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Synthesis of nanosized MFI zeolites using Cu-containing complexes

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15

16 Abstract

Nanosized MFI type zeolites were synthesized in the presence of Cu-containing 17 complexes. The use of ethylene diamine tetraacetic acid (EDTA) as a ligand promoted 18 19 the solubility and guaranteed the exclusive configuration of the copper-bearing chelate 20 in the precursor solutions. The EDTA-assisted MFI zeolite nanocrystals 21 (Cu-MFI-EDTA) was found to contain low amount of silanols due to formation of 22 flexible Si-O-Cu bonds. On the contrary, when ammonia (NH₃) was used as a ligand, 23 the copper species in the sample (Cu-MFI-NH₃) only present in the form of extra framework $[Cu^{\delta^+} \cdots O^{\delta^-} \cdots Cu^{\delta^+}]_n$ clusters. The introduction of transition metals assisted 24 by ligands permitted the preparation of nanocrystals with variable amount of silanols 25 26 and modified water affinity.

27

Keywords: Nanosized zeolite; Silanols; Copper complexes; Ethylene diamine 28 29 tetraacetic acid

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1 1. Introduction

Zeolite is crystalline microporous material consisting of 3D-connected tetrahedrally 2 coordinated (T) atoms (T = Si, Al, P, *etc.*).[1] Thanks to the tunable chemical 3 4 composition, high thermal stability and surface acidity, zeolite is becoming a 5 "game-changer" in the field of renewable energy and environmental improvement.[2] 6 In addition, via decreasing the size of the crystals from micron- to nano-scale, the 7 external surface area and diffusion are consistently increased.[3-5] However, 8 accompanied with the benign properties brought from nanosized zeolites, the amount 9 of silanols inside and/or outside the zeolite crystals is also inevitably increased.[6–8] 10 Such silanols sites are originated from the missing framework atoms in the zeolite 11 structure formed either during the synthesis or post-synthesis treatments.[9] The silanol 12 groups prefer to interact with water molecules to form "small H₂O clusters"[10], 13 lowering the hydrothermal stability of zeolites under harsh conditions.[11] From this 14 point, healing silanols is of interest to both improve zeolite stability and decrease the 15 water affinity.

16 Introducing transition metals into the framework of nanosized zeolite during synthesis 17 is a newly-developed environmentally-friendly approach to cope with the 18 above-mentioned problems.[12] On one hand, the silanols in zeolites were reported to 19 be efficiently healed after adding transition metal species.[13–15] On the other hand, 20 when transition metals are inserted in the zeolite framework, they are less likely to be 21 sintered.[16]

1 Although metal incorporation has received more and more attentions, the used 2 transition metal precursors were still restricted to the oxoacid anions. The synthesis of 3 (alumino)silicate zeolite is usually carried out under alkali conditions. The oxoacid 4 anions can maintain high solubility under alkali synthesis conditions for zeolites and 5 are not prone to precipitate. However, Cu usually exists in the form of hydrated cupric 6 cations in aqueous solutions. In such case, the cations easily precipitate with hydroxide 7 anions (Fig. S1(A) in Supporting Information (SI)). For this reason, effectively 8 incorporating Cu species, which has shown advantages in the field of catalysis such as 9 selective oxidation of methane into methanol [17], selective catalytic reduction (SCR) 10 of NO_x emission [18], *etc.*, is an interesting and is still a challenging task.[19] 11 Herein, a one-pot synthetic strategy for nanosized MFI zeolites via Cu-containing 12 complexes is reported. 13 **2. Experimental Section** 14 2.1 Chemicals 15 Tetrapropyl ammonium hydroxide (TPAOH, 1.0 mol/L aqueous solution) and copper 16 sulfate pentahydrate (CuSO₄ \cdot 5H₂O, >99 wt%) were purchased from Alfa Aesar Co. Ltd. Tetraethyl orthosilicate (TEOS, 98 wt%), and ethylene diamine tetra acetic acid 17 18 disodium salt (EDTA, >98 wt%) were purchased from Sigma-Aldrich Co. Ltd. All the

19 reagents were used without further purification.

1 2.2 Synthesis

2 2.2.1 Synthesis of copper-containing MFI nanosized zeolite with EDTA ligand (sample
3 Cu-MFI-EDTA)

4 Specifically, 9.8 g TPAOH, 0.055 g CuSO₄·5H₂O, and 0.165 g EDTA were mixed and 5 stirred for 2.5 hours. Afterwards, 5 g TEOS and 0.857 g double distillated water were 6 added sequentially. The precursor mixture was stirred at room temperature for 3 hours 7 and then placed on a shaker (250 rpm) for 16 hours to form a cerulean transparent 8 suspension (Fig. S1(B) in Supporting Information). Then the precursor mixture was 9 heated in an oven at 90 °C for 160 hours. In order to easily monitor the hydrothermal 10 crystallization process, the above precursor mixture was sealed in a polypropylene (PP) 11 bottle. Then the product was centrifuged, washed, dried. Finally, the as-synthesized 12 sample was calcinated at 550 °C for 6 hours. The SEM images and related histograms 13 of Cu-MFI-EDTA are shown in Fig. S2(A). The results unambiguously confirm that 14 the Cu-MFI-EDTA sample contains nanosized crystals with a mean particle diameter 15 of 90.1 nm.

16 2.2.2 Synthesis of copper-containing MFI nanosized zeolite with ammonia ligand
17 (sample Cu-MFI-NH₃)

In a typical synthesis process: 9.8 g TPAOH, 0.055 g $CuSO_4 \cdot 5H_2O$, 2.556 g NH_4OH mixed and stirred for 2.5 hours. Afterwards, 5 g TEOS was added drop by drop and then 0.857 g double-distillated water was added at once. The resulted precursor mixture was stirred at room temperature for 3 hours and then placed on a shaker (250 rpm) for 1 16 hours to form a violet transparent suspension (Fig. S1(C) in Supporting **Information**). The precursor mixture was then heated in an oven at 90 °C for 48 hours. 2 In order to avoid the possible volatilization of ammonia at 90 °C and the consequent 3 impact on the crystallization process, the above mixture was sealed in a stainless-steel 4 5 autoclave with a Teflon-lined container. The product was purified and dried and 6 calcinated at 550 °C for 6 hours. The SEM images and related histograms of 7 Cu-MFI-NH₃ are shown in **Fig. S2(B)**. The results unambiguously confirm that the 8 Cu-MFI-NH₃ sample contains nanosized crystals with a mean particle diameter of 9 135.2 nm.

10 2.2.3 Synthesis of pure siliceous nanosized silicalite-1 (reference sample Si-MFI)

11 The reference Si-MFI nanosized zeolite was prepared using the same precursor 12 suspension as the one used for synthesizing nanosized Cu-MFI-EDTA and 13 Cu-MFI-NH₃ zeolites, without introducing CuSO₄·5H₂O, EDTA or NH₄OH. In a 14 typical synthesis process: 5 g TEOS was added drop by drop into 9.8 g TPAOH. Then 15 0.857 g double-distillated water was added at once. The precursor mixture was 16 subjected to stirring at room temperature for 3 hours and then placed on a shaker for 16 hours. The colorless transparent precursor mixture was heated in an oven at 90 °C for 17 18 26 hours. In order to easily monitoring the hydrothermal crystallization process, the 19 above mixture was sealed in a PP bottle. After crystallization, the product was purified, 20 dried and calcined using the same procedure described above. The SEM images and 21 related histograms of Si-MFI are presented in Fig. S2(C). The results unambiguously confirmed that the Si-MFI sample contains nanosized crystals with a mean particle
 diameter of 83.5 nm.

3 2.3 Characterizations

The thermogravimetry analysis (TG) were conducted by a SETARAM SETSYS-B 4 microbalance with sensitivity of 0.1 µg. All the samples were calcinated before 5 6 conducting water adsorption tests to make sure that all the organics have been removed. The conditions for water adsorption were referred and modified from an ASTM 7 standard (ASTM D5758-01 2015). Specifically, the finely grinded samples were firstly 8 9 placed into an oven at 105 °C for 16 hours for removing pre-adsorbed water and other 10 impurities. Afterwards, they were transferred into a desiccator maintained at 58 % 11 relative humidity via saturated sodium bromide aqueous solution and stored at 25 °C for 12 72 hours.

The silanol group vibration modes of zeolite were characterized using a Nicolet Magna 550-FTIR spectrometer with 2 cm⁻¹ optical resolution equipped with an *in-situ* cell. The self-supported zeolite wafers were evacuated $(1.33 \times 10^{-4} \text{ Pa})$ and pretreated at 450 °C for 4 hours prior the measurements, and then the spectra were collected in the region of 4000-3000 cm⁻¹.

²⁹Si magic angle spinning nuclear magnetic resonance (²⁹Si MAS NMR) and {¹H}-²⁹Si
cross-polarized magic angle spinning nuclear magnetic resonance ({¹H}-²⁹Si CP MAS
NMR) were conducted on a Brucker Avance III-HD 500 (11.7 T) spectrometer using a
zirconia rotor with a diameter of 4 mm. The spinning frequency of the rotor was fixed

1	to 12 kHz. For ²⁹ Si MAS NMR, the spectrometer was operated at 99.3 MHz, and a
2	single pulse excitation (30° flip angle) was used with a recycle delay of 30 seconds.
3	While for ${}^{1}H$ - ${}^{29}Si$ CP MAS NMR, a contact time of 5 mi and a recycle delay of 2
4	seconds were used. Tetramethylsilane (TMS) was used as a reference for measuring
5	²⁹ Si chemical shifts.
6	Powder X-ray diffraction (XRD) patterns were recorded by a PANalytical X'Pert PRO
7	MPD diffractometer equipped with Cu K α radiation (45 kV, 40 mA, λ = 0.1541 nm) in
8	the 2theta range of 3-80°. The unit cell parameters of the samples were calculated from
9	their XRD patterns using JANA2006 software where Le Bail profile refinement, and
10	pseudo-Voigt function were selected.
11	Raman spectra were collected on a Jobin Yvon Labram 300 confocal Raman
12	spectrometer coupled with a microscope (objective: $50\times$) and a CCD detector. A 532
13	nm wavelength laser was used, and the spectra were accumulated 3 times for 60
14	seconds each.
15	The structural vibration modes of zeolite framework were collected using a Nicolet
16	Magna 550-FTIR spectrometer with 2 cm ⁻¹ optical resolution. Before testing, all
17	samples were mixed with potassium bromide and then pressed into self-supported

18 wafers.

19 UV-Vis spectra were recorded using a Varian Cary 4000 UV-Vis-NIR spectrometer in
20 the range from 800 to 200 nm. Prior to the tests, the sample powders were placed into a

cell equipped with a quartz window; magnesium hydroxide was used as a reference
 sample.

Scanning transmission electron microscopy (STEM) and Energy Dispersive 3 4 Spectroscopy (EDS) were performed using a double corrected JEOL ARM200 CFEG 5 TEM operated at 80 kV (to avoid the specimen damage by electron beam irradiation) equipped with a 100 mm² Centurio detector for the X-rays. For the imaging, the High 6 7 Angular Annular Dark Field (HAADF) detector was employed in order to accede the Z 8 chemical contrast in the imaging mode. A probe current of 0.1 nm was employed to 9 acquire images of 1024×1024 px at a speed of 12 µs/px. 256×256 px EDS chemical 10 maps were continuously acquired with an exposure of 0.02 ms/px and a 11 cross-correlation algorithm was applied to correct for the spatial drift every 30 seconds. 12 The nitrogen monoxide (NO) adsorption on the zeolite samples was followed using a Nicolet Magna 550-FTIR spectrometer with 2 cm^{-1} optical resolution with an *in situ* 13 14 cell. Prior the measurements, the self-supported zeolite wafers were evacuated $(1.33 \times 10^{-4} \text{ Pa})$ and pretreated at 450 °C for 4 hours. Then the spectra were collected at 15 16 room temperature (RT) under delivering different NO concentrations (3.0, 5.9, 8.9, 11.8, 14.7, and 17.6×10^{-3} mmol/g). 17

18 2.4 Density functional theory (DFT) calculations

19 Periodic DFT calculations were performed using the Perdew-Burke-Ernzerhof (PBE)

20 [20], exchange-correlation functional as the dispersion interactions was accounted for

21 empirical correction D2 (denoted as PBE+D2) [21] as implemented in Vienna Ab initio

1 Simulation Package (VASP) [22,23]. PAW pseudopotentials were employed, [24,25] 2 and the valence wave functions were expanded in a plane-wave basis with a cutoff 3 energy of 415 eV. The Brillouin zone was sampled using the Γ point only. [26] 4 2.4.1 Structure modelling of pure silica and copper-containing MFI zeolites 5 The framework structure of the Si-MFI sample was modeled using an orthorhombic 6 unit cell consisting of 96 T-atoms with the following unit cell parameters: a = 20.271 Å, b = 19.925 Å, c = 13.332 Å. All the T-atoms in the model were silicon. In order to 7 8 create a local imperfection (*i.e.*, a silanol nest composed of four silanols), one silicon 9 center was removed from the structure, and all the adjacent oxygen atoms were 10 saturated by hydrogen atoms. In order to reach the geometry optimization, all atoms were allowed to relax until the forces on each atom were less than 5×10^{-1} eV/nm. The 11 12 model structure corresponding to the Si-MFI sample was used and the Cu-species were 13 introduced to simulate the formation of Cu-containing MFI zeolites. 14 2.4.2 Calculations of the vibrational frequencies for nitrogen monoxide (NO) 15 molecules adsorbed on MFI nanosized zeolites 16 The N-O vibrational frequencies were calculated using a normal mode analysis where the elements of the Hessian were approximated as finite differences of gradients, 17 displacing each atomic center by 1.5×10^{-3} nm either way along each Cartesian 18 19 direction. The reported binding energies (BE) of the NO adsorbates were calculated

based on $BE = -E_{ad}-E_{sub}+E_{ad/sub}$, where E_{ad} is the total energy of the adsorbate in the gas

21 phase (ground state), E_{sub} is the total energy of the pristine zeolite system, and $E_{ad/sub}$ is

1	the total energy of the zeolite, together with the adsorbate in the optimized geometry.
2	With the above definition, negative values of <i>BE</i> imply favorable interactions.
3	3. Results and Discussion
4	In this work, EDTA and NH ₃ were used as ligands for the synthesis of nanosized
5	copper-containing MFI nanosized zeolites and the samples are denoted as
6	Cu-MFI-EDTA and Cu-MFI-NH ₃ , respectively. By finely tuning the synthesis
7	conditions, the copper-containing samples were synthesized with almost the same
8	amount of copper, i.e. 0.58 wt% and 0.57 wt% for samples Cu-MFI-EDTA and
9	Cu-MFI-NH ₃ , respectively (see Experimental Section). For comparison, pure siliceous
10	reference sample denoted as Si-MFI was also synthesized. All samples were calcinated
11	at 550 °C before being characterized (Table 1).
12	3.1 Reduced water affinity and decrease of silanols due to the Cu species insertion
13	into MFI framework
14	Reduced water affinity of Cu-MFI-EDTA over Si-MFI sample was demonstrated by
15	thermogravimetry (Fig. 1(A)). In order to guarantee the identical conditions for the
16	water vapor adsorption measurements, the two samples were pre-dehydrated and then
17	stored at 25 °C for 72 hours in a desiccator with 58 % relative humidity. The two
18	copper-containing zeolites show decreased water amount compared with the reference
19	sample Si-MFI (4 %), while both Cu-MFI-EDTA and Cu-MFI-NH ₃ samples contain
20	similar amount of Cu as determined by ICP-AES (Table S1 in Supporting
21	Information). The variation of water content in samples Cu-MFI-EDTA and 10

1	Cu-MFI-NH ₃ indicates the reduction of silanol groups resulted from the use of copper
2	ligands as confirmed by <i>in situ</i> FTIR spectroscopy (Fig. 1(B)). The IR spectrum of the
3	reference Si-MFI zeolite contains two absorption bands at 3740 cm ⁻¹ (terminal silanol
4	groups) and 3520 cm ⁻¹ (silanol nests),[27] indicating the presence of silanols though it
5	is highly crystalline (vide infra) and pure siliceous sample. While in the spectrum of
6	sample Cu-MFI-NH ₃ , the peak corresponding to silanol nests appears with very low
7	intensity and the peak corresponding to the terminal silanol groups shows diminished
8	intensity too. Whereas for sample Cu-MFI-EDTA, the band at 3520 cm ⁻¹ is not present
9	and the band at 3740 cm ⁻¹ with very low intensity corresponding to the terminal silanol
10	is observed. The results above suggest that the water adsorption capacity of the
11	Cu-MFI-EDTA and Cu-MFI-NH ₃ samples is decreased by introducing copper with the
12	help of the two ligands in the silanol sites. For sample Cu-MFI-EDTA, a considerable
13	decrease of the silanol nests and complete elimination of the terminal silanol groups
14	indicates less amount of defect sites within the crystals.

15 [INSERT FIG.1 HERE]

16 The reduced amount of silanol groups suggests that copper species can be introduced 17 into the framework of the MFI zeolite with the help of EDTA as a ligand, which can be 18 verified by ²⁹Si MAS NMR and related { ${}^{1}H$ }-²⁹Si CP MAS NMR spectra (**Fig. 2**). For 19 both samples Si-MFI and Cu-MFI-NH₃, two peaks at -113 ppm and -115 ppm with a 20 shoulder at -111 ppm, all related to the presence of Q⁴ species ((SiO)₄Si), are measured 21 by ²⁹Si MAS NMR. An additional Q³ signal ((SiO)₃SiOH) at -103 ppm is also detected

1	for both samples Si-MFI and Cu-MFI-NH ₃ (Fig. $2(A)$). Even an extremely weak Q^2
2	signal $((SiO)_2Si(OH)_2)$ at -93 ppm appears in the spectrum of the reference sample
3	Si-MFI. The Q^2 and Q^3 species reveal the presence of silanols with unsaturated
4	coordination in both samples, more pronounced for the reference pure silica sample
5	Si-MFI. In contrast, the Q^4 signals in the ²⁹ Si MAS NMR spectrum of sample
6	Cu-MFI-EDTA are well resolved, and at least eight peaks ranging from -110 ppm to
7	-120 ppm clearly appeared, which can be explained by a structure with very few
8	silanols.[10] In addition to the well-resolved Q ⁴ signals, another weak signal at -102
9	ppm appears in the spectrum of Cu-MFI-EDTA. However, no apparent signals in the
10	${^{1}H}^{-29}$ Si CP MAS NMR spectrum of sample Cu-MFI-EDTA are observed (Fig. 2(B)).
11	The appearance of this peak indicates that some of the silicon atoms in this sample are
12	bonded to another three silicon atoms plus one non-silicon atom via oxygen bridge
13	bonds (denoted as (SiO) ₃ -Si-O-X hereafter, where X refers to the non-silicon atom).
14	According to the Cu-MFI-EDTA synthesis recipe, the potential candidate for X atom
15	can be either hydrogen and/or copper. Nevertheless, if X atom were hydrogen atom, a
16	Q^3 peak should appear in the { ¹ H}- ²⁹ Si CP MAS NMR spectrum of Cu-MFI-EDTA,
17	just like the corresponding peak shown in the spectrum of Si-MFI. However, such a
18	peak is not observed in the ${}^{1}H$ - ${}^{29}Si$ CP MAS NMR spectrum of sample
19	Cu-MFI-EDTA (Fig. 2(B)), indicating that the X atom could be Cu. The Si MAS NMR
20	and related { ¹ H}- ²⁹ Si CP MAS NMR spectra indicate that the copper species in this
21	case are highly probable to be connected to the silicon via oxygen bridge (Si-O-Cu).

Such results are consistent with the previous reports on tungsten containing
 (W-MFI)[14] and molybdenum containing (Mo-MFI)[15] zeolites. Besides, the
 absence of peaks in {¹H}-²⁹Si CP MAS NMR spectrum of sample Cu-MFI-EDTA also
 indicates the low affinity to proton-containing species like water.

5 [INSERT FIG.2 HERE]

6 The insertion of copper atoms in the MFI framework with the help of the EDTA ligand 7 is further evidenced by the crystal symmetry change from orthorhombic to monoclinic for the MFI framework as shown in powder X-ray diffraction patterns (Fig. 3). The 8 peak at 24.5° 2 theta in the XRD pattern of sample Cu-MFI-EDTA splits, whereas only 9 10 one single peak appears in both samples Cu-MFI-NH₃ and Si-MFI. This indicates the 11 space group transformation from orthorhombic *Pnma* (Si-MFI and Cu-MFI-NH₃) to 12 monoclinic $P2_1/c$ (Cu-MFI-EDTA), inferring the symmetry downgrading originated 13 from the introduction of copper into the MFI framework. Compared with the reference sample Si-MFI, the Bragg peaks in the XRD pattern of sample Cu-MFI-EDTA (22-23° 14 15 2 Theta) are shifted. The unit cell parameters derived from Le Bail refinement of the 16 three patterns corresponding to samples Si-MFI, Cu-MFI-EDTA, and Cu-MFI-NH₃ are summarized **Table 1**. The unit cell volume increases from 5337.1 $Å^3$ for Si-MFI to 17 5340.5 Å³ for Cu-MFI-NH₃ and to 5352.0 Å³ for Cu-MFI-EDTA. 18 19 [INSERT FIG. 3 HERE]

20 [INSERT TABLE 1 HERE]

1	The addition of Cu into the zeolite crystal framework of Cu-MFI-EDTA sample is also
2	confirmed by Raman (Fig. 4) and FTIR (Fig. 5). Two weak bands symmetrically
3	located on both sides of the peak centered at 380 cm^{-1} (<i>c.a.</i> $330 \text{ and } 420 \text{ cm}^{-1}$, Fig. 4(B))
4	and a new band at 1038 cm ⁻¹ (Fig. 4(C)) for sample Cu-MFI-EDTA are clearly
5	observed. These peaks correspond to the M-O-Si vibration as reported previously for
6	Ti-, Fe-, W-, Mo-containing silicalite-1.[14,15,29] On the contrary, a band at 980 cm ⁻¹
7	present in both the Raman (Fig. $4(C)$) and FTIR (Fig. 5) spectra of Cu-MFI-NH ₃ and
8	Si-MFI, which is assigned to the O ₃ Si-OH stretching mode of silanol groups, does not
9	present in the spectra of sample Cu-MFI-EDTA. Such results further confirm silanols
10	removal from sample Cu-MFI-EDTA and is consistent with the results drawn from ²⁹ Si
11	MAS NMR and ${}^{1}H$ - ${}^{29}Si$ CP-MAS NMR study for both Si-MFI and Cu-MFI-EDTA
12	samples.
13	[INSERT FIG. 4 HERE]
14	[INSERT FIG. 5 HERE]
15	3.2 Role of EDTA ligand on healing silanols and promoting Cu species insertion in
16	MFI framework
17	The distinctive differences between samples Cu-MFI-EDTA and Cu-MFI-NH ₃ clearly
18	demonstrate the exceptional functions of the EDTA as a ligand for reinforcing the
19	copper atoms insertion into the MFI framework and simultaneously curing the silanols.
20	In order to unravel the role of the EDTA in the insertion of copper species in the zeolite
21	framework, scanning transmission electron microscopy (STEM) images acquired in 14

1	high angular annular dark field (HAADF) and energy dispersion spectroscopy (EDS)
2	show topographical features and Cu dispersion information for sample Cu-MFI-EDTA
3	(Fig. 6). Zeolite nanoparticles in sample Cu-MFI-EDTA are round-shaped with rather
4	smooth surface (Fig. $6(A)-6(E)$). The HAADF-STEM pictures showed the presence of
5	white spots in the zeolite crystals marked by the yellow arrows and circles in Fig.
6	6(B)-6(D). The corresponding magnified images are supplied in Fig. S3(A)-S3(C),
7	Supporting Information, respectively) and the high contrast in the STEM-EDS
8	mapping (green area) is seen in Fig. 6(H). Most of the bright spots associated with the
9	presence of high Z-contrast atoms are sited in the lattice fringes of the zeolite crystals
10	(Fig. 6(D). The corresponding magnified images are supplied in Fig. S3(C),
11	Supporting Information), indicating that the Cu species are incorporated in the MFI
12	framework, which is in a good correspondence with the NMR (Fig. 3), XRD (Fig. 4),
13	and theoretical results (vide infra). In order to confirm the abovementioned description,
14	the UV-vis spectroscopic study of the Cu-MFI-EDTA was conducted (Fig. 7). The
15	UV-vis spectrum of sample Cu-MFI-EDTA contains a peak centered at c.a. 260 nm
16	(Fig. 7(A)). This peak is assigned as the charge transfer transitions between oxygen in
17	the zeolite crystal lattice to isolated copper species. $(O^{2-}\rightarrow Cu^{2+})$ ligand to metal charge
18	transfer, LMCT). [30,31] No other bands assigned to the d-d transition of
19	$[Cu^{\delta^+}\cdots O^{\delta^-}\cdots Cu^{\delta^+}]_n$ species appear in the region 350 nm - 800 nm. [30,31]
20	Considering that crystallization time of the sample determines the amount of Cu
21	species incorporated in the zeolite framework (Table S3, Supplementary 15

1	Information), further investigation of the changes of the abovementioned absorption
2	peaks vs the amount of the incorporated Cu species in Cu-MFI-EDTA sample was
3	performed (Fig. $7(B)$ and $7(C)$). With increasing the copper content in sample
4	Cu-MFI-EDTA, the intensity of the " $O^{2-} \rightarrow Cu^{2+}$ LMCT" absorption peak gradually
5	increases and undergoes a blue shift in the corresponding UV-vis spectra. Based on
6	these results, it can be inferred that the copper species of sample Cu-MFI-EDTA should
7	be in the form of Si-O-Cu, rather than extra framework $[Cu^{\delta^+} \cdots O^{\delta^-} \cdots Cu^{\delta^+}]_n$ clusters.
8	In contrast with sample Cu-MFI-EDTA, the high-resolution STEM-HAADF study
9	reveals that the Cu-MFI-NH ₃ zeolite is highly coarse (Fig. $6(I)-6(L)$). High-resolution
10	STEM-HAADF and the STEM-EDS analyses indicate that the folded outer surface are
11	prone of being decorated by the copper species (yellow circles shown in Fig. 6(K) and
12	6(L), and the corresponding magnified images are supplied in Fig. S3(D)-S3(E),
13	Supporting Information). Although the UV-vis spectrum of sample Cu-MFI-NH ₃
14	does not contain the peak centered at c.a. 260 nm, there is an apparent band at
15	wavenumber larger than 550 nm showing the existence of extra framework
16	$[Cu^{\delta^+} \cdots O^{\delta^-} \cdots Cu^{\delta^+}]_n$ cluster species.(Fig.7 (A)). Considering the <i>Pmna</i> space group (a
17	single peak at 24.5° 2 theta in the XRD pattern shown in Fig. 3(C)) and Si-O-H
18	interactions (the Q^3 signal in the ${}^{1}H$ $-{}^{29}Si$ CP-MAS NMR spectrum shown in Fig.
19	2(A)) of sample Cu-MFI-NH ₃ , one can conclude that the Cu species are solely located
20	at the outer surface of the sample as extra framework $[Cu^{\delta^+} \cdots O^{\delta^-} \cdots Cu^{\delta^+}]_n$ cluster
21	species.

1 [INSERT FIG. 6 HERE]

2 [INSERT FIG. 7 HERE]

3 The unique role of EDTA in implanting the copper species into zeolite framework is 4 also analyzed via *in situ* FTIR study using nitrogen monoxide (NO) as a probe molecule to differentiate the copper species on both Cu-MFI-EDTA (Fig. 8(A)) and 5 6 Cu-MFI-NH₃ (Fig. 8(B)) samples. The theoretical calculations for NO adsorbed on both Cu-MFI-EDTA and Cu-MFI-NH₃ samples were performed for better 7 interpretation of the interactions among the copper species, silanol groups and NO 8 9 probe molecules. Detailed results are summarized in Table S2 in Supporting **Information**. Solely a wide band in the region 1940-1850 cm⁻¹ in the IR spectrum of 10 11 Cu-MFI-EDTA is present (Fig. 8(A)). This band corresponds to the N-O stretching 12 vibration and infers the presence of physically adsorbed NO [32,33]. Such assignment 13 is also confirmed by theoretical calculation and shown as inset of Fig. 8(A). The 14 binding energy of physically adsorbed NO is -114 kJ/mol, which is much lower than the 15 nitrosyl complexes, in particular 90 kJ/mol lower than the complex of NO with extra-framework Cu^{2+} cation. Therefore, the absence of the peaks for nitrosyl species in 16 17 sample Cu-MFI-EDTA suggests that there are no cationic extra-framework copper 18 species in this sample.

19 On the contrary, in the *in situ* IR spectrum of sample Cu-MFI-NH₃, four apparent peaks 20 from 1950 cm⁻¹ to 1840 cm⁻¹ appeared (**Fig. 8(B**)). The corresponding theoretical 21 calculation confirms that such four peaks are assigned to the NO adsorption on the

1	following four copper species in Cu-MFI-NH ₃ sample, with binding energy ranging
2	from -123 to -205 kJ/mol: (1) Structure where Cu^{2+} cation compensates two
3	deprotonated silanol groups (denoted as SN-Cu1): the cation interacts not only with
4	them, but also with one of the two intact silanols; (2) Structure where initially two
5	extra-framework Cu ²⁺ cations compensate two deprotonated silanol groups in the
6	silanol nest (denoted as SN-Cu2): in the optimized geometry, the silanol nest is healed
7	by one of the copper cations, which is incorporated in the zeolite framework, while the
8	other one remains as a charge compensating Cu^{2+} cation; (3) Structure with neutral
9	extra-framework copper-containing species Cu ²⁺ O ²⁻ , located inside the zeolite channel
10	close to a silanol nest (denoted as SN-CuO): interestingly, during the optimized
11	geometry, such $Cu^{2+}O^{2-}$ species interact with one of the H ⁺ cations originated from a
12	silanol group, thus $Cu^{2+}OH^{-}$ species and deprotonated SiO ⁻ group are formed; (4)
13	Structure with neutral extra-framework copper-containing species Cu ²⁺ (OH ⁻) ₂ , also
14	located inside the zeolite channel close to a silanol nest (denoted as SN-Cu(OH) ₂).
15	Obviously, none of the above four modes point to the existence of copper species
16	inserted in the framework of Cu-MFI-NH ₃ sample.

17 [INSERT FIG. 8 HERE]

18 *3.3 Effect of calcination and presence of sodium cations on the copper species in the*

19 *zeolite framework*

All above results indicate that the less water adsorption capacity of sample
Cu-MFI-EDTA is attributed to the introduction of atomically dispersed copper species

1	into the silanol sites of the MFI zeolite. All samples presented up to now are
2	characterized after the calcination. Considering the pivotal roles during zeolite
3	synthesis, it is necessary to understand the relationship between the calcination and the
4	silanols healing effect. Therefore, the XRD patterns of as-synthesized and calcined
5	Cu-MFI-EDTA samples are compared (Fig. 9). After the calcination, the position of the
6	Bragg peaks shifts downwards. Besides, in the calcined Cu-MFI-EDTA sample the
7	peaks at 23.3° and 24.5° 2 theta split (Fig. 9(A)). Correspondingly, the FTIR spectra
8	also show that the band at 980 cm ⁻¹ (silanol sites in zeolite framework, Fig. $9(B)$)
9	disappeared during the calcination process. This indicates that the silanol sites are
10	healed during the calcination of the Cu-MFI-EDTA sample.

11 [INSERT FIG. 9 HERE]

12 Due to the low solubility of H₂EDTA, the disodium salt form, Na₂EDTA, is instead 13 chosen for introducing the EDTA ligand into the synthesis. Therefore, it is of interest to 14 investigate the effect of sodium cations on the formation of the Cu-MFI-EDTA and the 15 location of the Cu-EDTA chelate. The possibility for confining the Na₂[Cu-EDTA] 16 coordination compound in the channel intersections of MFI framework in vicinity of 17 the silanol nests was modeled; this corresponds to the as-synthesized Cu-MFI-EDTA sample. The structure was optimized, which suggests that the bulky coordination 18 19 compound can be well accommodated in the zeolite channels (Fig. 10(A)). Interestingly, the incorporation of the bulky compound does not affect the zeolite 20 21 framework, which remains essentially unchanged, except the hydroxyl groups in the

1	silanol nests. The Si-Si distance of the structure with and without Na ₂ [Cu-EDTA] is
2	shown in Fig. S4. The coordination compound itself is sufficiently flexible, as shown
3	earlier,[34] and this allows to fit in the available channel intersection. The calculated
4	binding energy with respect to isolated Na ₂ [Cu-EDTA] coordination compound and
5	empty zeolite model is large (-317 kJ/mol). In order to understand the effect of
6	additional sodium cations, an MFI zeolite consisting of 96 Si atoms was constructed as
7	a basic model structure for accommodating the guest Cu-containing species. The
8	results show that the Cu^{2+} cation can be incorporated into the zeolite framework at the
9	position of the silanol nest. Two charge-compensating Na^+ cations from the
10	Na ₂ [Cu-EDTA] are located in the vicinity, which is consistent with the Cu/Na molar
11	ratio close to 0.5 shown in Table S1, i.e. 0.58 wt % and 0.43 wt % for Cu and Na in
12	sample Cu-MFI-EDTA respectively. Thus, all four protons from the silanol nest
13	hydroxyls are replaced by copper or sodium ions. Among them, three of the oxygen
14	centers from the silanol groups are coordinated to the copper ion while the sodium
15	cations are coordinated to the fourth oxygen center and surrounding oxygen atoms (Fig.
16	10(B)).

17 [INSERT FIG. 10 HERE]

Based on the abovementioned results, a possible explanation on the unique function of the Cu-EDTA complex (sample Cu-MFI-EDTA) on healing the silanols is presented (Scheme 1). Silanols are unavoidably created during the crystallization of nanosized zeolites. For the synthesis of nanosized Cu-MFI-EDTA zeolite, the used aqueous

1	precursor suspension is highly alkaline: the pH value of the precursor suspension after
2	adding the EDTA is 13.75 (Table S1). Under such condition, the EDTA mainly exists
3	in the form of EDTA ⁴⁻ ion, with a distribution coefficient in aqueous solution not less
4	than 0.998.[35,36] Due to the chelate effect of $EDTA^{4-}$ ion and the help of Na^{+} as
5	counter cation, Cu ²⁺ exclusively forms Na ₂ [Cu-EDTA] complex stoichiometrically
6	with a ratio of 1:1, regardless of the initial molar ratio between Cu^{2+} and $EDTA^{4-}$. Based
7	on the theoretical result, the Na ₂ [Cu-EDTA] coordination compound is prone of being
8	confined in the channel intersections of MFI frameworks. When the confined
9	Na ₂ [Cu-EDTA] is in vicinity of the silanol nests, Cu species becomes part of the MFI
10	framework by forming flexible Cu-O-Si bonds. In contrast, the [Cu-NH ₃] cannot be
11	finely fixed and confined within the channel intersections of the MFI framework. In
12	this case, the copper species in Cu-MFI-NH ₃ sample only exist in the form of various
13	extra-framework clusters $[Cu^{\delta^+} \cdots O^{\delta^-} \cdots Cu^{\delta^+}]_n$ and do not have the ability to repair the
14	silanol-based defects of the Cu-MFI-NH ₃ sample. From this point of view, Na ₂ EDTA
15	can achieve the purpose of healing silanols of nanosized MFI zeolites, while
16	introduction of ammonia as ligand cannot play such a role even though it also does
17	promote the solubility of copper species in the synthesis mixture (see Fig. S1(B)and
18	S1(C))

19 [INSERT SCHEME 1 HERE]

1 **4. Conclusions**

Copper containing nanosized MFI zeolite crystals with reduced water affinity were 2 3 synthesized via one-pot synthesis method. The addition of Na₂EDTA ligand into the synthesis suspension guarantees the formation of octahedral Na₂[Cu-EDTA] 4 5 coordination compound that is likely to be confined in the channel intersection of MFI 6 framework or deposited on the outer surface. During the calcination, the confined 7 Na₂[Cu-EDTA] in vicinity of the silanol nests become part of the MFI framework via 8 flexible Cu-O-Si interactions and heal the silanols with the help of sodium cations. On 9 the contrary, the [Cu-NH₃] compounds cannot be confined within zeolite channel intersections, leading to various extra-framework $[Cu^{\delta^+} \cdots O^{\delta^-} \cdots Cu^{\delta^+}]_n$ clusters that 10 11 cannot cure the silanols of the Cu-MFI-NH₃ sample. 12 References

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1 Figures and Tables



Fig. 1. Water content in calcinated Si-MFI, Cu-MFI-EDTA, and Cu-MFI-NH₃
nanosized zeolites stored at 58 % relative humidity for 3 days measured by

- 1 thermogravimetry (A); In-situ FTIR spectra of calcined Si-MFI, Cu-MFI-EDTA, and
- 2 Cu-MFI-NH₃ nanosized zeolites (B) in the region 4000-3000 cm⁻¹.



Fig. 2. Solid-state ²⁹Si MAS NMR spectra (A) and the corresponding {¹H}-²⁹Si
CP-MAS NMR spectra (B) of Si-MFI, Cu-MFI-EDTA, and Cu-MFI-NH₃ nanosized
zeolites.



- **Fig. 3.** Powder XRD patterns of (A) Si-MFI, (B) Cu-MFI-EDTA, and (C) Cu-MFI-NH₃
- 2 calcined nanosized zeolites



- 1 Fig. 4. Raman spectra of Si-MFI, Cu-MFI-EDTA, and Cu-MFI-NH₃ nanosized zeolites
- 2 in the ranges (A) 200-1500 cm⁻¹(B) 200-650 cm⁻¹ (B), and (C) 900-1400 cm⁻¹.



Fig. 5. FTIR spectra of Si-MFI, Cu-MFI-EDTA, and Cu-MFI-NH₃ nanosized zeolites.



Fig. 6. STEM-HAADF micrographs (A-E, arrows and circles in B-D show the copper
species) and STEM-EDS elemental maps (F: Si (orange), G: O (blue), and H: Cu
(green)) of Cu-MFI-EDTA nanosized zeolites; STEM-HAADF micrographs (I-M,
arrows in J-L show the copper species) and STEM-EDS elemental maps (N-P; N: Si
(orange), O: O (blue), and P: Cu (green)) of Cu-MFI-NH₃ nanosized zeolites.



Fig. 7. UV-Vis spectra of Si-MFI, Cu-MFI-EDTA, and Cu-MFI-NH₃ nanosized
zeolites in the range of 200-800 nm(A); UV-Vis spectra of Si-MFI, Cu-MFI-EDTA

1 samples after different crystallization time in the ranges (B) 200-800 nm and (C)

2 250-300 nm.



Fig. 8. *In-situ* FTIR spectra of Cu-MFI-EDTA nanosized zeolite recorded at different
concentrations of nitrogen monoxide (3.0, 5.9, 8.9, 11.8, 14.7, and 17.6×10⁻³ mmol/g)
at room temperature. The inset illustrates the modeled physically adsorbed NO on the
Cu-MFI-EDTA nanosized zeolite (A); *In-situ* FTIR spectrum of Cu-MFI-NH₃

nanosized zeolite recorded at different concentrations of nitrogen monoxide (3.0, 5.9,
 8.9, 11.8, 14.7, and 17.6×10⁻³ mmol/g) at room temperature. The insets illustrate the
 modeled adsorbed NO mode on the Cu-MFI-NH₃ nanosized zeolite (B).





2 Fig. 9. XRD patterns (A) and FTIR spectra (B) of Cu-MFI-EDTA and Si-MFI

3 nanosized zeolites before and after calcination





Fig. 10. The Na₂[Cu-EDTA] coordination compound in the channel intersection of
MFI zeolite from different points of view (A); location of Cu and Na in the modeled
Cu-MFI-EDTA structure from two points of view (B) (Color coding: Si—blue,
Cu—yellow, O—red, Na—cyan, N—light yellow, and C—brown).



1

2 Scheme 1 Graphical illustration of the distinctive effects of the Cu using EDTA (A) or

- 3 NH₃ (B) as ligands for healing the silanols in nanosized MFI zeolites.
- 4

Table 1 Unit cell parameters of nanosized zeolites Si-MFI and Cu-MFI-EDTA. Unit

2	cell parameters	were calculated	from powder	diffraction	data based o	on a Le Bail	profile

	Space	а	b	С	β	V	
Sample	group	[Å]	[Å]	[Å]	[°]	[Å ³]	
Si-MFI	Pnma	20.0630	19.8836	13.3788	90.000	5337.1	
Cu-MFI-EDTA	$P2_1/n$	20.1129	19.8790	13.3865	90.544	5352.0	
Cu-MFI-NH ₃	Pnma	20.0622	19.8833	13.3876	90.000	5340.5	

3 refinement and Pseudo-Voigt profile function using the JANA2006 software.