side reactions at high temperatures, which is unfavorable for NH$_3$-SCR. The chemical environment and distribution of active Cu species in Cu-based zeolites are often related to their Si/Al ratios, as the cationic Cu species need to electrostatically balance the negative charge generated by the AlO$_4^-$ tetrahedral structure in the zeolites [32–35]. When the Si/Al ratio of a zeolite
is fixed, there should be an optimal Cu loading in Cu/zeolite catalysts, which can not only ensure the formation of enough active Cu species to guarantee high NH$_3$-SCR activity, but also stabilize the zeolite framework, thereby improving the hydrothermal stability of catalysts [36–38]. For example, the first generation of commercial Cu/SSZ-13 catalyst developed by BASF company had a Si/Al ratio of 17.5 and an optimal Cu content of 2.8 wt% with 100% Cu$^{2+}$ ion-exchange degree [16]. Further, the Si/Al of Cu/SSZ-13 catalyst was optimized to about 10 to guarantee enough acid sites in catalysts, as acid sites are also important for the NH$_3$-SCR process; besides, the ion exchange degree of Cu$^{2+}$ on Cu/SSZ-13 was adjusted to about 60% (Cu content is 2.8 wt%) to obtain the best catalytic activity and hydrothermal stability in NH$_3$-SCR [31,39].

Therefore, in this work, a series of xCu/MCM-22 zeolites with Si/Al ratios of about 15 (to ensure enough acid sites) and different Cu loadings (2–10 wt%) were prepared by incipient wetness impregnation method in order to investigate their catalytic activities and hydrothermal stability in NH$_3$-SCR. The physicochemical properties of xCu/MCM-22 zeolites were investigated by powder X-ray diffraction (XRD), N$_2$ physical adsorption, NH$_3$ temperature-programmed desorption (NH$_3$-TPD), H$_2$ temperature-programmed reduction (H$_2$-TPR), inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible diffuse reflectance spectra (UV-vis) experiments. The optimal Cu loading for H-MCM-22 with Si/Al ratio of 15 and the hydrothermal stability of xCu/MCM-22 zeolites in NH$_3$-SCR were clarified. The insights shown in this work should be of great benefit to the development of better NH$_3$-SCR catalysts and the understanding of reaction processes.

2. Materials and Methods

2.1. Catalyst Preparation

Parent H-MCM-22 zeolite (with Si/Al ratio of 15) was hydrothermally synthesized according to the previous procedures [22,23] by using sodium meta-aluminate (NaAlO$_2$, 41 wt% Al$_2$O$_3$, 41 wt% Na$_2$O, Sinopharm Chem. Reagent Co., Ltd. Shanghai, China), silica sol (40.5 wt% SiO$_2$, Qingdao Haiyang Chem. Co., Ltd. Qingdao, China), hexamethyleneimine (HMI, 98 wt%, Aladdin industrial Co., Ltd. Shanghai, China), boric acid (99.8 wt%, Sinopharm Chem. Reagent Co., Ltd. Shanghai, China), sodium hydroxide (NaOH, 96 wt%, Sinopharm Chem. Reagent Co., Ltd. Shanghai, China) and deionized water. The synthesis gel had a molar composition of SiO$_2$:0.033Al$_2$O$_3$:0.9H$_3$BO$_3$:1HMI:0.3NaOH:3H$_2$O. The synthesis process was as follows: 0.73 g of NaOH, 0.80 g of NaAlO$_2$ and 5.57 g of H$_3$BO$_3$ were dissolved in 45 g of deionized water. After stirring the mixture at room temperature for 10 min, 9.92 g of HMI was introduced under stirring. Finally, 14.81 g of silica sol was slowly added and it was further stirred for 3 h. The synthesis gel was then crystallized in a Teflon-lined stainless-steel autoclave at 170 °C for 5 days under rotation. The obtained products were filtered and washed to neutral. Then, the obtained products were dried overnight at 100 °C, and calcined at 560 °C for 10 h in air to remove the template molecules in the zeolites. H-MCM-22 (MCM-22 in hydrogen form) was prepared by ion-exchanging the calcined samples twice with NH$_4$NO$_3$ (99 wt%, Sinopharm Chem. Reagent Co., Ltd. Shanghai, China) aqueous solution (for example, 1 g zeolites were mixtures with 45 mL 1 mol/L NH$_4$NO$_3$ solution) at 80 °C for 5 h, which was then calcined in air at 550 °C for 6 h.

Cu-based MCM-22 zeolites were prepared by incipient wetness impregnation method. Typically, Cu(NO$_3$)$_2$·3H$_2$O solution (0.38–1.89 g of Cu(NO$_3$)$_2$·3H$_2$O (99–102%, Sinopharm Chem. Reagent Co., Ltd. Shanghai, China) dissolved in 23 mL deionized water) was mixed with 5 g of H-MCM-22 samples under constant stirring. The mixture solution was first treated at 40 KHz by ultrasound for 20 min and then stirred for 24 h at room temperature. After that, the products were dried at 100 °C for 12 h and then calcined in air at 550 °C for 6 h to obtain the xCu/MCM-22 catalyst, where x represents the Cu loadings (x = 2, 4, 6, 8, 10 wt%, respectively). Hydrothermal aging treatment of xCu/MCM-22 catalysts: portions of xCu/MCM-22 zeolites were placed in a tube furnace, and then hydrothermally aged in air containing 10% water for 10 h at 750 °C; the obtained samples were denoted as xCu/MCM-22-aged catalysts.
2.2. Catalyst Characterization

The X-ray powder diffraction (XRD) patterns collected on a PANalytical X’pert Pro MPD X-ray diffractometer (Philips, Eindhoven, Netherlands) was adjusted to a Cu Kα radiation of 154.06 pm in the range of 2θ from 3° to 50° with a scan speed of 4°/min. Using a paper by Xing and co-workers [40], the relative crystallinity (RC) of metal modified zeolites was obtained by dividing the sums of their diffraction peak intensities at 2θ of 14.3°, 22.7°, 23.7° and 26.0° by that of the reference sample (H-MCM-22 zeolite with a assumed 100% crystallinity).

The practical atomic composition of catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Autoscan16, TJA, Seymour Fisher Corporation, USA).

Nitrogen adsorption/desorption isotherms were collected on a TriStar II 3020 gas adsorption analyzer (Micromeritics, Norcross, GA, USA). Before the measurement, zeolite samples were degassed for 8 h under high vacuum at 300 °C. The BET surface area (S_BET) was calculated by Brunauer–Emmett–Teller (BET) method (focused on adsorption curve in the relative pressure range of 0.05 to 0.25). Total pore volume (V_total) was determined at a nitrogen relative pressure of 0.99. The external surface area (S_ext) and micropore volume (V_micro) were calculated by t-Plot method. The micropore surface area (S_micron) and mesopore volume (V_meso) were calculated by the differences between S_BET and S_ext, and between V_total and V_micro, respectively.

With the assistance of field emission scanning electron microscope (Quanta 400 FEG, FEI Electron Optics, Hillsboro, OR, USA), scanning electron microscopy (SEM) images were taken to analyze the surface morphology of zeolite samples.

The ultraviolet-visible diffuse reflectance spectra (UV-vis) in 200–800 nm were collected on a Cary 5000 UV-vis-DRS spectrophotometer (Agilent Technologies Inc., Santa Clara, CA, USA, the diffuse reflectance was attached with a BaSO₄ integrating sphere).

Prior to the H₂ temperature-programmed reduction performed on a Chem Star chemisorption analyzer (Quantachrome Instrument Crop., Boynton Beach, FL, USA), 0.2 g of sample fixed in a quartz U-tube was pre-treated at 350 °C for 1 h and then cooled down to 50 °C (by a heating rate of 10 °C/min under Ar flow (30 mL/min)). Afterwards, in 10% H₂/Ar (30 mL/min) flow, the temperature increased to 900 °C with a ramp of 10 °C/min. The signal fluctuation of H₂ was recorded by using a thermal conductivity detector (TCD).

Before the temperature-programmed desorption of NH₃ (NH₃-TPD) experiment operated on a Chem Star chemisorption analyzer (Quantachrome Instrument Crop., Boynton Beach, FL, USA), 0.2 g catalysts were pre-treated with the same procedures as in H₂-TPR experiments. Afterwards, samples were flushed with 10% NH₃/He flow (30 mL/min) for 1 h at 50 °C, followed by pure He purging for 30 min to eliminate the gaseous/physically adsorbed NH₃ species. Finally, catalysts were heated to 900 °C at a ramp of 10 °C/min in He flow (30 mL/min), during which the signal of NH₃ was monitored by a TCD detector.

Aimed at investigating the surface properties and valence state, X-ray photoelectron spectroscopy (XPS) was collected on a Thermo ESCALAB 250 system (Thermo Fisher Scientific, Waltham, MA, USA) with Al Kα radiation (hv = 1486.6 eV). The C 1s (284.6 eV) was referenced so as to calibrate the binding energy.

2.3. Reaction Measurements

The catalytic performance of NH₃-SCR was investigated in a fixed-bed flow reactor equipped with a quartz tube. Typically, 0.3 g 20-40 mesh catalyst was pre-treated in 5% O₂/N₂ flow (75 mL/min) at 120 °C for 30 min before increasing to 550 °C at a ramp of 10 °C/min. One hour later it was cooled down to 100 °C. Then the feed gas (300 mL/min) contained 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, and balanced N₂ was introduced. The standard NH₃-SCR was tested from 100 to 550 °C with 50 °C as a step. At each target temperature, a minimum maintenance time of 45 min was set to reach a steady state. Both the inlet and outlet concentrations of NOₓ (NO and NO₂) were analyzed using a...
flue gas analyzer (KM950, Kane International Limited, Welwyn Garden City, UK). NO\textsubscript{x} conversion was calculated on the basis of:

\[
\text{NO\textsubscript{x} conversion (\%)} = \frac{C\text{in}_{\text{NO\textsubscript{x}}} - C\text{out}_{\text{NO\textsubscript{x}}}}{C\text{in}_{\text{NO\textsubscript{x}}}} \times 100\% \quad (1)
\]

For NO oxidation experiments, the experimental steps are similar to the standard NH\textsubscript{3}-SCR experiments, while the feed gas was: 500 ppm NO, 5 vol.% O\textsubscript{2} and balanced N\textsubscript{2}. The NO conversion was calculated on the basis of:

\[
\text{NO conversion (\%)} = \frac{C\text{in}_{\text{NO}} - C\text{out}_{\text{NO}}}{C\text{in}_{\text{NO}}} \times 100\% \quad (2)
\]

The subscripts “in” and “out” in Equations (1) and (2) represent the inlet and outlet concentrations of NO\textsubscript{x} or NO, respectively.

3. Results and Discussions

3.1. Textural and Structural Properties

Figure 1 shows the SEM images of H-MCM-22 (Figure 1a) and xCu/MCM-22 zeolites (Figure 1b–f). All the zeolites had the disk-like shape of typical MWW zeolites with a similar particle size of around 1 \( \mu \)m in diameter and 50–100 nm in thickness, illustrating that the introduction of copper caused only minor changes in the textural properties of MCM-22 crystals. The XRD patterns of H-MCM-22 and xCu/MCM-22 zeolites are shown in Figure 2, which exhibit typical diffraction peaks for MWW framework structures without impurities [23]. As shown in Table 1, the relative crystallinities (RC) of all the zeolites are similar and in the range of 93–102\%, supporting that the introduction of copper into H-MCM-22 zeolites does not destroy the framework structure of MCM-22 zeolites.

![Figure 1](image1.png)

**Figure 1.** SEM images of H-MCM-22 (a) and xCu/MCM-22 zeolites: (b) 2Cu/MCM-22, (c) 4Cu/MCM-22, (d) 6Cu/MCM-22, (e) 8Cu/MCM-22, (f) 10Cu/MCM-22.
When Cu loading exceeded 4 wt%, the loss percentages of BET surface area and total pore volume for $\textit{xCu}/\text{MCM-22}$ were close to their theoretical values (0, 2, 4, 6, 8, 10 wt%, respectively), illustrating that the Cu contents gradually increased with Cu loadings in $\textit{xCu}/\text{MCM-22}$. As displayed in Table 1 and Figure S2, in comparison with parent H-MCM-22, both the BET surface area and total pore volume in $\textit{xCu}/\text{MCM-22}$ decreased about 20%. When further increasing the Cu loading to 4 wt%, the loss percentage values in Figure S2B for $4\text{Cu}/\text{MCM-22}$ only slightly changed. However, when Cu loading exceeded 4 wt%, the loss percentages of BET surface area and total pore volume for $6\text{Cu}/\text{MCM-22}$, $8\text{Cu}/\text{MCM-22}$ and $10\text{Cu}/\text{MCM-22}$ dramatically decreased to 30–40%, which suggests that the formation of aggregated CuO species caused severe pore blockage in MCM-22 zeolites, supported by XRD results in Figure 2. Moreover, as shown in Table 1, the external surface area ($S_{\text{ext}}$) and mesopore volume ($V_{\text{meso}}$) only slightly changed from $2\text{Cu}/\text{MCM-22}$ to $10\text{Cu}/\text{MCM-22}$, which demonstrates that aggregated CuO species mainly block the micropores in MCM-22 zeolites. Furthermore, comparing the loss of BET surface area ($S_{\text{BET}}$) with micropore surface area ($S_{\text{micro}}$) in Figure S2A, or the loss of total pore volume ($V_{\text{total}}$) with micropore volume ($V_{\text{micro}}$) in Figure S2B, it can be concluded that when

![Figure 2. XRD patterns of H-MCM-22 and $\textit{xCu}/\text{MCM-22}$ zeolites.](image)

| Zeolites     | Cu $^d$ (wt%) | RC $^b$ (%) | Surface Area $^c$ ($m^2 \cdot g^{-1}$) | Pore Volume $^c$ ($cm^3 \cdot g^{-1}$) |
|-------------|---------------|-------------|----------------------------------------|----------------------------------------|
| H-MCM-22    | 0             | 100         | 500                                    | 0.50                                   |
| 2Cu/MCM-22  | 2.1           | 93          | 404                                    | 0.40                                   |
| 4Cu/MCM-22  | 3.7           | 100         | 404                                    | 0.40                                   |
| 6Cu/MCM-22  | 6.7           | 100         | 391                                    | 0.39                                   |
| 8Cu/MCM-22  | 8.5           | 93          | 365                                    | 0.38                                   |
| 10Cu/MCM-22 | 10.4          | 102         | 290                                    | 0.34                                   |

Cu contents of all the zeolites were measured by ICP-AES. Relative crystallinity (RC) of $\textit{xCu}/\text{MCM-22}$ was estimated by comparing the sum of the peak intensities of each zeolite at 2θ of 14.3°, 22.7°, 23.7° and 26.0° with that of H-MCM-22 as a reference, according to Xing and co-workers [40]. Surface area and pore volume of each of the zeolites were determined by nitrogen physisorption experiments. $S_{\text{BET}}$, $S_{\text{micro}}$ and $S_{\text{ext}}$ represent the BET surface area, micropore surface area and external surface area, respectively. $V_{\text{total}}$, $V_{\text{micro}}$ and $V_{\text{meso}}$ represent the total pore volume, micropore volume and mesopore volume, respectively.

In addition, as shown in Figure 2, small diffraction peaks at 2θ of 35.6°, 38.7° and 48.8° gradually emerge with the increasing of Cu contents, which indicates the formation of CuO nanoparticles in $\textit{xCu}/\text{MCM-22}$ zeolites [41,42]. As displayed in Table 1, the actual copper contents in $\textit{xCu}/\text{MCM-22}$ were close to their theoretical values (0, 2, 4, 6, 8, 10 wt%, respectively), illustrating that the Cu contents in $\textit{xCu}/\text{MCM-22}$ zeolites can be easily adjusted through incipient wetness impregnation method. As shown in Figure S1, a positive relationship between Cu content and the intensity of diffraction peak representing CuO was observed, indicating that the concentration of aggregated CuO nanoparticles gradually increased with Cu loadings in $\textit{xCu}/\text{MCM-22}$.

The quantitative results of nitrogen physisorption experiments are shown in Table 1 and Figure S2. As displayed in Table 1 and Figure S2, in comparison with parent H-MCM-22, both the BET surface area and total pore volume in $2\text{Cu}/\text{MCM-22}$ decreased about 20%. When further increasing the Cu loading to 4 wt%, the loss percentage values in Figure S2B for $4\text{Cu}/\text{MCM-22}$ only slightly changed. However, when Cu loading exceeded 4 wt%, the loss percentages of BET surface area and total pore volume for $6\text{Cu}/\text{MCM-22}$, $8\text{Cu}/\text{MCM-22}$ and $10\text{Cu}/\text{MCM-22}$ dramatically decreased to 30–40%, which suggests that the formation of aggregated CuO species caused severe pore blockage in MCM-22 zeolites, supported by XRD results in Figure 2. Moreover, as shown in Table 1, the external surface area ($S_{\text{ext}}$) and mesopore volume ($V_{\text{meso}}$) only slightly changed from $2\text{Cu}/\text{MCM-22}$ to $10\text{Cu}/\text{MCM-22}$, which demonstrates that aggregated CuO species mainly block the micropores in MCM-22 zeolites. Furthermore, comparing the loss of BET surface area ($S_{\text{BET}}$) with micropore surface area ($S_{\text{micro}}$) in Figure S2A, or the loss of total pore volume ($V_{\text{total}}$) with micropore volume ($V_{\text{micro}}$) in Figure S2B, it can be concluded that when
Cu loading exceeds 6 wt%, the losses of \( S_{\text{micro}} \) and \( V_{\text{micro}} \) are much larger than those of \( S_{\text{BET}} \) and \( V_{\text{total}} \), which indicates the severe blockage of microporous pore in zeolites at high Cu loadings.

In general, xCu/MCM-22 zeolites with different Cu loadings have similar relative crystallinities, crystal size and surface morphology. However, aggravated CuO nanoparticles gradually formed with increasing Cu loadings, which led to the decrease of micropore surface area and micropore pore volume in xCu/MCM-22. The pore blockage effect of CuO species in xCu/MCM-22 was significant when the Cu loadings exceeded 4 wt%, which meant xCu/MCM-22 lost 30–40% of BET surface area and total pore volume.

3.2. Acidity of Catalysts

A good NH\(_3\)-SCR catalyst should have appropriate amounts of acid sites to promote ammonia adsorption and activation at the active sites during the reaction processes [36,43,44]. Thus, the temperature-programmed desorption of NH\(_3\) (NH\(_3\)-TPD) was performed in order to investigate the acid properties of H-MCM-22 and xCu/MCM-22 zeolites used in this work.

As shown in Figure 3, three TPD peaks were observed at about 145, 210 and 450 °C in H-MCM-22 zeolite, which can be attributed to NH\(_3\) desorbed from the weak, medium and strong acid sites, respectively [45]. As all of the samples in Figure 3 have similar Si/Al ratios, the different acid densities of xCu/MCM-22 zeolites can be mainly attributed to their different Cu loadings. In comparison with H-MCM-22, the TPD peak at 450 °C in 2Cu/MCM-22 dramatically decreased while the peak at 343 °C increased, which suggests that the introduced Cu species not only covered some of the strong acid sites but also formed some medium acid sites in 2Cu/MCM-22 [46]. When further increasing Cu loading to 10 wt% (from 2Cu/MCM-22 to 10Cu/MCM-22), the peak in 343 °C gradually changed to 383 °C, and two peaks at about 450 °C and 600 °C obviously emerged. As the intensities of peaks at 450 and 600 °C gradually increased with Cu loadings, we deduced that they may be related with Cu species.

![Figure 3. NH\(_3\)-TPD profiles of H-MCM-22 and xCu/MCM-22 zeolites.](image-url)

According to the above speculations, the NH\(_3\)-TPD profiles in Figure 3 were deconvoluted into three or six peaks, as shown in Figure S3. Correspondingly, the quantitative results of NH\(_3\)-TPD experiments are summarized in Table 2. All the zeolites in Table 2 have similar total acid density (in the range of 1062 to 1276 µmol/g). However, the concentrations of weak, medium and strong acid sites in H-MCM-22 and xCu/MCM-22 are apparently different. As the Cu loadings increased from 0 to 10 wt% (from H-MCM-22 to 10Cu/MCM-22), the densities of weak and medium acid sites gradually decreased from 255 µmol/g to 102 µmol/g, and from 446 µmol/g to 140 µmol/g, respectively. In contrast, the density of strong acid sites dramatically increased from 361 µmol/g to 1034 µmol/g. According to the literature [22,47–50], the results in Table 2 demonstrate that some of the weak and medium acid sites were covered by Cu species, but the introducing of Cu species also led to the increasing of strong
acid sites. As shown in Figure 3, the shift of TPD peaks towards higher temperatures also confirms that the global acid strength of xCu/MCM-22 zeolites gradually increases with Cu loadings, which is in agreement with the quantitative results in Table 2.

Table 2. Quantitative results of acid densities in H-MCM-22 and xCu/MCM-22 zeolites.

| Zeolites     | Acid Sites Density (μmol/g) |
|--------------|-----------------------------|
|              | Total \(^{a}\) | Weak \(^{a}\) | Medium \(^{b}\) | Strong \(^{b}\) |
| H-MCM-22     | 1062          | 255           | 446          | 361          |
| 2Cu/MCM-22   | 1216          | 207           | 328          | 681          |
| 4Cu/MCM-22   | 1124          | 202           | 247          | 674          |
| 6Cu/MCM-22   | 1152          | 173           | 265          | 714          |
| 8Cu/MCM-22   | 1197          | 96            | 323          | 778          |
| 10Cu/MCM-22  | 1276          | 102           | 140          | 1034         |

\(^{a}\) Total acid density of each sample was determined by NH₃-TPD experiments in Figure 3. \(^{b}\) Densities of weak, medium and strong acid sites were calculated based on the deconvoluted relative percentages of the peaks at around 140, 210 and 460 °C in Figure 3 and Figure S3, respectively.

It should be noted that the parent H-MCM-22 zeolite contains boron elements because H₃BO₃ was used in the synthesis process of H-MCM-22 in order to increase the crystallinity and yield of H-MCM-22 zeolites. However, as boron can only form extremely weak acid sites, and can be easily removed in the following NH₄NO₃ ion-exchange procedures [22], it should have minor effects on the acidity of H-MCM-22 and xCu/MCM-22 zeolites.

In general, the content of Cu in H-MCM-22 has little influence on the total acid density of xCu/MCM-22 zeolites, but the global acid strength of xCu/MCM-22 zeolites increases with Cu loadings, which may result in different NH₃ adsorption and activation abilities of xCu/MCM-22 zeolites in NH₃-SCR.

3.3. Characterization of Cu Species

The existing states of Cu species in xCu/MCM-22 zeolites were characterized by UV-vis spectroscopy, as shown in Figure 4. According to previous literature [51,52], the UV bands at around 13,100 cm⁻¹ can be attributed to the d–d transitions of Cu²⁺ in a distorted octahedral configuration; the broad bands at around 35,000 and 48,000 cm⁻¹ were caused by O²⁻→Cu²⁺ charge transfer transitions; all of those bands are characteristic of the isolated Cu²⁺ species. The UV bands near 22,500 and 40,000 cm⁻¹ are assigned to the d–d transition and charge transfer transition of Cu with octahedral environment in CuO₃ species [42,53–55].

![Figure 4. UV-vis spectra of xCu/MCM-22 zeolites with different copper contents.](image-url)
As shown in Figure 4, the UV band at around 48,000 cm⁻¹ representing isolated Cu²⁺ species was observed for 2Cu/MCM-22 zeolite, while no bands at 22,500 and 40,000 cm⁻¹ corresponding to CuOₓ species were observed, which suggests that most of the Cu species in 2Cu/MCM-22 were isolated Cu²⁺ species, in accordance with XRD results in Figure 2. With the increase of Cu loadings, the UV band at 40,000 cm⁻¹ in 4Cu/MCM-22 emerged, indicating the formation of CuOₓ species. By further increasing Cu loadings (from 4Cu/MCM-22 to 10Cu/MCM-22), the UV absorption bands at 40,000 and 22,500 cm⁻¹ rapidly increased; meanwhile, the band intensity at 40,000 cm⁻¹ exceeds that at 48,000 cm⁻¹. Those results illustrate that for xCu/MCM-22 zeolites with high Cu loadings (6–10 wt%), most of the Cu species in the zeolites are CuOₓ species, though the concentrations of isolated Cu²⁺ species in xCu/MCM-22 also increase with Cu loadings, as reflected by the increased intensity of the bands at 13,100 cm⁻¹. As a whole, the UV-vis results reveal that both isolated Cu²⁺ and CuOₓ species in xCu/MCM-22 increase with Cu loadings; besides, Cu species are mainly in the form of isolated Cu²⁺ species for 2Cu/MCM-22, while for xCu/MCM-22 with high Cu loadings (>4 wt%), CuOₓ species become dominant.

Temperature-programmed reduction with hydrogen (H₂-TPR) experiments were conducted in order to further investigate the Cu species in xCu/MCM-22 zeolites. As shown in Figure 5, no obvious reduction peak was observed for parent H-MCM-22 zeolite. In contrast, the reduction peaks of five xCu/MCM-22 zeolites are complex. For example, four reduction peaks at about 200, 250, 410 and 583 °C can be distinguished in 2Cu/MCM-22, while for 8 Cu/MCM-22 and 10 Cu/MCM-22, only severely overlapped reduction peaks were observed. According to the literature [56,57], the peak at 250 °C in 2Cu/MCM-22 can be attributed to the reduction of CuO nanoparticles to Cu⁰, which indicates that highly dispersed CuO nanoparticles exist in 2Cu/MCM-22, even though they cannot be observed by XRD (Figure 2) due to the detection limitation. On the other hand, the reduction of isolated Cu²⁺ species in zeolites needs two steps due to the strong electrostatic interactions between isolated Cu²⁺ species and the zeolite framework [58]: the isolated Cu²⁺ first be reduced into Cu⁺ and then Cu⁺ be reduced into Cu⁰ at higher temperatures during H₂-TPR experiments. Thus, the reduction peak at 200 °C in 2Cu/MCM-22 can be attributed to the reduction of Cu²⁺ to Cu⁺; the peaks at 410 °C and 583 °C resulted from the reduction of Cu⁺ to Cu⁰ species [9,31,59]. The reason for the occurrence of two reduction peaks in the reduction of Cu⁺ to Cu⁰ may be due to multiple channel systems of MCM-22 zeolites, which form multiple ion-exchange sites for isolated Cu²⁺ species with significantly different reducibility. According to Wasowicz and co-workers [60], there are at least three different ion-exchange sites of Cu²⁺ ions in MCM-22 zeolite, among which the most favorable sites of Cu²⁺ ions are located near the five-ring presented in the intralayer of the two-dimensional sinusoidal channel system and in the interlayer large supercages.

Figure 5. H₂-TPR profiles of H-MCM-22 and xCu/MCM-22 zeolites.
With the increase of Cu loading, the reduction peaks of xCu/MCM-22 zeolites in Figure 5 gradually shift to lower temperatures, though the total peak area increases. For 4Cu/MCM-22, four reduction peaks at around 167, 235, 400 and 550 °C can be distinguished, and only three peaks at 177, 235 and 363 °C were observed for 6Cu/MCM-22. As proven in previous studies [57,58], the reduction of Cu species becomes easier with the increase of nearest neighbor Cu species. Therefore, the reduction peak at about 177 °C in 6Cu/MCM-22 may be contributed to from both the reduction of CuO to Cu\(^{0}\) and of Cu\(^{2+}\) reduced to Cu\(^{+}\). By further increasing Cu loading to 10 wt%, the reduction peak of Cu\(^{2+}\) to Cu\(^{+}\) decreases to 152 °C; meanwhile, the peaks in the range of 200–300 °C dramatically increase and become severely overlapped. According to the literature [56,57], the overlapped peaks between 200 and 300 °C can be attributed to the reduction of CuO to Cu\(^{0}\) in different pore systems of MCM-22 zeolites, as their peak intensities greatly increase with Cu loadings.

Based on the above assignments, the peak deconvolution results of H\(_2\)-TPR experiments are displayed in Figure S4 and Table 3. Due to the complexity of Cu reduction behaviors in high Cu loadings, the results in Table 3 are just semi-quantitative because of the highly overlapped peaks, especially in 8Cu/MCM-22 and 10Cu/MCM-22. As shown in Figure 5, the reduction process I (Table 3) is easily overlapped with reduction process II, so we tentatively take the reduction process III as the representative of isolated Cu\(^{2+}\) species. As shown in Table 3, from 2Cu/MCM-2 to 10Cu/MCM-22, the relative peak area percentages of CuO increase from 14% to 58%, while the relative peak area percentages of isolated Cu\(^{2+}\) species decrease from 65% to 13%, both of which are consistent with the UV-vis results in Figure 4.

| Catalyst | Reduction Process 1\(^{a}\) (Cu\(^{2+}\) to Cu\(^{+}\)) | Reduction Process 2\(^{a}\) (CuO to Cu\(^{0}\)) | Reduction Process 3\(^{a}\) (Cu\(^{+}\) to Cu\(^{0}\)) | \(H_2\) Consumption\(^{b}\) (µmol/g) | \(H_2/\text{Cu}\) r |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2Cu/MCM-22 | 196 21 | 256 14 | 386 65 | 241 | 0.73 |
| 4Cu/MCM-22 | 170 23 | 235 19 | 417 58 | 428 | 0.74 |
| 6Cu/MCM-22 | 177 34 | 235 31 | 580 35 | 622 | 0.59 |
| 8Cu/MCM-22 | 170 27 | 260 48 | 500 25 | 792 | 0.59 |
| 10Cu/MCM-22 | 161 29 | 242 58 | 338 13 | 976 | 0.60 |

\(^{a}\) Relative quantitative results of each Cu/MCM-22 zeolite according to the deconvoluted peaks shown in Figure S4. Reduction processes 1, 2, and 3 represent the reductions of Cu\(^{2+}\) to Cu\(^{+}\), CuO to Cu\(^{0}\), and Cu\(^{+}\) to Cu\(^{0}\), respectively.

\(^{b}\) Total \(H_2\) consumption of each sample was recorded by a thermal conductivity detector (TCD). \(H_2/\text{Cu}\) ratio was calculated from the total \(H_2\) consumption value divided by the Cu concentration in each Cu/MCM-22 zeolite (Table 1).

The quantitative \(H_2\) consumption results of Figure 5 are also presented in Table 3. The \(H_2/\text{Cu}\) ratios of xCu/MCM-22 zeolites were less than 1 (the theoretical \(H_2/\text{Cu}\) ratio for the reduction process of Cu\(^{2+}\) to Cu\(^{0}\)), which decreased from 0.73 to 0.60 with increasing Cu loadings. According to Yue and co-workers [61], the low \(H_2/\text{Cu}\) ratios may be caused by the existence of unreducible copper species in xCu/MCM-22 zeolites. As proven by Figure S5, no obvious peak can be observed for 6Cu/MCM-22, even when reduced at 900 °C during the \(H_2\)-TPR experiment, which suggests that unreducible copper species indeed exist in xCu/MCM-22, as the highly aggravated Cu species should be hardly accessible to \(H_2\) molecules and thus hard to be fully reduced.

In general, \(H_2\)-TPR experiments illustrated that three kinds of Cu species—i.e., isolated Cu\(^{2+}\), CuO nanoparticles and unreducible copper species—exist in xCu/MCM-22 zeolites. In addition, with the increment of Cu loadings, CuO nanoparticles gradually become the predominant Cu species in xCu/MCM-22. Moreover, the reduction temperatures of xCu/MCM-22 gradually shift to lower values with increasing Cu loadings, which may indicate the increase of reducibility for xCu/MCM-22 in NH\(_3\)-SCR.
The content of surface Cu species and their chemical environment were further investigated by X-ray photoelectron spectroscopy (XPS). As presented in Figure 6A, at least five peaks can be distinguished in the Cu 2p XPS spectra of xCu/MCM-22 zeolites. According to the literature [62–65], the Cu 2p3/2 peak at around 933 eV, the Cu 2p1/2 peak at around 953 eV and the 2p → 3d satellite peak at around 944 eV confirm the existence of CuO species in xCu/MCM-22 zeolites, which is in accordance with the above XRD, UV-vis and H₂-TPR results. Moreover, the asymmetry of the Cu 2p3/2 peak at about 933 eV can be deconvoluted into two contributions centered around 933 and 935 eV (as shown in Figure 6B–F), corresponding to dispersed CuO and CuO species which have electrostatic interactions with MCM-22 zeolite framework, respectively, according to previous reports [63–65]. Those results suggest that most of the Cu species existing on the surfaces of xCu/MCM-22 zeolites are CuO nanoparticles, even for 2Cu/MCM-22 with the lowest Cu loading.

![Figure 6. Cu 2p XPS spectra of xCu/MCM-22 with different Cu contents: (A) original spectra and deconvolution spectra of (B) 2Cu/MCM-22, (C) 4Cu/MCM-22, (D) 6Cu/MCM-22, (E) 8Cu/MCM-22 and (F) 10Cu/MCM-22.](image)

The quantitative XPS results of xCu/MCM-22 are displayed in Table 4, in comparison with the ICP-AES results. As shown in Table 4, the Si/Al ratios of xCu/MCM-22 derived from XPS are slightly lower than those from ICP-AES, suggesting that aluminum species are slightly rich on the surface of xCu/MCM-22 zeolites. According to Zhu and co-workers [66], the enrichment of aluminum species on the surface of xCu/MCM-22 after Cu introduction, especially in xCu/MCM-22 with high Cu loadings (from 4Cu/MCM-22 to 10Cu/MCM-22), may be due to the formation of extra-framework Al species and migration of Al species to the surface of MCM-22 zeolites during the calcination process. On the contrary, the Si/Cu ratios of xCu/MCM-22 obtained from XPS are apparently higher than those from ICP-AES, which indicates that most of the Cu species in xCu/MCM-22 are concentrated in the bulk rather than on the surface. As shown in Table 1 and Figure S2B, the decreased BET surface areas and
3.4. NH3-SCR Catalytic Performance

As shown in Figure 7, the catalytic behaviors of five xCu/MCM-22 zeolites are typical for NH3-SCR reactions. NOx conversions first increase with temperature, reaching the maximum conversions at 200–300 °C and then decrease with temperature after 300 °C, as the oxidation of ammonia with oxygen is highly favored at high temperatures [67].

Compared with 2Cu/MCM-22, the NOx conversions of 4Cu/MCM-22 at a low temperature range (<300 °C) increased, but at above 300 °C apparently decreased. In addition, the NOx conversion curves of 6Cu/MCM-22, 8Cu/MCM-22 and 10Cu/MCM-22 zeolites are almost overlapping, indicating their similar SCR activity in spite of difficult Cu loadings. Those results suggest that the NH3-SCR activity of xCu/MCM-22 can be affected only at low Cu loadings (≤4 wt%); once Cu loading exceeds 4%, the catalytic activity has little association with Cu contents. In general, 4Cu/MCM-22 shows the best NH3-SCR activity among the five xCu/MCM-22 zeolites, which exhibits higher than 80% NOx conversion in a wide temperature window (160–430 °C).

The active Cu species in NH3-SCR over Cu-based zeolites are quite complex, especially in the low temperature range (<300 °C) [14,15]. Gao and co-workers [32,37] found that [Cu(OH)]+ and dimer Cu2+ species were the main active centers in NH3-SCR below 300 °C due to the solvation effects between Cu2+ species and H2O at low temperatures. Besides, an ammonia inhibition effect was also observed on the rate-limiting copper re-oxidation step in NH3-SCR below 250 °C [68], which could suppress the oxidation of Cu+ to Cu2+ species and thus inhibit the NH3-SCR reactions. In contrast, the NH3-SCR reactions at high temperature (>300 °C) are less affected by the H2O solvation and ammonia inhibition.
effects; isolated Cu$^{2+}$ species are widely accepted as the primary active sites \[32,37\]. However, the ammonia oxidation side reactions are highly favored at high temperatures, which are mainly catalyzed by aggregated CuO$_x$ species and can ultimately cause the decrease of NO$_x$ conversions.

As illustrated by UV-vis and H$_2$-TPR experiments, concentrations of both of the isolated Cu$^{2+}$ and CuO$_x$ species increased with Cu loadings. In addition, H$_2$-TPR profiles in Figure 5 also reveal that the reducibility of xCu/MCM-22 zeolites gradually increases with Cu loadings. Then, it is reasonable to expect that the NO$_x$ conversions of xCu/MCM-22 in NH$_3$-SCR below 300 °C should increase with Cu loadings. However, the results in Figure 7 contradict that assumption. According to the NH$_3$-TPD results in Section 3.2, the acid strength of xCu/MCM-22 zeolites increases with Cu loadings. As high acid strength may favor ammonia inhibition effect in low temperature NH$_3$-SCR reactions \[68\], it can be suggested that the ammonia inhibition effect may be one of the causes for the decreased NO$_x$ conversions in xCu/MCM-22 with increasing Cu loadings in NH$_3$-SCR below 300 °C.

Moreover, as shown in Figure S2, due to the pore blockage effect, the BET surface areas and total pore volumes of xCu/MCM-22 zeolites dramatically decrease when Cu loadings exceed 4 wt%, which may be another factor affecting the SCR activity of catalysts. In order to verify this speculation, NO oxidation experiments were conducted on 4Cu/MCM-22, 6Cu/MCM-22 and 10Cu/MCM-22. As shown in Figure 8, the NO conversions of all the catalysts first increased with temperature and then rolled over above 350 °C, due to thermodynamic limitations of NO oxidation reaction, in accordance with previous studies \[69,70\].

According to references \[71–73\], NO oxidation reactions are predominately catalyzed by dimer Cu$^{2+}$ species and CuO$_x$ species; the isolated Cu$^{2+}$ species have little NO oxidation activity. From XRD, UV-vis, H$_2$-TPR and XPS results, the concentration of CuO$_x$ species in xCu/MCM-22 significantly increases with Cu loadings, which should lead to increased NO oxidation activity. However, the NO conversions of three catalysts in Figure 8 are in the order of 6Cu/MCM-22 > 10Cu/MCM-22 > 4Cu/MCM-22. As shown in Figure S2 and Table 1, 10Cu/MCM-22 shows apparently lower total pore volume (0.34 cm$^3$ g$^{-1}$) and surface area (290 m$^2$ g$^{-1}$) than 4Cu/MCM-22 (0.40 cm$^3$ g$^{-1}$ and 404 m$^2$ g$^{-1}$) and 6Cu/MCM-22 (0.39 cm$^3$ g$^{-1}$ and 391 m$^2$ g$^{-1}$), which means that the pore blockage effect is more severe in 10Cu/MCM-22 than other two zeolites. Therefore, though more CuO$_x$ species exist in 10Cu/MCM-22, large amounts of aggregated CuO$_x$ nanoparticles severely block the pore systems of 10Cu/MCM-22 zeolites, which makes most of the active sites in 10Cu/CMM-22 inaccessible to reactant molecules and ultimately leads to decreased NO oxidation activity. As NO oxidation is one of the reactions occurring in NH$_3$-SCR, it is reasonable to believe that the pore blockage effect also has a significant impact in NH$_3$-SCR over xCu/MCM-22 zeolites, especially when Cu loadings exceed 4 wt%.
Therefore, the complex NH3-SCR performances of xCu/MCM-22 zeolites with different Cu loadings in Figure 7 may have resulted from a combination of multiple factors, such as Cu loadings, the ammonia inhibition effect and the pore blockage effect. At low Cu loadings (≤4 wt%), the NH3-SCR activity of xCu/MCM-22 is mainly affected by the concentration of active isolated Cu²⁺ species and the ammonia inhibition effect. The increase of isolated Cu²⁺ species with Cu loadings in xCu/MCM-22 will promote the NH3-SCR reactions. However, the increased acid strength with Cu loadings (as proven by NH3-TPD) may cause a severe ammonia inhibition effect, which will deteriorate the NH3-SCR reactions, especially in a low temperature range (<250 °C). When Cu loading exceeded 4 wt%, due to the formation of large amounts of aggregated CuO species, the pore blockage effect became a dominant factor deciding the NH3-SCR performance of xCu/MCM-22 zeolites, which resulted in the similar NH3-SCR performances of 6Cu/MCM-22, 8Cu/MCM-22 and 10Cu/MCM-22 in Figure 7. As a result, 4Cu/MCM-22 showed the best NH3-SCR activity among the five xCu/MCM-22 zeolites by balancing different influencing factors.

3.5. Hydrothermal Stability of xCu/MCM-22 in NH3-SCR

The NH3-SCR activities of xCu/MCM-22 zeolites before and after hydrothermal aging are displayed in Figure 9. After hydrothermal aging in air containing 10% water at 750 °C for 10 h, the NOx conversions of xCu/MCM-22 only slightly decreased, indicating that xCu/MCM-22 zeolites have high hydrothermal stability in NH3-SCR.

![Figure 9](image-url)

**Figure 9.** Comparison of NH3-SCR activity of xCu/MCM-22 (before hydrothermal aging) and xCu/MCM-22-aged (after hydrothermal aging) with different Cu contents: (A) 2Cu/MCM-22 and 2Cu/MCM-22-aged; (B) 4Cu/MCM-22 and 4Cu/MCM-22-aged; (C) 6Cu/MCM-22 and 6Cu/MCM-22-aged; (D) 8Cu/MCM-22 and 8Cu/MCM-22-aged; (E) 10Cu/MCM-22 and 10Cu/MCM-22-aged.
In comparison with 2Cu/MCM-22, the NO\textsubscript{x} conversion of 2Cu/MCM-22-aged at 100–200 °C significantly increased, as shown in Figure 9A. According to the literature [74–77], some of CuO\textsubscript{x} species (with low activity in NH\textsubscript{3}-SCR) on the surface of Cu-SAPO-34 may migrate into the ion-exchange sites of SAPO-34 zeolite to form active isolated Cu\textsuperscript{2+} species during the hydrothermal aging process, thereby causing an increase of NH\textsubscript{3}-SCR activity for Cu-SAPO-34 after hydrothermal aging. This may be one of the reasons for the enhanced activity of 2Cu/MCM-22 in NH\textsubscript{3}-SCR after hydrothermal aging. For 4Cu/MCM-22, the NO\textsubscript{x} conversion slightly decreases in low temperatures (100–200 °C) and increases in high temperatures (300–500 °C) after hydrothermal aging, as shown in Figure 9B. Peden and co-workers [78] had also observed similar results on Cu/Beta zeolites in NH\textsubscript{3}-SCR. They attributed the increased NO\textsubscript{x} conversion at high temperatures for Cu/Beta after hydrothermal aging to the transformation of CuO\textsubscript{x} species into CuAlO\textsubscript{3} species, as CuAlO\textsubscript{3} species have higher activity than CuO\textsubscript{x} species at high temperatures in NH\textsubscript{3}-SCR. As for the decreased NO\textsubscript{x} conversions in NH\textsubscript{3}-SCR at low temperatures after hydrothermal aging, they found that some of isolated Cu\textsuperscript{2+} species in Cu/Beta which were highly active transformed into less active CuO\textsubscript{x} species or CuAlO\textsubscript{3} species during the hydrothermal aging process. Peden’s observations may explain the change in NO\textsubscript{x} conversion in Figure 9B for 4Cu/MCM-22 before and after hydrothermal aging.

As shown in Figure 9C–E, when Cu loadings exceed 4 wt\%, hydrothermal aging treatment has almost no influence on the performance of xCu/MCM-22 zeolites, which indicates that high Cu loadings are beneficial for the hydrothermal stability of xCu/MCM-22 zeolites. As discussed above, aggregated CuO\textsubscript{x} species formed in high Cu loadings caused severe blockage of the pore system in xCu/MCM-22, which may have hindered the diffusion of H\textsubscript{2}O molecules in zeolites during the hydrothermal aging process and prevented the attack of H\textsubscript{2}O on the zeolite framework, and ultimately improved the hydrothermal stability of xCu/MCM-22 zeolites [38,49]. The detailed mechanism behind the hydrothermal stability of xCu/MCM-22 zeolites in Figure 9 is still ambiguous now, which is currently under study. In general, xCu/MCM-22 zeolites have high hydrothermal stability in NH\textsubscript{3}-SCR. In addition, the hydrothermal stability of xCu/MCM-22 in NH\textsubscript{3}-SCR is related to Cu loading: when Cu loading ≤ 4 wt\%, hydrothermal aging treatment slightly affects the NH\textsubscript{3}-SCR activity of xCu/MCM-22 zeolites; once Cu loading exceeds 4 wt\%, hydrothermal aging treatment has little effect on the performance of xCu/MCM-22 zeolites in NH\textsubscript{3}-SCR.

4. Conclusions

A series of xCu/MCM-22 zeolites with different Cu loadings were prepared by incipient wetness impregnation method and their activity and hydrothermal stability in NH\textsubscript{3}-SCR were investigated. SEM and XRD experiments demonstrated that Cu loading has no significant influence on the surface morphology and crystallinity of xCu/MCM-22 zeolites. However, nitrogen physisorption experiments illustrated that the pore surface areas and pore volumes of xCu/MCM-22 gradually decrease with Cu loadings due to the formation of aggravated CuO\textsubscript{x} nanoparticles, which cause the blockage of pore system in xCu/MCM-22, especially when Cu loadings exceed 4 wt\%. NH\textsubscript{3}-TPD experiments showed that the total acid densities of all the xCu/MCM-22 zeolites are similar, and the global acid strength of xCu/MCM-22 increases with Cu loadings. UV-vis, H\textsubscript{2}-TPR and XPS results demonstrated that three different types of Cu species exist in xCu/MCM-22 zeolites: isolated Cu\textsuperscript{2+} species, aggregated CuO\textsubscript{x} species and unreducible copper species. In addition, the concentrations of both isolated Cu\textsuperscript{2+} and CuO\textsubscript{x} species in xCu/MCM-22 increase with Cu loadings, but the increment of CuO\textsubscript{x} species is more distinct, especially in high Cu loadings (> 4 wt\%).

Catalytic performance experiments illustrated that the NH\textsubscript{3}-SCR activity of xCu/MCM-22 can only be affected at low Cu loadings (≤ 4 wt\%); when Cu loading exceeds 4 wt\%, the NO\textsubscript{x} conversions of xCu/MCM-22 in NH\textsubscript{3}-SCR have little association with Cu loadings, due to the pore blockage effects caused by aggregated CuO\textsubscript{x} species. In general, 4Cu/MCM-22 showed the best NH\textsubscript{3}-SCR activity among the five xCu/MCM-22 zeolites, which exhibited higher than 80% NO\textsubscript{x} conversions in a wide
temperature window (160–430 °C), owing to its medium Cu loading which can not only ensure enough active isolated Cu$^{2+}$ species but also suppress the formation of aggregated CuO$_x$ species.

The hydrothermal stability of $x$Cu/MCM-22 zeolite in NH$_3$-SCR is related to its Cu loading. After hydrothermal aging in air containing 10% water at 750 °C for 10 h, the NO$_x$ conversions of 2Cu/MCM-22 in NH$_3$-SCR at low temperatures (100–200 °C) obviously increased. As for 4Cu/MCM-22, the NO$_x$ conversions at low temperatures (100–200 °C) slightly decreased, but at high temperatures (300–500 °C) increased after hydrothermal aging. When Cu loading exceeds 4 wt%, hydrothermal aging treatment has almost no influence on the performances of xCu/MCM-22 zeolites. In general, all of the five xCu/MCM-22 zeolites with different Cu loadings showed high hydrothermal stability in NH$_3$-SCR. The detailed mechanism for the high hydrothermal stability of xCu/MCM-22 zeolites in NH$_3$-SCR is currently under investigation.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2079-4991/10/11/2170/s1. Figure S1: Relationship between the intensity of CuO diffraction peaks and Cu contents over xCu/MCM-22 zeolites. Figure S2: Correlations between the loss percentages of (A) surface areas (SBET, BET surface area, and Smicro, micropore surface area) and (B) pore volumes (Vtotal, total pore volume, and Vmicro, micropore volume) with Cu contents over xCu/MCM-22 zeolites. Figure S3: Deconvolution of the NH3-TPD profiles of H-MCM-22 and xCu/MCM-22 zeolites. Figure S4: Deconvolution of the H2-TPR profiles of xCu/MCM-22 with different copper contents. Figure S5: H2-TPR profile of 6Cu/MCM-22.

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