This journal is © The Royal Society of Chemistry 2011

Electronic Supplementary Information

Designed Copper-amine Complex as an Efficient Template for One-pot Synthesis of Cu-SSZ-13 Zeolite with Excellent Activity for Selective Catalytic Reduction of NOx by NH_3

Limin Ren, Longfeng Zhu, Chengguang Yang, Yanmei Chen, Qi Sun, Haiyan Zhang, Caijin Li, Faisal Nawaz, Xiangju Meng, and Feng-Shou Xiao*

Synthesis procedure:

Tetraethylenepentamine (TEPA) was the amine complexed with $CuSO_4 \cdot 5H_2O$ to form a Cu-TEPA complex. All chemicals were obtained from commercial suppliers and used without further purification. The chemical composition of the starting gels and the corresponding products are given in Table 1. As a typical run for the synthesis of Cu-ZJM-1-10, $NaAlO_2$ (0.471 g) and NaOH (0.250 g) were dissolved in water. Then $CuSO_4 \cdot 5H_2O$ (0.999 g) was added to this solution followed by adding TEPA (0.841 g). After one hour stirring, silica sol (3.21 mL, 31.5 wt %) was added in the above gel drop wise under vigorously stirring. After being stirred for three hours, the final gel was transferred to a Teflon-lined stainless steel autoclave and heated at 140 °C for 4 days. The product was collected by filtration, washed with deionized H_2O, and dried under 80 °C for 24 hours.

Characterization:

The X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). The step size was 0.02°, and the scanning speed was 3°/min. The ratio of Si/Al and copper content were determined by inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). The ^{29}Si MAS NMR spectra were recorded on a Varian Infinity Plus 400 spectrometer, and chemical shifts were referenced to tetramethylsilane (TMS). The sample morphology was observed with a field emission scanning electron microscope (JEOS JSM 6700F). Surface area and pore volume of the sample obtained were measured by nitrogen adsorption–desorption isotherms at 77K using a micromeritics ASAP2020M system. FTIR spectra were recorded using a Bruker 66V FTIR spectrometer. DTA–TG analysis was carried out on a NETZSCH STA 449C in air at a heating rate of 10 K/min from room temperature to 1000 °C. Elemental analysis was performed on a Perkin-Elmer 2400 element analyzer. UV/Vis spectra were measured on a PERKIN ELMER Lambda 20 spectrophotometer.

Theoretical calculation:

Density functional theory (DFT), with the B3LYP hybrid exchange-correlation functional, was used to perform theoretical calculations. Geometry optimizations were all performed with the Gaussian 03 program, and a DGDZVP basis set was used. For all the systems considered we have determined equilibrium geometries in the gas phase and have evaluated vibrational frequencies. The solvation effect has been investigated with Polarizable Continuum Model (PCM) solvent method implemented in the Gaussian 03 package. The PCM has been reported.[1-3]

Catalytic test:

Selective catalytic reduction (SCR) of NOx with NH_3 was measured in a flow-through powder reactor system using gas mixtures containing 1000 ppm NO, 1000 ppm NH_3, and 10% O_2 with a balance of Ar. The total flow rate was held at 44 mL/min, over the 200 mg catalyst powder samples (SV~30,000 h^{-1}). The temperature was varied from 108 to 550 °C in approximately 50 °C steps, as measured by a thermocouple of the catalyst powder bed.

REFERENCES

(1) Miertuš, S.; Scrocco, E.; Tomasi, J. Chem. Phys 1981, 55, 117-129.
(2) Miertuš, S.; Tomasi, J. Chem. Phys 1982, 65, 239-245.
(3)Tomasi, J.; Mennucci, B.; Cammi, R. Chem. Rev. 2005, 105, 2999-3093.

This journal is © The Royal Society of Chemistry 2011

Supporting Tables and Figures Captions:

Table S1. Products synthesized from the starting aluminosilicate gel in the absence of Cu-TEPA complex.

Table S2. Products synthesized from the aluminosilicate gel ($x$$Na_2O$/1$Al_2O_3$/200$H_2O$/10$SiO_2$/2TEPA) in the absence of Cu^{2+}.

Table S3. Textural parameters of products synthesized from the starting aluminosilicate gels in the presence of Cu-TEPA complexes with SiO_2/Al_2O_3 ratios.

Table S4. Products synthesized from the aluminosilicate gel ($x$$Na_2O$/1$Al_2O_3$/200$H_2O$/10$SiO_2$/2Cu-TETA) in the presence of Cu-TETA complex.

Fig. S1 Optimized geometry of Cu-TEPA complex.

Fig. S2 ^{29}Si NMR spectra of the samples synthesized from the starting aluminosilicate gels in the presence of Cu-TEPA complex with SiO_2/Al_2O_3 ratios at (a) 10, Cu-ZJM-1-10; (b) 15, Cu-ZJM-1-15; (c) 25, Cu-ZJM-1-25; and (d) 35, Cu-ZJM-1-35, respectively.

Fig. S3 IR spectra of (a) as-synthesized and (b) protonated Cu-ZJM-1-25 products.

Fig. S4 TG-DTA curves of as-synthesized Cu-ZJM-1-10.

Fig. S5 UV-Vis spectra of (a) Cu-TEPA complex in solution, (b) as-synthesized Cu-ZJM-1-10, and (c) protonated Cu-ZJM-1-10.

This journal is © The Royal Society of Chemistry 2011

Table S1. Products synthesized from the starting aluminosilicate gel in the absence of Cu-TEPA complex.

Sample	$Na_2O/Al_2O_3/H_2O/SiO_2$	Products of zeolites
A	3.1/1.0/200/10	GME + PHI
B	3.3/1.0/200/15	GME + PHI + ANA
C	3.5/1.0/200/25	PHI + ANA
D	3.8/1.0/200/35	ECR-1 + PHI + ANA

Table S2. Products synthesized from the aluminosilicate gel ($x$$Na_2O/1Al_2O_3/200H_2O/10SiO_2/2$TEPA) in the absence of Cu^{2+}.

Run	$Na_2O:Al_2O_3$	Products
1	1.4	Amorphous + MOR + LTA
2	2.0	P + GME
3	2.8-4.0	P + GME + ANA
4	4.0-4.5	P + ANA

Table S3. Textural parameters of products synthesized from the starting aluminosilicate gels in the presence of Cu-TEPA complexes with SiO_2/Al_2O_3 ratios.

Sample	$S_{BET}(m^2/g)^a$	$V_{Micropore}(cm^3/g)^a$
Cu-ZMM-1-10	586	0.27
Cu-ZMM-1-15	524	0.23
Cu-ZMM-1-25	558	0.25
Cu-ZMM-1-35	540	0.24

[a] BET surface areas and microporous volumes of samples after twice ion-exchange with NH_4NO_3 and calcination at 550 °C for 8 h

Table S4. Products synthesized from the aluminosilicate gel (xNa$_2$O/1Al$_2$O$_3$/200H$_2$O/10SiO$_2$/2Cu-TETA) in the presence of Cu-TETA.

Run	$Na_2O:Al_2O_3$	Products
1	2.6-3.9	Amorphous
2	3.9-4.5	Amorphous + LTA
3	4.5-4.8	P + GME + ANA
4	4.8-5.2	P+ANA

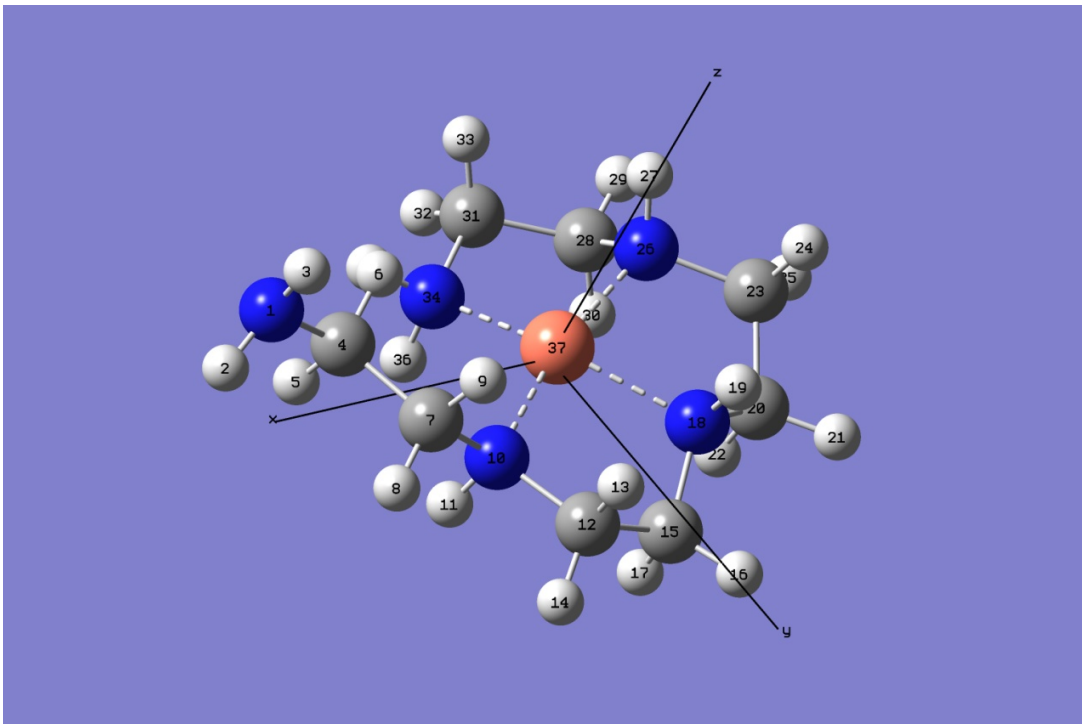

Fig. S1. Optimized geometry of Cu-TEPA complex.

This journal is © The Royal Society of Chemistry 2011

Number	Atoms	x	y	z
1	N	4.40620400	-1.24824700	0.66946300
2	H	5.19584700	-0.91951700	0.12021400
3	H	4.54389500	-0.99827300	1.64509400
4	C	3.12234400	-0.85597500	0.13843400
5	H	3.06378000	-1.21025200	-0.90009100
6	H	2.34810900	-1.38557000	0.71328200
7	C	2.80244900	0.65549800	0.17729200
8	H	3.59870200	1.21842800	-0.32450700
9	H	2.75092800	1.00165700	1.21353400
10	N	1.48962500	0.98822700	-0.47997800
11	H	1.60685700	0.80110100	-1.48022200
12	C	1.13955300	2.44589600	-0.33671400
13	H	1.38476500	2.74354000	0.68678700
14	H	1.74913700	3.05750700	-1.00956500
15	C	-0.34750400	2.65786500	-0.60222600
16	H	-0.63050600	3.70066900	-0.42015800
17	H	-0.60750500	2.41822400	-1.63814300
18	N	-1.09538700	1.72572100	0.28982500
19	H	-1.00033400	2.04833700	1.25766800
20	C	-2.54176000	1.49711200	-0.00521600
21	H	-3.14000900	2.39118100	0.20338000
22	H	-2.63471700	1.27953200	-1.07374900
23	C	-3.01333300	0.31652200	0.84535900
24	H	-3.04692400	0.60040000	1.90110400
25	H	-4.02382700	0.01070300	0.55814200
26	N	-2.04728500	-0.82757400	0.71126400
27	H	-1.93770800	-1.26737600	1.62840200
28	C	-2.41588500	-1.89806600	-0.26535100
29	H	-3.28506100	-2.46590100	0.08453200
30	H	-2.68752600	-1.42117900	-1.21263700
31	C	-1.20818000	-2.81322300	-0.44075800
32	H	-1.40796000	-3.58263200	-1.19150300
33	H	-0.97158200	-3.32045500	0.49878800
34	N	-0.01421300	-1.98095800	-0.82270700
35	H	0.84636900	-2.48340400	-0.59136800
36	H	0.00977300	-1.87119300	-1.84107500
37	Cu	-0.21114500	-0.10274100	0.05283100

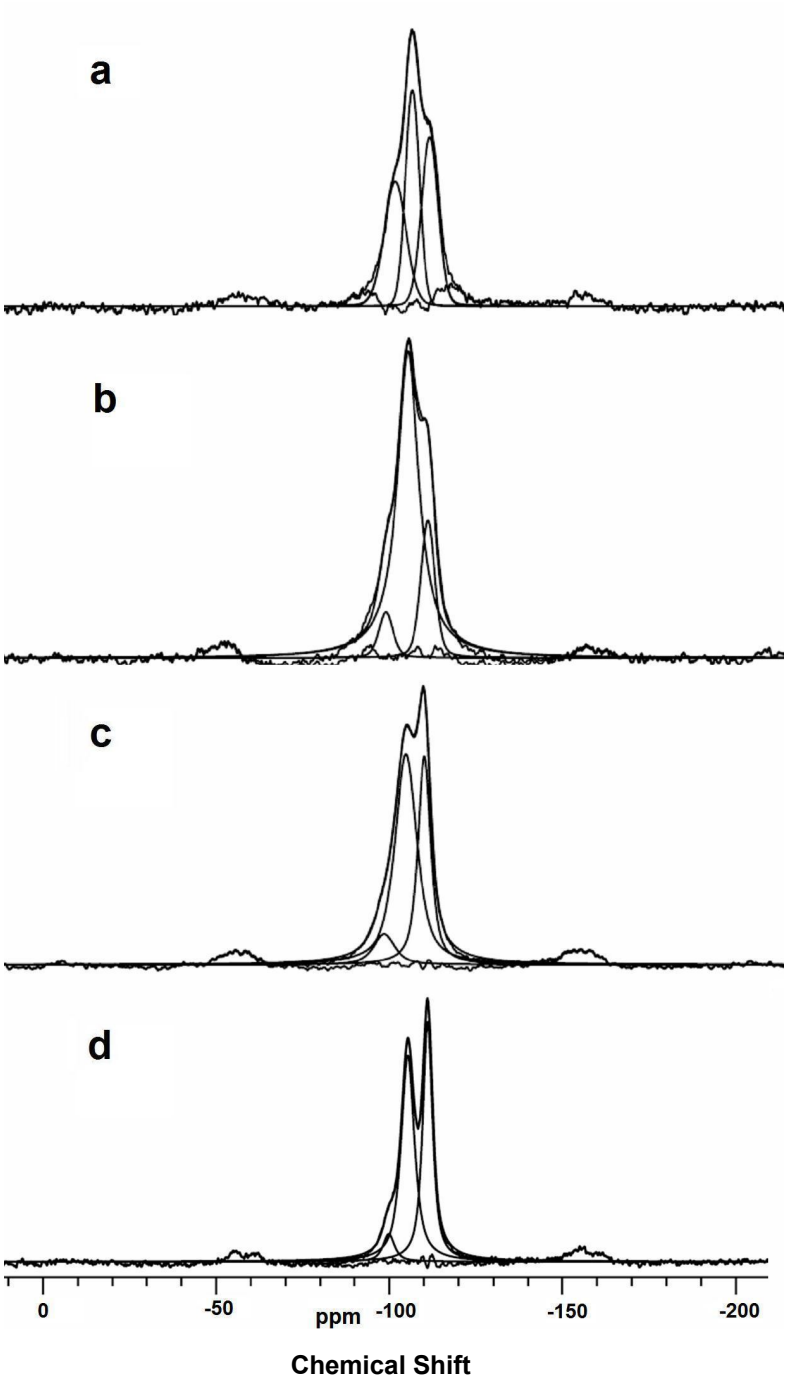

Fig. S2 ^{29}Si NMR spectra of the samples synthesized from the starting aluminosilicate gels in the presence of Cu-TEPA complex with SiO_2/Al_2O_3 ratios at (a) 10, Cu-ZJM-1-10; (b) 15, Cu-ZJM-1-15; (c) 25, Cu-ZJM-1-25; and (d) 35, Cu-ZJM-1-35, respectively.

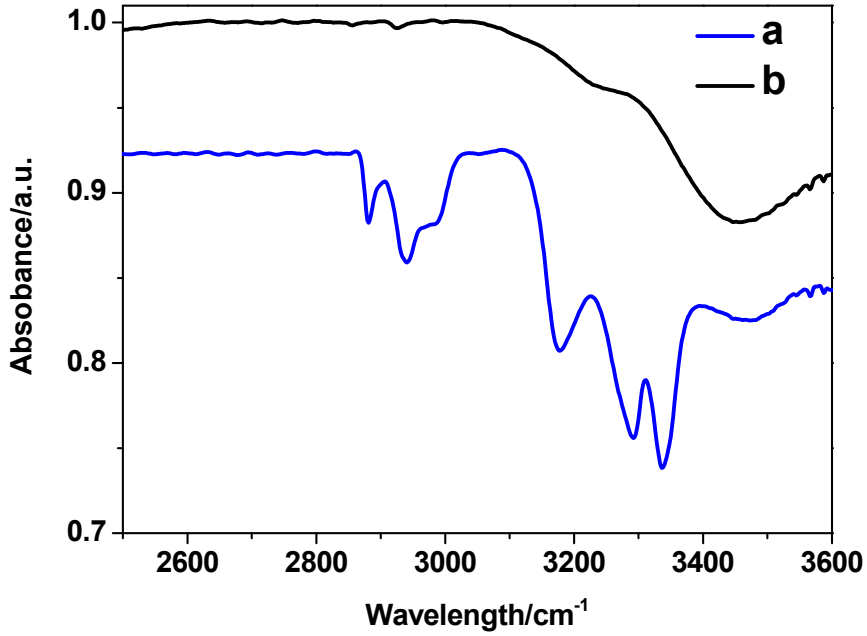

Fig. S3 IR spectra of (a) as-synthesized and (b) protonated Cu-ZJM-1-25 products.

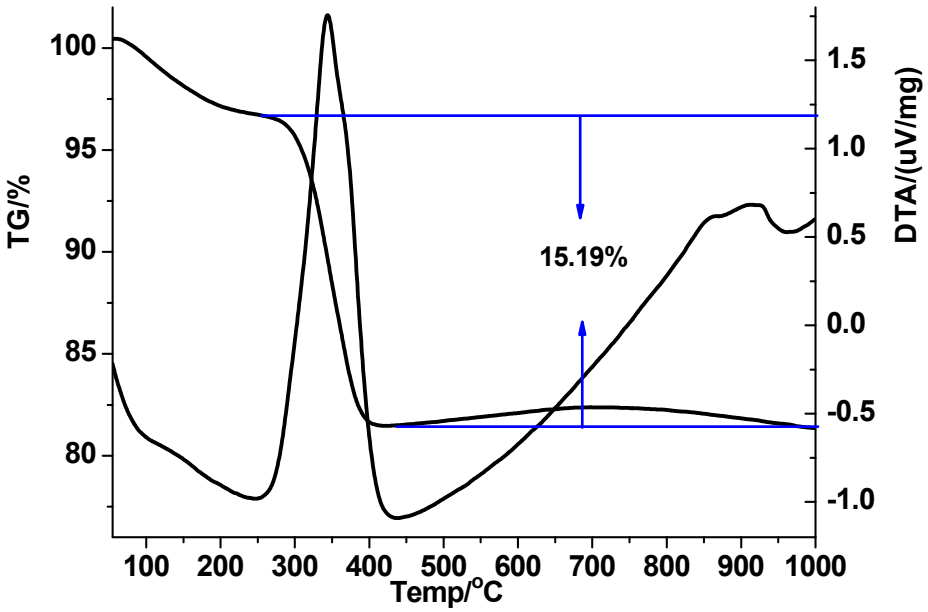

Fig. S4 TG-DTA curves of as-synthesized Cu-ZJM-1-10.

This journal is © The Royal Society of Chemistry 2011

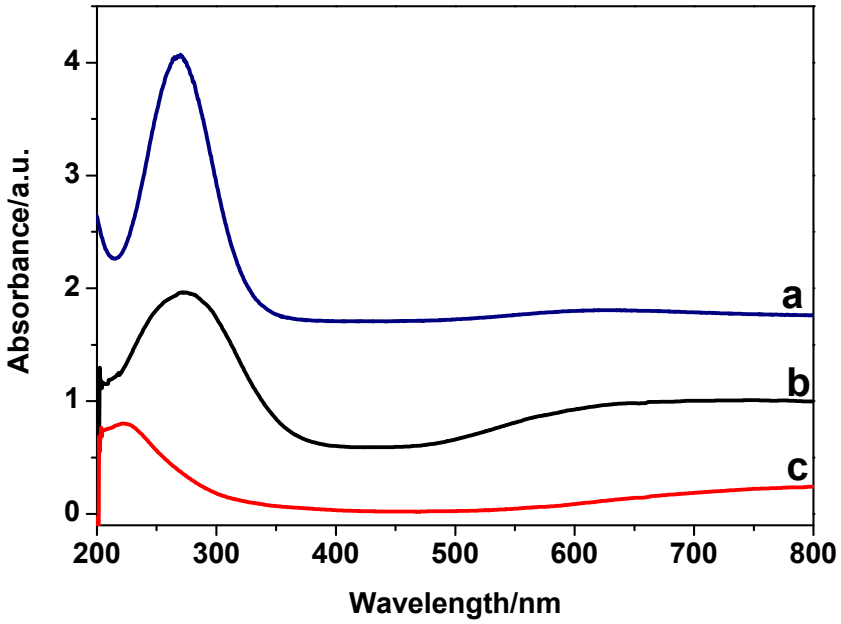

Fig. S5 UV-Vis spectra of (a) Cu-TEPA complex in solution, (b) as-synthesized Cu-ZJM-1-10, and (c) protonated Cu-ZJM-1-10.