由新型铜胺络合物模板剂设计合成活性优异的 Cu-SSZ-13 分子筛

任利敏², 张一波³, 曾尚景², 朱龙凤², 孙 琦¹, 张海燕², 杨承广²,
孟祥举¹, 杨向光³, 肖丰收^{1,*}

¹ 浙江大学催化研究所, 浙江杭州 310028

² 吉林大学无机合成与制备国家重点实验室, 吉林长春 130012

³ 中国科学院长春应用化学研究所, 吉林长春 130022

摘要: 以低廉的铜胺络合物为新型模板剂, 成功地合成了含铜的 SSZ-13 沸石分子筛 (Cu-ZJM-1)。在合成过程中, 铜胺络合物既是模板分子, 又是催化活性组分铜物种的直接来源。理论计算表明, 该模板分子的构型与尺寸恰好与构成 SSZ-13 分子筛结构的 CHA 笼相匹配, 因而可以成功地导向该沸石分子筛结构。采用 X 射线衍射、扫描电镜、氮气吸附、红外、紫外-可见吸收光谱、差热-热重分析、氨气程序升温脱附及氢气程序升温还原等手段对样品的性质及模板分子的状态进行了系统表征。结果表明, 所制 Cu-ZJM-1 样品为结晶度很高的 SSZ-13 沸石结构, 硅铝比和铜负载量可调且铜处于高分散状态, 在 NH₃ 选择催化还原氮氧化物反应中表现出优异的催化性能。

关键词: 新型模板剂; 铜胺络合物; 设计合成; Cu-SSZ-13; 理论计算; 氨还原消除氮氧化物反应

中图分类号: O643/X7

文献标识码: A

收稿日期: 2011-08-04. 接受日期: 2011-09-12.

*通讯联系人. 电话: (0431)85168590; 传真: (0431)85168624; 电子信箱: fsxiao@zju.edu.cn

基金来源: 国家自然科学基金 (20973079, 21003107); 国家重点基础研究发展计划 (973 计划, 2009CB623507).

本文的英文电子版(国际版)由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).

Design and Synthesis of a Catalytically Active Cu-SSZ-13 Zeolite from a Copper-Amine Complex Template

REN Limin², ZHANG Yibo³, ZENG Shangjing², ZHU Longfeng², SUN Qi¹, ZHANG Haiyan²,
YANG Chengguang², MENG Xiangju¹, YANG Xiangguang³, XIAO Feng-Shou^{1,*}

¹ Department of Chemistry, Zhejiang University, Hangzhou 310028, Zhejiang, China

² State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, Jilin, China

³ Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China

Abstract: The modern synthesis of zeolites typically uses organic structure-directing agents. Therefore, the developing of new templates is part of zeolite research. The design and synthesis of Cu-SSZ-13 using a novel template of a low-cost copper amine complex (Cu²⁺ coordinated with tetraethylenepentamine) were reported, where the copper amine complex is both a template for synthesizing the SSZ-13 structure and a source of copper species in the zeolite. The calculated size of the complex (0.728 nm × 0.922 nm) matches well with the CHA cages (0.73 nm × 1.2 nm), which are the building units of the SSZ-13 zeolite. Various techniques were used to investigate the chemical and physical properties of the synthesized zeolite. The results showed that the sample has the SSZ-13 zeolite structure, high crystallinity, adjustable Si/Al ratios, and controllable copper loading. Catalytic tests using the selective catalytic reduction of NO_x with NH₃ showed that the Cu-SSZ-13 was a superior catalyst, and it can be important for the abatement of environmentally harmful NO_x.

Key words: novel template; copper amine complex; designed synthesis; Cu-SSZ-13; theoretical calculation; selective catalytic reduction of NO_x with NH₃

Received 4 August 2011. Accepted 12 September 2011.

*Corresponding author. Tel: +86-431-85168590; Fax: +86-431-85168624; E-mail: fsxiao@zju.edu.cn

This work was supported by the National Natural Science Foundation of China (20973079 and 21003107) and the National Basic Research Program of China (973 Program, 2009CB623507).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

沸石分子筛材料,尤其是硅铝沸石分子筛材料,具有规则的微孔孔道、大的比表面积、较高的热稳定性及水热稳定性,是目前应用于石油化工领域最广泛的多相催化材料^[1~4]。在现代沸石分子筛合成中,有机模板剂的使用起着非常重要的作用,新拓扑结构沸石分子筛的开发以及新的合成路线的探索都与新型模板分子密切相关^[5~14],如 Corma 课题组报道的 ITQ 系列分子筛^[5~7]以及 Zones 课题组报道的 SSZ 系列分子筛^[8~11]。通常,模板分子在沸石分子筛的合成中起着结构导向、孔道填充以及平衡骨架电荷的作用^[4]。在选择有机模板剂时,一般需考虑其构型、大小、可溶解性、电荷等因素^[2~4]。早期,比较典型的模板剂有季铵盐等^[1~4],而近年来模板剂种类得到不断拓展,如 Morris 等^[15~16]报道的既可用作模板又可作为溶剂的离子液体;Ryoo 等^[19,20]报道的既可用作微孔模板又可导向有序介孔结构的两亲有机硅长链分子;Corma 等^[21]报道的有机膦基化合物以及 Davis 等^[22,23]报道的金属络合物等。

值得指出的是,金属络合物作为模板剂被广泛应用于多种磷铝骨架结构沸石分子筛的合成^[24~30],如 AFI, AlPO₄-16 和 CHA 等^[24~26];Wilkinson 课题组又采用该方法成功合成了手性镓磷结构分子筛^[27,28];Wright 等^[29,30]采用金属 Ni 与芳杂环得到的络合物分子制备了 STA-6 及 STA-7 分子筛。但是对于硅铝骨架沸石分子筛,仅成功合成了十四元环 UTD-1 沸石分子筛^[22,23],其合成使用了络合物二茂钴[bis(pentamethylcyclopentadienyl) cobalt (III) hydroxide, (Cp*)₂Co(OH)]作为模板剂。由于硅铝分子筛的合成通常是在强碱性水热条件下,大部分金属络合物可能已经发生分解。因此,使用普通的金属络合物合成硅铝分子筛仍然是一个很大的挑战。

另一方面,近年来具有高硅铝比和八元环孔道结构的 SSZ-13 沸石分子筛在 MTO 反应中具有较高的催化活性和选择性,因而广受关注^[31~33]。高的硅铝比赋予了产品更高的热稳定性及水热稳定性,而八元环的孔道结构使其在 MTO 反应中具有良好的择形性^[34]。最近,人们还发现 Cu 交换的 SSZ-13 沸石在以 NH₃ 为还原剂的消除氮氧化物(NO_x)污染

的反应(NH₃-SCR)中,显示出比其它分子筛(Cu-ZSM-5, Cu-Beta 等)更为优异的催化活性和选择性^[35~38]。但是,由于 SSZ-13 沸石分子筛较小的孔道尺寸以及交换容量的限制,Cu 负载量不高,从而限制了其催化活性的提高。更值得指出的是,当前用于合成 SSZ-13 沸石分子筛的模板剂只有 N,N,N'-三甲基-1-1-金刚烷氢氧化铵(TMAA-OH)^[9,14],该试剂价格昂贵,使得该分子筛应用受到限制。因此,使用廉价易得的模板剂来合成 SSZ-13 沸石分子筛,并使其具有高度分散且担载量可控的金属活性物种显得十分重要。

最近,本课题组曾以铜胺络合物(Cu²⁺和四乙烯五胺,Cu-TEPA)为模板分子,合成了 Cu-SSZ-13 沸石分子筛(Cu-ZJM-1)^[39],本文则详细报道了 Cu-ZJM-1 的设计合成、系统表征及其用于 NH₃-SCR 反应的性能。

1 实验部分

1.1 样品的合成与处理

1.1.1 Cu-ZJM-1 沸石分子筛的合成

Cu-ZJM-1 沸石分子筛是在投料摩尔比为 3.1~3.8Na₂O:1.0Al₂O₃:10~35SiO₂:200H₂O:2.0~3.0Cu-TEPA 的初始凝胶体系中合成的,典型的过程如下。首先将 0.514 g NaAlO₂ (CP, 国药集团化学试剂有限公司)溶于 4.722 g 去离子水中,再加入 1.149 g CuSO₄·5H₂O (99%, 北京化工厂)。搅拌 0.5 h 之后,滴加 1.07 g 四乙烯五胺 (95%, 国药集团化学试剂有限公司),经充分搅拌再加入 0.38 g NaOH (96%, 北京化工厂),搅拌 0.5 h 之后,再加入 3.6 ml 质量分数为 31.5% 的硅溶胶(杭州银湖化学有限公司),搅拌 2~3 h 后,装入聚四氟乙烯内衬的钢制反应釜中,于 140 °C 反应 3~6 d。反应完成后,将产物用去离子水洗涤,并在 100 °C 干燥 12 h,得到 Cu-ZJM-1-x 样品。x 代表起始物种的 SiO₂/Al₂O₃ 比值。

1.1.2 Cu-ZJM-1 沸石分子筛的处理

用于催化反应的样品需经铵交换和焙烧等处理,具体操作如下。将 1 g Cu-ZJM-1 样品加到 100 ml 的硝酸铵溶液 (1 mol/L) 中,在 80 °C 水浴条件下

交换 12 h 后, 充分洗涤, 过滤并于 100 °C 干燥 12 h, 再在空气中于 550 °C 焙烧 8 h, 所得样品命名为 Cal-Cu-ZJM-1.

1.1.3 常规离子交换法制备 Con-Cu-SSZ-13 样品

参照文献 [35], 采用离子交换法制备 Con-Cu-SSZ-13. 具体操作如下. 将氢型的 SSZ-13 沸石分子筛 (骨架摩尔比 Si/Al = 4.2) 加到 0.1 mol/L 的硝酸铜溶液中, 该溶液中含有分子筛饱和和交换量 2 倍的铜离子. 在室温搅拌 24 h 后, 经洗涤、过滤、烘干, 再重复一次上述交换操作. 干燥后样品在空气条件下于 500 °C 焙烧 4 h, 该样品命名为 Con-Cu-SSZ-13.

1.2 催化性能测试

NH₃-SCR 反应在固定床流动反应体系中进行, 催化剂用量 0.2 g. 原料气组成: 0.1% NO, 0.1% NH₃, 10% O₂, 5% 水蒸气, Ar 平衡气, 流量为 44 ml/min. 尾气组分采用四级杆质谱仪在线检测. 测试前, 所有样品均需在 500 °C 活化 4 h.

1.3 样品的表征

X 射线衍射 (XRD) 谱由 Rigaku D/MAX 2550 型 X 射线衍射仪 (40 kV, 200 mV, Cu K α , 以 0.02 间隔阶梯扫描, 扫描速度 3°/min) 测定; ²⁹Si 高分辨魔角旋转核磁共振 (MAS NMR) 谱图在 Varian Infinity Plus 400 型核磁共振仪上测得; 元素分析在 Perkin-Elmer 3300 DV ICP (电感耦合等离子体) 分析仪上进行; 电镜为日本电子 JSM6300 型扫描电子显微镜 (SEM, 加速电压 4~5 kV, JEOL 2010F); 氮气吸附/脱附实验在液氮温度 (-196 °C) 下进行, 由 Micromeritics ASAP 2020M 分析仪完成, 实验前, 样品在 200 °C 真空条件下处理 10 h; 样品的红外光谱 (FT-IR) 在 Nicolet Impact 410 型 FT-IR 光谱仪上测定, 采用 KBr 压片 (样品占 1%), 测试范围 400~4000 cm⁻¹; 样品的差热热重 (TG-TDA) 曲线由 NETZSCH STA 449C 仪器测定, 在空气条件下进行,

测试范围为室温到 1000 °C, 升温速率为 10 °C/min; C, H, N 元素分析的仪器型号为 Perkin-Elmer 2400; 紫外可见吸收光谱 (UV-Vis) 由 Perkin-Elmer Lambda 20 光谱仪得到; NH₃ 程序升温脱附 (NH₃-TPD) 和 H₂ 程序升温还原 (H₂-TPR) 数据均在 Micromeritics AutoChem II 2920 型自动化学吸附分析仪上测定.

1.4 理论计算

计算利用 B3LYP 杂化交换关联函数的密度泛函理论进行. 结构优化使用基组为 DGDZVP 的 Gaussian 03 软件. 对于气相中的平衡构型计算了振动频率, 所有的计算都采用 Gaussian 03 包中的极化连续模型 (PCM) 来描述分子所处的水溶液环境.

2 结果与讨论

2.1 Cu-ZJM-1 沸石分子筛的设计合成

2.1.1 模板剂的设计

本文选择 CuSO₄·5H₂O 和 TEPA 络合产物 (Cu-TEPA) 作为模板分子, 进行 Cu-ZJM-1 沸石分子筛的设计合成. 主要原因有以下几点. (1) 铜离子和 TEPA 可以形成很稳定的络合物, 其络合常数 (lg*K*, 20 °C) 为 23.1, 远远高于 Cu(OH)₄²⁻ 的 18.5, 因而确保了其在碱性合成条件下稳定存在. (2) Cu-TEPA 络合物带有两个正电荷, 因而可更好地与体系中带负电荷的硅物种进行相互作用. (3) 在该络合物分子中, 一个铜离子与一个 TEPA 分子进行配合, 铜原子可以满足稳定的四配位构型. 理论计算表明, Cu-TEPA 络合物分子的大小 (0.728 nm × 0.922 nm) 与构型恰好和构成 ZJM-1 沸石分子筛的 CHA 笼 (0.73 nm × 1.20 nm) 相匹配^[34,40].

2.1.2 Cu-ZJM-1 沸石分子筛的合成

通过调节起始凝胶的配比, 可制得不同硅铝比的 Cu-ZJM-1 沸石分子筛, 见表 1. 在该合成体系中, Cu-TEPA 与 SiO₂ 的比值保持在 0.1~0.2, 通过调节

表 1 不同摩尔配比的起始凝胶得到的产物的硅铝比、铜含量及比表面积

Table 1 Starting composition of the gels, SiO₂/Al₂O₃ ratios, and Cu content in the as-synthesized solid products

Sample	Na ₂ O:Al ₂ O ₃ :H ₂ O:SiO ₂ :Cu-TEPA molar ratio	SiO ₂ /Al ₂ O ₃ ratio		Cu content (%)	<i>A</i> _{BET} / (m ² /g)	Crystallization time (d)
		ICP	²⁹ Si NMR			
Cu-ZJM-1- <i>x</i> ^a						
<i>x</i> = 10	3.1:1.0:200:10:2	8.1	8.0	9.5	586	3
<i>x</i> = 15	3.3:1.0:200:15:2	8.6	8.4	9.8	524	4
<i>x</i> = 25	3.5:1.0:200:25:3	10.7	11.0	10.2	558	4.5
<i>x</i> = 35	3.8:1.0:200:35:3	15.3	15.0	10.1	540	6

^a*x* stands for the SiO₂/Al₂O₃ ratio in the initial gel.

体系中的碱度 ($\text{Na}_2\text{O}/\text{SiO}_2$) 来得到 Cu-ZJM-1 分子筛的纯相。体系中碱度过高时, 较易伴随出现 P 沸石杂相; 体系中碱度过低时, 则出现大量无定形产物。另外, 反应温度也对产物的最终结构影响很大。较低的反应温度下 ($100\text{ }^\circ\text{C}$), 产物倾向于生成 FAU 沸石结构; 较高的反应温度条件下 ($180\text{ }^\circ\text{C}$), 易产生 P 沸石杂相; 在 $140\text{ }^\circ\text{C}$ 生长 3~6 d 最终可得到 Cu-ZJM-1 (CHA 沸石结构) 的纯相产物, 并且产物的晶化时间随着投料硅铝比的升高而延长 (见表 1)。还可以发现, 随着投料中硅铝比的升高, 产物硅铝比也在逐渐提高。

图 1 为不同起始凝胶组成下, 原始合成的 Cu-ZJM-1 样品和经过铵交换并焙烧的 Cal-Cu-ZJM-1 样品的 XRD 谱。可以看出它们都具有典型的 CHA 沸石结构 ($2\theta = 9.5^\circ, 14.0^\circ, 16.1^\circ, 17.8^\circ, 20.7^\circ, 25.0^\circ$)^[41], 且具有较高的结晶度。图 2 为各 Cu-ZJM-1 样品在 $2\theta = 20^\circ \sim 26^\circ$ 区间的 XRD 谱。由图可见, 随着起始凝胶硅铝比的增加, 样品衍射峰从 $2\theta = 20.75^\circ$ 偏移至 20.88° , 这与骨架中因 Al 的减少

图 1 不同起始凝胶投料情况下原始合成的样品 Cu-ZJM-1 及焙烧后的样品的 XRD 谱

Fig. 1. XRD patterns of as-synthesized (a) and calcined (b) Cu-ZJM-1 samples with different initial Si/Al ratios.

图 2 Cu-ZJM-1-10, Cu-ZJM-1-25 及 Cu-ZJM-1-35 样品的 XRD 谱

Fig. 2. XRD patterns of Cu-ZJM-1-10, Cu-ZJM-1-25, and Cu-ZJM-1-35 samples.

而导致晶胞参数的减小有关, 更进一步证明了样品硅铝比的提高^[42]。

图 3 为不同 Cu-ZJM-1 样品的 ^{29}Si NMR 谱。谱图经分峰拟合后可用于精确计算样品的硅铝比^[4]。可以看出, 随着投料硅铝比的增加, 产物的 Q1

图 3 Cu-ZJM-1-10, Cu-ZJM-1-15, Cu-ZJM-1-25 和 Cu-ZJM-1-35 的 ^{29}Si NMR 以及它们的拟合谱

Fig. 3. ^{29}Si NMR and their fitted spectra of Cu-ZJM-1-10, Cu-ZJM-1-15, Cu-ZJM-1-25, and Cu-ZJM-1-35 samples.

[Si(3Al), $\delta = -96.5$] 及 Q2 [Si(2Al), $\delta = -99.9$] 物种的比例不断降低, 而 Q3 [Si(1Al), $\delta = -104.93$] 及 Q4 [Si(0Al), $\delta = -110.8$] 物种的比例不断增加, 与 ICP 结果 (见表 1) 基本一致。

图 4 为不同 Cu-ZJM-1 样品的 SEM 照片。由图可见, 样品因硅铝比的变化而呈现出不同的形貌, 如 Cu-ZJM-1-10 为 300 nm 左右的、规整的立方晶体, 而 Cu-ZJM-1-25 则为几个微米大小的花朵形状。结果同样表明产物具有很高的结晶度。由此可见, 通过控制起始凝胶的硅铝比, 可以得到硅铝比可控的 Cu-ZJM-1 样品。

图 4 Cu-ZJM-1-10, Cu-ZJM-1-15, Cu-ZJM-1-25 和 Cu-ZJM-1-35 样品的 SEM 照片

Fig. 4. SEM images of Cu-ZJM-1-10 (a), Cu-ZJM-1-15 (b), Cu-ZJM-1-25 (c), and Cu-ZJM-1-35 (d) samples.

从外观上看, 所有样品都呈蓝色, 说明 Cu 物种包含在沸石分子筛中。如表 1 所示, 在原始合成出的样品中 Cu 含量可高达 10%, 大大高于采用离子交换法得到的 Con-Cu-SSZ-13 的 Cu 含量 (2.9%)^[35–37]。即使经过两次硝酸铵溶液处理并焙烧, 仍有 6.12% 的 Cu 存在于沸石中, 高于普通交换法得到的 Con-Cu-SSZ-13。值得指出的是, 铜含量高时, 原始合成的样品及焙烧处理后的样品的 XRD 谱中并未出现任何 CuO ($2\theta = 35.6^\circ$ 和 38.8°) 或者 Cu₂O ($2\theta = 36.44^\circ$)^[43] 的特征峰, 这表明 Cu-ZJM-1 中 Cu 的分散状态良好。通过控制硝酸铵交换及焙烧的次数, 样品的 Cu 含量可以控制在 0~10%。如经两次硝酸铵交换并焙烧即可使样品的 Cu 含量达 6.12%。若继续进行硝酸铵交换, 样品中的 Cu 含量

便降低至 3.1%。

特别值得提出的是, 在合成 Cu-ZJM-1 中原位引入 Cu 大大提高了铜源利用率。经过计算, 当产物中 Cu 含量为 10% 时, 原料中大约有 86% 的 Cu 物种留在 Cu-ZJM-1 中。即使经过两次硝酸铵交换后, 此时产物中 6.12% 的 Cu 含量仍对应着 55% 的原料利用率。而离子交换法通常需要大量的铜溶液^[35–37], 原料的利用率较低。等体积浸渍法^[44]的原料利用率较高, 但不利于金属离子的分散, 所得到的产物经常出现聚集态的氧化铜。

2.2 铜胺络合物模板剂在 Cu-ZJM-1 中的状态

图 5 为 Cu-ZJM-1-10 和 Cal-Cu-ZJM-1-10 样品的 N₂ 吸附等温线。由图可见, 原始合成样品的 N₂ 吸附量基本为 0。经 2 次硝酸铵交换, 并在空气中 550 °C 焙烧, 所得样品为典型的 I 型等温线, 其比表面积为 586 m²/g (见表 1), 与普通 SSZ-13 沸石 (580 m²/g) 类似。表明 Cu-TEPA 模板剂确实存在于原始合成的样品中, 经焙烧除去模板剂后则得到了开放孔道的产物。

图 5 Cu-ZJM-1-10 和 Cal-Cu-ZJM-1-10 样品的氮气吸附等温线

Fig. 5. N₂ adsorption-desorption isotherms of the Cu-ZJM-1-10 and Cal-Cu-ZJM-1-10 samples.

为了比较 Cu-ZJM-1 和普通 SSZ-13 的孔径分布, 本文将比压的横坐标取对数, 得到如图 6 的曲线。可以看出 Cal-Cu-ZJM-1 的等温线拐点对应的横坐标具有比 H-SSZ-13 更小的数值, 说明前者孔径更小^[45]。可能是由孔道中存在较大尺寸的 Cu 物种所致。

为了进一步理解样品中铜胺模板剂的状态, 本文采用多种手段对样品进行分析。图 7 为

图 6 Cal-Cu-ZJM-1-10 和 H-SSZ-13 在横坐标比压数值取对数后的氮气吸附等温线

Fig. 6. N_2 adsorption isotherms of Cal-Cu-ZJM-1-10 (1) and H-SSZ-13 (2) using a logarithmic x-axis.

Cu-ZJM-1-25 和 Cal-Cu-ZJM-1-25 样品的 FT-IR 谱. 可以看出, Cu-ZJM-1-25 样品于 $2800\sim 3000\text{ cm}^{-1}$ 出现对应于亚甲基的振动峰, $3100\sim 3400\text{ cm}^{-1}$ 之间的三个峰为胺基的振动引起的. 这说明 Cu-ZJM-1-25 含有亚甲基和胺基基团, 这与 TEPA 分子组成一致. 处理并焙烧后的样品 Cal-Cu-ZJM-1-25 的有机基团全部消失.

图 7 Cu-ZJM-1-25 和 Cal-Cu-ZJM-1-25 的 FT-IR 谱
Fig. 7. FT-IR spectra of Cu-ZJM-1-25 and Cal-Cu-ZJM-1-25.

图 8 为 Cu-ZJM-1-10 样品的 TG-DTA 曲线. 可以看出, 在 $250\text{ }^{\circ}\text{C}$ 之前, 样品出现少量失重, 可归属于沸石分子筛中吸附的水分子, 在 $250\sim 500\text{ }^{\circ}\text{C}$ 之间, 只出现一个位于 $343\text{ }^{\circ}\text{C}$ 的放热峰, 对应的热失重为 15.19% , 这与四乙烯五胺模板分子分解有关. 对于 $500\text{ }^{\circ}\text{C}$ 后出现的放热峰并伴随有 1.5% 的增重, 则归属为产物中铜物种的氧化. 元素分析结果显示, 产物中有机物含量为 14.7% , 与 TG-DTA 的结果接近, 且产物中 C/N 摩尔比为 1.57 , 与模板剂

图 8 Cu-ZJM-1-10 样品的 TG-DTA 曲线
Fig. 8. TG-DTA curves of Cu-ZJM-1-10.

TEPA 分子 (1.6) 很接近. 这进一步表明四乙烯五胺分子完整地存在于 Cu-ZJM-1-10 沸石分子筛孔道中.

图 9 为 Cu-ZJM-1-10 样品和 Cu-TEPA 溶液的 UV-Vis 谱. Cu-ZJM-1-10 样品在 270 nm 处出现明显的吸收峰, 与 Cu-TEPA 溶液 (268 nm) 十分接近, 这说明铜胺络合物分子以完整的配合状态存在于分子筛孔道中. 硝酸铵交换并焙烧后的样品吸收峰位于 225 nm , 可归属于单分散的 Cu^{2+} 物种.

图 9 Cu-TEPA 溶液、Cu-ZJM-1-10 和 Cal-Cu-ZJM-1-10 样品的紫外可见吸收光谱

Fig. 9. UV-Vis spectra of Cu-TEPA complex in solution, Cu-ZJM-1-10, and Cal-Cu-ZJM-1-10.

2.3 Cu-TEPA 对合成 Cu-ZJM-1 的结构导向作用

综上所述, 铜和四乙烯五胺的络合物完整地存在于 Cu-SSZ-13 分子筛的孔道中. 但是, 其模板导向作用还未完全了解. 因此, 我们首先在未加 Cu-TEPA 络合物的条件下, 调节起始凝胶的配比 (主要是 $\text{Na}_2\text{O}/\text{SiO}_2$ 比值), 但没有制得任何 CHA 结构的沸石分子筛样品 (见表 2, 实验 1~4). 这表明该

表 2 不含 Cu-TEPA 模板剂或者只在 TEPA 存在的情况下得到的产物

Table 2 Products obtained from the gel in the absence of Cu-TEPA template or in the presence of TEPA

Run	Na ₂ O:Al ₂ O ₃ :H ₂ O:SiO ₂ :TEPA	Product
1	3.1:1.0:200:10:0	GME + PHI
2	3.3:1.0:200:15:0	GME + PHI + ANA
3	3.5:1.0:200:25:0	PHI + ANA
4	3.8:1.0:200:35:0	ECR-1 + PHI + ANA
5	1.4:1.0:200:10:2	amorphous + MOR + LTA
6	2.0:1.0:200:10:2	P + GME
7	2.8-4.0:1.0:200:10:2	P + GME + ANA
8	4.0-4.5:1.0:200:10:2	P + ANA

络合物分子在 Cu-ZJM-1 沸石分子筛的合成过程中起到了重要的结构导向作用。

由于四乙烯五胺可用作模板剂合成 ZSM-5 分子筛^[46], 为了考察只有 TEPA 存在时能否合成 ZJM-1 沸石, 在体系中不加铜离子, 经过一系列配比的调变, 产物中也未出现任何 ZJM-1 沸石相 (表 2, 实验 5~8)。这表明只有在铜胺络合物整体存在的情况下才能够合成 CHA 结构的 ZJM-1 沸石。在 TEPA 单独存在的条件下, TEPA 是以长链的形式存在于体系中, 大约长度为 1.82 nm^[46], 这种长链构型与 CHA 笼是不相匹配的, 因此, 不能够合成出 CHA 结构的 ZJM-1 沸石产品。

为了验证 Cu-TEPA 络合物作为模板分子的专属性, 我们也采用了其它有机胺与铜离子进行络合。三乙烯四胺 (TETA) 具有与四乙烯五胺相似的长链结构, 并且同样具有很高的络合常数 ($\lg k = 20.4$)。用 Cu-TETA 来尝试合成 SSZ-13 分子筛时, 经过一系列配比的调变, 始终没有出现任何具有 CHA 结构沸石产物 (见表 3)。这也可通过模板剂的构型与沸

表 3 Cu-TETA 存在的情况下调节凝胶配比 ($x\text{Na}_2\text{O}:1\text{Al}_2\text{O}_3:200\text{H}_2\text{O}:10\text{SiO}_2:2\text{Cu-TETA}$) 得到的样品

Table 3 Products obtained from the aluminosilicate gel in the presence of Cu-TETA ($x\text{Na}_2\text{O}:1\text{Al}_2\text{O}_3:200\text{H}_2\text{O}:10\text{SiO}_2:2\text{Cu-TETA}$)

Run	Na ₂ O:Al ₂ O ₃	Product
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

TETA—triethylenetetramine.

石分子筛 CHA 笼结构的匹配与否来解释。上述结果充分证明 Cu-TEPA 在 Cu-ZJM-1 沸石分子筛的合成上具有专属性。

2.4 Cu-ZJM-1 分子筛的催化性能

近年来, NO_x 消除反应逐渐成为人们关注的热点, 其中含 Cu 或 Fe 物种的沸石分子筛因其高的热稳定性及优异的催化性能而成为研究的重心^[35–38,47–50]。与常见的 Cu-ZSM-5 和 Cu-Beta 沸石相比, Cu-SSZ-13 沸石具有适合的孔道结构及良好的水热稳定性, 在 NH₃-SCR 反应中表现出了更高的反应活性及抗失活能力^[35–38]。

分子筛的酸性中心有利于还原剂 NH₃ 的吸附活化, 是 NH₃ 还原 NO_x 能力的一个重要影响因素^[51]。NH₃-TPD 曲线中 NH₃ 脱附温度可反映分子筛酸性强弱。通常, 250 °C 前的脱附峰可以归属为弱酸吸附 NH₃ 的脱附, 而 250 °C 之后的脱附峰为强酸位上 NH₃ 脱附峰^[52]。图 10(a) 为 Cal-Cu-ZJM-1-10 及 Con-Cu-SSZ-13 的 NH₃-TPD 曲线。可以看出, Cal-Cu-ZJM-1-10 样品于 196 °C 出现脱附峰, 对应弱酸中心, 而 348 °C 处对应强酸中心。值得指出的是, Cal-Cu-ZJM-1-10 在 530 °C 和 625 °C 处出现了明显的脱附峰, 这可能与分子筛中铜原子和 NH₃

图 10 Cal-Cu-ZJM-1-10 和 Con-Cu-SSZ-13 的 NH₃-TPD 和 H₂-TPR 曲线

Fig. 10. NH₃-TPD (a) and H₂-TPR (b) curves of Cal-Cu-ZJM-1-10 (1) and Con-Cu-SSZ-13 (2).

分子的吸附作用相关. 类似的脱附峰 (498 °C) 也出现在 Con-Cu-SSZ-13 中. 与 Con-Cu-SSZ-13 相比, Cal-Cu-ZJM-1-10 的高温脱附峰的滞后说明其中铜物种的稳定性更高. 另外, Con-Cu-SSZ-13 样品在 767 °C 明显出现脱附峰, 这是由于该温度下分子筛骨架崩塌所致, 但在 Cal-Cu-ZJM-1-10 中并未出现此峰. 由此可见, 即使骨架硅铝比相似, Cal-Cu-ZJM-1-10 分子筛具有更高的骨架热稳定性.

在 NH_3 -SCR 反应中, 沸石分子筛中金属物种的还原性决定了 NO_x 的转化程度. 在含铜沸石分子筛的 NH_3 -SCR 反应中, Cu 的含量及其在沸石分子筛中的分布状态决定了还原反应发生的难易程度^[53,54]. 图 10(b) 为 Cal-Cu-ZJM-1 及 Con-Cu-SSZ-13 样品的 H_2 -TPR 图. 可以看出, Cal-Cu-ZJM-1 样品还原峰面积远远大于 Con-Cu-SSZ-13, 这与其具有较高铜含量一致. 两个样品分别在 245 °C 及 269 °C 出现低温还原峰, 通常, 低温还原峰为 Cu^{2+} 还原为 Cu^+ 所致, 峰温越低说明样品中 Cu 物种越容易被还原, 从而具有更高的 NH_3 -SCR 反应活性; 而 Cal-Cu-ZJM-1 及 Con-Cu-SSZ-13 产物的高温还原峰 606 °C 及 526 °C 则对应于 Cu^+ 到 Cu^0 的变化, 文献报道认为, 高温还原峰对应的温度越高, 分子筛中的铜活性物种稳定性越高, 这在 NH_3 -SCR 反应中则表现为较好的抗高温失活能力^[54].

图 11 为 Cal-Cu-ZJM-1-10 分子筛在 NH_3 -SCR 反应中 NO 转化率随温度的变化. 与具有同样硅铝比的、由传统交换法制得的 Con-Cu-SSZ-13 沸石相比, 该样品可较快达到高转化率, 即在 180 °C 时反

图 11 Cal-Cu-ZJM-1-10 和 Con-Cu-SSZ-13 在不同温度下 NH_3 -SCR 反应中 NO 的转化率

Fig. 11. NO conversion in the NH_3 -SCR reaction over Cal-Cu-ZJM-1-10 (1) and Con-Cu-SSZ-13 (2).

应转化率达 98%, 而 Con-Cu-SSZ-13 则在 270 °C 才可达到. 另外, Cal-Cu-ZJM-1 沸石分子筛高活性可持续到 450 °C, 而 Con-Cu-SSZ-13 沸石高活性仅持续到 380 °C. 这可能得益于 Cu-ZJM-1 沸石分子筛中较高的铜含量和良好的铜物种分散状态有关.

3 结论

设计了一种新型的铜胺络合物 Cu-TEPA 作为模板剂来直接合成 CHA 结构的 Cu-SSZ-13 沸石 (Cu-ZJM-1). 在该样品的合成过程中, Cu-TEPA 既起到了结构导向作用, 也提供了活性中心铜. 理论计算结果表明, Cu-TEPA 络合物分子的大小和构型恰好与构成 ZJM-1 沸石分子筛的结构单元 CHA 笼相匹配. 对比实验也证明铜离子和四乙烯五胺络合物作为模板剂合成 Cu-ZJM-1 沸石分子筛有其专属性和不可替代性. 该方法得到的样品含铜量高, 铜分散状态好, 在 NH_3 -SCR 反应中表现出了优异的催化性能. 该方法有可能为新型沸石分子筛合成提供新的路线, 并且 Cu-ZJM-1 沸石在 NH_3 -SCR 反应中的优异性能对于消除环境污染具有重要意义.

参 考 文 献

- 1 Corma A. *Chem Rev*, 1995, **95**: 559
- 2 Davis M E. *Nature*, 2002, **417**: 813
- 3 Cundy C S, Cox P A. *Chem Rev*, 2003, **103**: 663
- 4 Xu R, Pang W, Yu J, Huo Q, Chen J. *Chemistry of Zeolite and Related Porous Materials*. Singapore: Wiley, 2007. 1
- 5 Corma A, Rey F, Rius J, Sabater M J, Valencia S. *Nature*, 2004, **431**: 287
- 6 Corma A, Diaz-Cabanas M J, Jorda J L, Rey F, Sastre G, Strohmaier K G. *J Am Chem Soc*, 2008, **130**: 16482
- 7 Sun J, Bonneau C, Cantin A, Corma A, Diaz-Cabanas M J, Moliner M, Zhang D, Li M, Zou X. *Nature*, 2009, **458**: 1154
- 8 Lobo R F, Pan M, Chan I, Li H X, Medrud R C, Zones S I, Crozier P A, Davis M E. *Science*, 1993, **262**: 1543
- 9 Zones S I. US 4 544 538. 1985
- 10 Wagner P, Nakagawa Y, Lee G S, Davis M E, Elomari S, Medrud R C, Zones S I. *J Am Chem Soc*, 2000, **122**: 263
- 11 Jackowski A, Zones S I, Hwang S-J, Burton A W. *J Am Chem Soc*, 2009, **131**: 1092
- 12 Lee J H, Park M B, Lee J K, Min H-K, Song M K, Hong S B. *J Am Chem Soc*, 2010, **132**: 12971
- 13 Hong S B, Min H-K, Shin C-H, Cox P A, Warrender S J, Wright P A. *J Am Chem Soc*, 2007, **129**: 10870
- 14 Diaz-Cabanas M J, Barrett P A, Cambor M A. *Chem Commun*, 1998: 1881
- 15 Cooper E R, Andrews C D, Wheatley P S, Webb P B,

- Wormald P, Morris R E. *Nature*, 2004, **430**: 1012
- 16 Parnham E R, Drylie E A, Wheatley P S, Slawin A M Z, Morris R E. *Angew Chem, Int Ed*, 2006, **45**: 4962
- 17 Wei Y, Tian Z, Gies H, Xu R, Ma H, Pei R, Zhang W, Xu Y, Wang L, Li K, Wang B, Wen G, Lin L. *Angew Chem, Int Ed*, 2010, **49**: 5367
- 18 Fayad E J, Bats N, Kirschhock C E A, Rebours B, Quoineaud A-A, Martens J A. *Angew Chem, Int Ed*, 2010, **49**: 4585
- 19 Choi M, Cho H S, Srivastava R, Venkatesan C, Choi D-H, Ryoo R. *Nature Mater*, 2006, **5**: 718
- 20 Choi M, Na K, Kim J, Sakamoto Y, Terasaki O, Ryoo R. *Nature*, 2009, **461**: 246
- 21 Simancas R, Dari D, Velamazán N, Navarro M T, Cantín A, Jordá J L, Sastre G, Corma A, Rey F. *Science*, 2010, **330**: 1219
- 22 Freyhardt C C, Tsapatsis M, Lobo R F, Balkus K J, Davis M E. *Nature*, 1996, **381**: 295
- 23 Lobo R F, Tsapatsis M, Freyhardt C C, Khodabandeh S, Wagner P, Chen C-Y, Balkus K J Jr, Zones S I, Davis M E. *J Am Chem Soc*, 1997, **119**: 8474
- 24 Wheatley P S, Love C J, Morrison J J, Shannonb I J, Morris R E. *J Mater Chem*, 2002, **12**: 477
- 25 Balkus Jr K J, Gabrielov A G, Shepelev S. *Microporous Mater*, 1995, **3**: 489
- 26 Garcia R, Shannon I J, Slawin A M Z, Zhou W, Cox P A, Wright P A. *Microporous Mesoporous Mater*, 2003, **58**: 91
- 27 Gray M J, Jasper J D, Wilkinson A P, Hanson J C. *Chem Mater*, 1997, **9**: 976
- 28 Stalder S M, Wilkinson A P, Hanson J C. *Chem Mater*, 1997, **9**: 2168
- 29 Wright P A, Maple M J, Slawin A M Z, Patinec V, Aitken R A, Welsh S, Cox P A. *J Chem Soc, Dalton Trans*, 2000: 1243
- 30 Garcia R, Philp E F, Slawin A M Z, Wright P A, Cox P A. *J Mater Chem*, 2001, **11**: 1421
- 31 Zhu Q, Kondo J N, Tatsumi T, Inagaki S, Ohnuma R, Kubota Y, Shimodaira Y, Kobayashi H, Domen K. *J Phys Chem C*, 2007, **111**: 5409
- 32 Zhu Q, Kondo J N, Ohnuma R, Kubota Y, Yamaguchi M, Tatsumi T. *Microporous Mesoporous Mater*, 2008, **112**: 153
- 33 Bleken F, Bjørgen M, Palumbo L, Bordiga S, Svelle S, Lillerud K-P, Olsbye U. *Top Catal*, 2009, **52**: 218
- 34 Baerlocher C, Meier W M, Olson D H. *Atlas of Zeolite Framework Types*. 6th Ed. Amsterdam: Elsevier, 2007. 96
- 35 Kwak J H, Tonkyn R G, Kim D H, Szanyi J, Peden C H F. *J Catal*, 2010, **275**: 187
- 36 Korhonen S T, Fickel D W, Lobo R F, Weckhuysen B M, Beale A M. *Chem Commun*, 2011, **47**: 800
- 37 Fickel D W, D'Addio E, Lauterbach J A, Lobo R F. *Appl Catal B*, 2011, **102**: 441
- 38 Fickel D W, Lobo R F. *J Phys Chem C*, 2010, **114**: 1633
- 39 Ren L, Zhu L, Yang C, Chen Y, Sun Q, Zhang H, Li C, Nawaz F, Meng X, Xiao F-Sh. *Chem Commun*, 2011, **47**: 9789
- 40 Hereijgers B P C, Bleken F, Nilsen M H, Svelle S, Lillerud K-P, Bjørgen M, Weckhuysen B M, Olsbye U. *J Catal*, 2009, **264**: 77
- 41 Treacy M M J, Higgins J B. *Collection of Simulated XRD Patterns for Zeolites*. 5th Ed. Amsterdam: Elsevier, 2007. 112
- 42 Delprato F, Delmotte L, Guth J L, Huve L. *Zeolites*, 1990, **10**: 546
- 43 Chanquía C M, Sapag K, Rodríguez-Castellón E, Herrero E R, Eimer G A. *J Phys Chem C*, 2010, **114**: 1481
- 44 Chen C-K, Chen Y-W, Lin C-H, Lin H-P, Lee C-F. *Chem Commun*, 2010, **46**: 282
- 45 Guo X, Han Y, Zou Y, Li D, Yu J, Qiu S, Xiao F-Sh. *Microporous Mesoporous Mater*, 2001, **42**: 325
- 46 Pellegrino C, Aiello R, Testa F, Crea F, Tuel A, Nagy J B. *Microporous Mesoporous Mater*, 2001, **47**: 85
- 47 Long R Q, Yang R T. *J Catal*, 2002, **207**: 274
- 48 刘福东, 单文坡, 石晓燕, 张长斌, 贺泓. 催化学报 (Liu F D, Shan W P, Shi X Y, Zhang Ch B, He H. *Chin J Catal*), 2011, **32**: 1113
- 49 林涛, 张秋林, 李伟, 龚茂初, 幸怡汛, 陈耀强. 物理化学学报 (Lin T, Zhang Q L, Li W, Gong M C, Xing Y X, Chen Y Q. *Acta Phys-Chim Sin*), 2008, **24**: 1127
- 50 刘致强, 唐磊, 常丽萍, 王建成, 鲍卫仁. 催化学报 (Liu Zh Q, Tang L, Chang L P, Wang J Ch, Bao W R. *Chin J Catal*), 2011, **32**: 546
- 51 Rodríguez-González R, Hermes F, Bertmer M, Rodríguez-Castellón E, Jiménez-López A, Simon U. *Appl Catal A*, 2007, **328**: 174
- 52 Long R Q, Yang R T. *Catal Lett*, 2001, **74**: 201
- 53 Kieger S, Delahay G, Coq B, Neveu B. *J Catal*, 1999, **183**: 267
- 54 Sultana A, Nanba T, Sasaki M, Haneda M, Suzuki K, Hamada H. *Catal Today*, 2011, **164**: 495

英 译 文

English Text

Zeolites, especially aluminosilicates, are probably the most important heterogeneous acid catalysts in industry due to their large surface area, high adsorption capacity, uniform and intricate channels, high thermal and hydrothermal stabilities, and well-defined micropores that give excellent shape selectivity in catalysis [1–4]. In the modern synthesis of zeolites, the organic template plays an important role. Novel templates are used to create zeolites with new topological structures [5–14]. For example, the ITQs zeolites prepared by Corma and coworkers [5–7] and the SSZs zeolites prepared by Zones and coworkers [8–11] typically involve a series of new organic templates. The organic template molecules have the following functions: directing the assembly pathway, filling the pore space, and balancing the charges of zeolite framework [4]. Amines and quaternary

ammonium molecules were the typical organic templates for synthesizing zeolite structures [2–4]. Recently, the types of molecular templates for synthesizing zeolites have been greatly expanded. For example, ionic liquids reported by Morris et al. [15–18] are both templates and solvents during the synthesis, long chain amphiphilic organosilane templates first reported by Ryoo's group [19,20] function as both micropore templates and useful directing agents for ordered mesoporous structures, phosphazene-based compounds reported by Corma et al. [21] are successful templates for the boggside structure with 10- and 12-ring intersecting channels, and the cobalt complex reported by Davis et al. [22,23] has been used to template a super-large microporous zeolite.

Metal complexes are widely used to direct the aluminophosphate framework of zeolites [24–30] such as the aluminophosphate frameworks of AFI, $\text{AlPO}_4\text{-16}$, and CHA [24–26]. Wilkinson and coworkers [27,28] have expanded this route to the synthesis of chiral gallophosphate structures. Wright et al. [29,30] have used nickel complexed within an azamacrocyclic as a structure directing agent to synthesize aluminophosphates of STA-6 and STA-7. However, it is difficult to synthesize aluminosilicate zeolites by using a metal complex as template with the exception of the successful synthesis of a 14-ring UTD-1 zeolite (DON structure) by a special cobalt compound of bis(pentamethylcyclopentadienyl)cobalt(III) hydroxide [22,23]. This may be attributed to the relatively low stability and weak solubility of metal complexes in the strong alkaline media used for synthesizing aluminosilicate zeolites, as compared with the metal complexes used for synthesizing aluminophosphate zeolites in near neutral media. Therefore, the synthesis of aluminosilicate zeolites templated from a metal complex still remains a challenge.

It has been reported that the high silica CHA-type aluminosilicate zeolite SSZ-13 with CHA cages connected by small 8-rings is highly active and selective for the methanol-to-olefin (MTO) reaction [31–33]. The higher silicon to aluminum ratio is benefit for thermal stability and hydrothermal stability, and the 8-ring channel endows the zeolite with a better selectivity than other zeolites [34]. Recently, the superior activity and selectivity of a copper ion-exchanged SSZ-13 zeolite in the selective catalytic reduction of NO_x with NH_3 ($\text{NH}_3\text{-SCR}$) was observed [35–38], but controlling the Cu loading in the SSZ-13 zeolite was not easy due to the small pore openings and limited ion exchanged capacity. It should be pointed out that the SSZ-13 zeolite was synthesized by using the template of *N,N,N*-trimethyl-1-1-adamantammonium hydroxide (TMAdaOH), which is very expensive [9,14]. This strongly limits the wide application of the SSZ-13 zeolite in industry. Therefore, it is highly desirable to synthesize this high silica CHA-type zeolite with a controllable metal loading using low cost templates.

Recently, we briefly reported the synthesis of a Cu-SSZ-13 zeolite (designated as Cu-ZJM-1) using a low cost copper complex (Cu^{2+} and tetraethylenepentamine, Cu-TEPA) as template [39]. Here, we give the details of the design, synthesis, and characterization of the Cu-ZJM-1 zeolite, which had a high and controllable copper content and high dispersion of the copper species and was a superior $\text{NH}_3\text{-SCR}$ reaction catalyst.

1 Experimental

1.1 Synthesis and treatment

1.1.1 Synthesis of Cu-ZJM-1 zeolite

Cu-ZJM-1 samples were synthesized from aluminosilicate gels with the molar ratio of $3.1\text{--}3.8\text{Na}_2\text{O}:1.0\text{Al}_2\text{O}_3:10\text{--}35\text{SiO}_2:200\text{H}_2\text{O}:2.0\text{--}3.0\text{Cu-TEPA}$. All chemicals were obtained from commercial suppliers and used without further purification. As a typical synthesis of Cu-ZJM-1-10, NaAlO_2 (0.514 g) and NaOH (0.380 g) were dissolved in water. Then, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (1.149 g) was added to this solution followed by the addition of TEPA (1.07 g). After 1 h stirring, silica sol (3.6 ml, 31.5 wt%) was added into the above gel dropwise with vigorous stirring. After stirring for 2–3 h, the final gel was transferred to a Teflon-lined stainless steel autoclave and heated at 140 °C for 3–6 d. The product was collected by filtration, washed with deionized H_2O , and dried at 100 °C for 12 h. The products obtained were designated as Cu-ZJM-1-*x*, where *x* presents the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the initial gels.

1.1.2 Treatment of Cu-ZJM-1 zeolite

The treatment of Cu-ZJM-1 was performed by ion exchange with NH_4NO_3 and calcination at 550 °C for 8 h. In a typical treatment, 1 g of Cu-ZJM-1 was ion exchanged with 100 ml of NH_4NO_3 solution (1 mol/L) at 80 °C for 12 h. After washing with deionized H_2O and drying at 100 °C for 12 h, the products obtained were calcined at 550 °C for 8 h in air. The final product was designated as Cal-Cu-ZJM-1.

1.1.3 Synthesis of conventional Cu-SSZ-13

A conventional Cu-SSZ-13 zeolite was obtained from the ion exchange of H-SSZ-13 (Si/Al molar ratio = 4.2) with $\text{Cu}(\text{NO}_3)_2$ solution and calcination at 550 °C for 8 h [35]. In a typical procedure, 1.5 g H-SSZ-13 was added into 100 ml 0.1 mol/L $\text{Cu}(\text{NO}_3)_2$ solution. After stirring for 24 h at room temperature, the product was filtered, washed with deionized water, and dried at 100 °C overnight. After repeating this process, the sample was calcined at 500 °C in air for 4 h. This

sample was designated as Con-Cu-SSZ-13.

1.2 Catalytic test

The NH_3 -SCR was performed in a flow reactor using gas mixtures containing 0.1% NO , 0.1% NH_3 , 10% O_2 , and 5% H_2O with a balance of Ar. The total flow rate was 44 ml/min and 200 mg catalyst powder samples were used. The temperature was varied from 108 to 550 °C in approximately 5 °C/min steps using a thermocouple in the catalyst powder bed. The catalysts were pre-calcined at 500 °C in air for 4 h before reaction.

1.3 Characterization

X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The step size was 0.02°, and the scanning speed was 3°/min. ^{29}Si MAS NMR spectra were recorded on a Varian Infinity Plus 400 spectrometer, and chemical shifts were referenced to tetramethylsilane (TMS). The Si/Al ratio and copper content were determined by inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). The sample morphology was observed with a field emission scanning electron microscope (SEM, JEOS JSM 6700F). The surface area and pore volume of the samples were measured by nitrogen adsorption-desorption isotherms at −196 °C using a Micromeritics ASAP 2020M system. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker 66V FTIR spectrometer. Thermogravimetry-differential thermal analysis (TG-DTA) was carried out on a NETZSCH STA 449C at a heating rate of 10 °C/min from room temperature to 1000 °C in air. Elemental analysis was performed on a Perkin-Elmer 2400 element analyzer. UV-Vis spectra were measured on a Perkin-Elmer Lambda 20 spectrophotometer. The temperature-programmed desorption of ammonia (NH_3 -TPD) experiments were performed using a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. H_2 -temperature-programmed reduction (H_2 -TPR) was performed on a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a TCD in 10% H_2 -90%He flow of 40 ml/min by heating the catalyst from 35 °C with a heating rate of 10 °C/min and holding it at the desired final temperature for 1 h.

1.4 Theoretical calculation

Density functional theory (DFT) with the B3LYP hybrid exchange-correlation functional was used to perform theoretical calculations. Geometry optimization was performed with the Gaussian 03 program. A DGDZVP basis set was

used. The equilibrium geometries in the gas phase and vibrational frequencies were calculated for all the systems. The solvation effect was investigated with the polarizable continuum model (PCM) solvent method implemented in the Gaussian 03 package.

2 Results and discussion

2.1 Design and synthesis of Cu-ZJM-1

2.1.1 Design of the template

From an analysis of the factors that are important in selecting an appropriate template (conformation, size, solubility, and charge) [4], we chose TEPA to coordinate with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to form a Cu-TEPA complex. The reasons were: (1) Cu-TEPA has a large $\lg K$ (23.1), which was higher than that (18.5) of $\text{Cu}(\text{OH})_4^{2-}$, and which suggested that Cu-TEPA would have good stability in a strongly alkaline media and the metal complexes would not be decomposed in the synthesis; (2) A positive charge on the copper complex would promote the interaction between the template with negatively charged silica species in the strongly alkaline media; (3) A size match between the copper complex and zeolite framework would play a critical role in the structure directing effect, and the theoretical calculations showed that there is a good match between the stable molecular configuration of Cu-TEPA (0.728 nm × 0.922 nm) and the CHA cages (0.73 nm × 1.20 nm), which are the building units of ZJM-1 zeolite [34,40].

2.1.2 Synthesis of Cu-ZJM-1 zeolites

By adjusting the chemical composition of the starting gels, Cu-ZJM-1 was successfully synthesized with various Si/Al ratios. The results are presented in Table 1. During the synthesis, the Cu-TEPA/ SiO_2 ratio was between 0.1–0.2. The adjusting of the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio was important: if the alkalinity was too high, zeolite P as an impurity would be produced, and on the other hand, very low alkalinity would lead to the formation of an amorphous aluminosilicate phase. In addition, the crystallization temperature was also an important factor in the crystallization of Cu-ZJM-1. At the low temperature of 100 °C, the FAU structure would be formed instead of the CHA structure. At the high temperature of 180 °C, zeolite P would appear. It was when the crystallization temperature was 140 °C that a pure phase of Cu-ZJM-1 zeolite (CHA structure) was obtained by crystallization for 3–6 d. Interestingly, the Si/Al ratios in Cu-ZJM-1 and required crystallization time increase with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in the initial gels. The results are presented in Table 1.

Figure 1 shows the XRD patterns of the as-synthesized

Cu-ZJM-1 and the ion exchanged and calcined Cal-Cu-ZJM-1 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in the starting gels. All the samples gave the typical peaks of the CHA zeolite structure [41], which also showed they had good crystallinity. Figure 2 shows the XRD patterns of various Cu-ZJM-1 samples from 20° to 26° , which clearly showed that the major peak shifted from 20.75° to 20.88° with the changing of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the initial gel from 10 to 35. This was because the cell parameter decreased with increasing Si/Al ratios and was in good agreement with the literature [42].

Figure 3 shows the ^{29}Si NMR spectra of various Cu-ZJM-1 samples, which can be used to get the Si/Al ratio in the zeolite framework [4]. With increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the initial gel, Q1 [Si(3Al), $\delta = -96.5$] and Q2 [Si(2Al), $\delta = -99.9$] species were decreased, and at the same time, Q3 [Si(1Al), $\delta = -104.93$] and Q4 [Si(0Al), $\delta = -110.8$] species were increased. This behavior was related to the increase of the Si/Al ratio in the zeolite framework. The values of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio estimated from the ^{29}Si NMR spectra are presented in Table 1. These were consistent with the values obtained from the ICP analysis.

Figure 4 shows SEM images of Cu-ZJM-1 samples with various Si/Al ratios. Clearly, the different samples had different morphologies. For example, Cu-ZJM-1-10 was composed of regular cubic crystals with sizes of about 300 nm, while the Cu-ZJM-1-25 sample was composed of flower-like morphologies with sizes of several micrometers. The SEM images also confirmed that the Cu-ZJM-1 samples have high crystallinity.

All the Cu-ZJM-1 samples were blue, which indicated that copper cations existed in the samples. The elemental analysis by ICP technique showed that the Cu loading in the Cu-ZJM-1 samples was as high as 9.5–10.2 wt% (Table 1), which was much higher than that (2.9 wt%) in Cu-SSZ-13 prepared by an aqueous Cu^{2+} ion exchange method [35–37]. Even a double ion exchange of Cu-ZJM-1-10 with NH_4NO_3 solution and calcination gave Cu-ZJM-1-10 with a Cu loading of 6.12 wt%. It is noteworthy that even with high Cu content, we did not find the CuO ($2\theta = 35.6^\circ$ and 38.8°) or Cu_2O ($2\theta = 36.44^\circ$) phases [43] in the Cu-ZJM-1 samples (Fig. 1), suggesting that the copper species were highly dispersed in the micropores of the Cu-ZJM-1 zeolites. Interestingly, the Cu loading in the Cu-ZJM-1 zeolites could be adjusted in the range of 0–10 wt% by ion exchange of the Cu-ZJM-1 zeolites with NH_4NO_3 solution. For example, after three times ion exchange with NH_4NO_3 solution and calcination, the Cu loading in Cu-ZJM-1-10 could be adjusted to 3.1 wt%. These results indicated that catalytically active components could be easily controlled in the synthesis of zeolites by the use of the templates of the metal complexes reported here.

It was observed that the direct route for introducing Cu^{2+} species into the zeolites used here greatly enhanced the efficiency of loading the copper species in the synthesis. For example, when Cu-TEPA was used as the template, 86% of the copper cations remained in the Cu-ZJM-1 product. In contrast, when the conventional ion exchange method was used to prepare Cu-SSZ-13 zeolite, the cations remaining in the final product was only 3.9% in the work of Kwak et al. [35–37]. When the equivalent volume impregnation method was used [44], these were present as a bulky CuO phase, which was not good for the NH_3 -SCR reaction.

2.2 Cu-TEPA template in Cu-ZJM-1 samples

Figure 5 shows the N_2 adsorption isotherms of the Cu-ZJM-1-10 and Cal-Cu-ZJM-1-10 samples. It should be noted that Cu-ZJM-1-10 showed no adsorption. After treatment with NH_4NO_3 solution and calcination, Cal-Cu-ZJM-1-10 exhibited the typical Langmuir-type adsorption, indicating the presence of uniform micropores. This sample had a BET surface area of $586 \text{ m}^2/\text{g}$, which was very close to that ($580 \text{ m}^2/\text{g}$) of a SSZ-13 zeolite. These results suggested that the micropores of the as-synthesized Cu-ZJM-1-10 were completely filled by Cu-TEPA, and after calcination, Cal-Cu-ZJM-1-10 had completely opened micropores. It is shown in Table 1 that all the Cu-ZJM-1 samples had a high surface area after their treatment, which supported the view that Cu-TEPA was a template for the formation of Cu-ZJM-1 zeolites.

It is known [45] that the pore size distribution in the zeolite can be obtained from the low pressure region of the isotherm. The adsorption isotherms of Cal-Cu-ZJM-1-10 and protonated SSZ-13 (H-SSZ-13) are compared using logarithmic x-axis in Fig. 6. The logarithmic form made their difference more obvious. The smaller micropore size distribution of Cal-Cu-ZJM-1-10 was shown by the occurrence of the inflection point of the curve at a lower $\log(p/p_0)$ as compared with H-SSZ-13. This can be interpreted as due to the loading of Cu atoms.

To get information on the chemical state of Cu-TEPA in Cu-ZJM-1, various techniques (FT-IR, TG-DTA, CHN analysis, UV-Vis spectroscopy) were used. Figure 7 shows the IR spectra of Cu-ZJM-1-25 and Cal-Cu-ZJM-1-25. Cu-ZJM-1-25 showed three bands at $2800\text{--}3000 \text{ cm}^{-1}$ and three bands at $3100\text{--}3400 \text{ cm}^{-1}$, which were assigned to the ethyl group and amine group, respectively. These organic groups are in TEPA. After treatment with NH_4NO_3 solution and calcination, all the bands associated with the organic species disappeared for Cal-Cu-ZJM-1-25.

The TG-DTA (Fig. 8) curves of Cu-ZJM-1-10 showed a mass loss of 15.19%. One main exothermic peak at 343°C was detected. These features were due to the decomposition

of the Cu-TEPA template. A slight increase in mass (about 1.5%) at 450–850 °C was found, which was due to the partial oxidation of the copper species. CHN analysis of the sample gave the result that the mass of the organic species was about 14.7%, and the C/N molar ratio of the template was 1.57, which was in good agreement with the nominal C/N ratio (1.6) of TEPA molecules. These results indicated that the Cu-TEPA complex was intact in the micropores of the Cu-ZJM-1 zeolites.

Figure 9 shows the UV-Vis spectrum of as-synthesized Cu-ZJM-1-10. For comparison, the spectrum of a Cu-TEPA complex solution was measured. Cu-ZJM-1-10 exhibited a strong band at 270 nm, which was almost the same as that (268 nm) of Cu-TEPA in the solution. These results suggested that the Cu-TEPA complex was retained inside the Cu-ZJM-1 zeolite. After NH_4^+ ion exchange and calcination, Cu-ZJM-1 showed one main peak at 225 nm, which was assigned to a highly dispersed Cu^{2+} species.

2.3 Structure directing effect of the Cu-TEPA complex

The above characterization showed clearly the state of the Cu-amine complex in the final products. In most samples, this was maintained intact inside the framework, where it would play a role as a structure directing agent.

To understand the role of Cu-TEPA in the synthesis of Cu-ZJM-1, a series of comparative experiments were performed. At first, when there was no Cu-TEPA complex in the synthesis, even when the alkalinity was changed in a wide range, we did not get any CHA-type ZJM-1 zeolite, as shown in Table 2 (Runs 1–4). These results indicated the structure directing role of the Cu-TEPA complex for synthesizing ZJM-1 zeolite.

It has been reported that TEPA is an effective template for synthesizing zeolites Nu-10 and ZSM-5 [46]. In our experiments, when TEPA was introduced in the absence of Cu^{2+} , we could not get the ZJM-1 zeolite (Table 2, Runs 5–8). TEPA is a linear molecule that has a length of 1.82 nm [46], which does not match the CHA cage (0.73 nm $\times$ 1.20 nm), which are the building units of Cu-ZJM-1 zeolites.

To confirm the specificity of TEPA, a smaller molecule of triethylenetetramine (TETA) with a similar long chain as TEPA was used to form Cu-TETA ($\lg K = 20.4$). This Cu-TETA complex did not direct any CHA structure in a wide composition range, as shown in Table 3. This can be explained by the non-match of the conformation of Cu-TETA with the CHA cages. These results confirmed that the Cu-TEPA complex is an effective and special structure directing agent for synthesizing CHA-type Cu-ZJM-1 zeolites.

2.4 Catalytic performance of Cu-ZJM-1

Recently, much attention has been paid to catalytic reactions for the abatement of environmentally harmful NO_x compounds (NO , NO_2 , and N_2O). Fe and Cu-containing zeolites were widely investigated because of their excellently catalytic activities [35–38, 47–50]. A superior activity and selectivity of a Cu ion-exchanged SSZ-13 zeolite in the NH_3 -SCR was observed, which were better than those of Cu-Beta and Cu-ZSM-5 zeolites, because of its appropriate pore size and high stability [35–38].

The acidic sites of zeolites are the sites for the adsorption and activation of the NH_3 reductant. Acidity is one of the most important parameters that determine the extent of NO_x reduction with ammonia over zeolite catalysts [51]. The NH_3 desorption temperature of NH_3 -TPD curves are useful for providing acidity information of the zeolites. Usually, an ammonia desorption peak below 250 °C is considered as due to weakly bonded ammonia and that above 250 °C is considered as due to strongly bonded ammonia from ammonia bonded to protons of the zeolite [51,52].

Figure 10(a) shows the NH_3 -TPD curves of Cal-Cu-ZJM-1-10 and Con-Cu-SSZ-13. The peak at 196 °C for the Cal-Cu-ZJM-1-10 sample was attributed to a weakly acidic site, and the peak centered at 348 °C was due to desorbed strongly bonded ammonia. Compared with H-SSZ-13, the peak areas of the strongly acidic sites were decreased. This is due to the partially replacement of Brønsted acid sites by Cu^{2+} [52]. Interestingly, two clear peaks at 530 °C and 625 °C were observed for Cal-Cu-ZJM-1-10. These two peaks were assigned to NH_3 interacting with copper species. A similar desorption peak was found with the Con-Cu-SSZ-13 sample at 498 °C. Compared with Con-Cu-SSZ-13, the Cal-Cu-ZJM-1-10 sample showed higher desorption temperatures, which suggested that the copper species in Cu-ZJM-1-10 were more stable. It was also worth mentioning that there was a clear desorption peak at 767 °C observed with the Con-Cu-SSZ-13 sample, which was attributed to zeolite framework collapse, while no such peak was found with the Cal-Cu-ZJM-1-10 sample. This indicated that with the same framework Si/Al ratio, the Cu-ZJM-1-10 sample had the better framework stability.

In the NH_3 -SCR reaction over metal-containing zeolites, the redox property of the metal species is another important factor that influenced NO_x conversion. In Cu-loaded zeolites, the redox property depends on the copper content, copper species distribution, and zeolite structure [53,54]. Figure 10(b) gives the H_2 -TPR profiles of the Cal-Cu-ZJM-1 and Con-Cu-SSZ-13 samples. For all the desorption peaks, the Cal-Cu-ZJM-1 sample has a significant larger area than the Con-Cu-SSZ-13 sample. This is in line with the much higher copper content of the Cal-Cu-ZJM-1 sample. The redox peaks were at 245 and 269 °C for Cal-Cu-ZJM-1 and Con-Cu-SSZ-13, respectively. Generally, the low tempera-

ture redox peak is attributed to the reduction of Cu^{2+} species to Cu^+ species. A lower temperature for this redox peak meant more active copper species and better NH_3 -SCR activity. Peaks 606 °C and 526 °C were the high temperature redox peaks for Cal-Cu-ZJM-1 and Con-Cu-SSZ-13, respectively. These were attributed to the reduction of Cu^+ species to Cu^0 species. It was reported that a higher temperature for this redox peak indicated a more stable state of the Cu^{2+} species, and this could be associated with a better high temperature NH_3 -SCR catalytic performance [54].

Figure 11 shows the NO_x conversion as a function of reaction temperature between 100 and 550 °C over the Cal-Cu-ZJM-1-10 and Con-Cu-SSZ-13 zeolites. Clearly, as compared with Con-Cu-SSZ-13, Cal-Cu-ZJM-1-10 gave the maximum conversion at a lower temperature, higher activity before 300 °C, and a longer life time. The superior activity was probably due to the high dispersion of Cu^{2+} species and high loading of Cu species in Cu-ZJM-1 zeolite (Fig. 9).

3 Conclusions

A low cost copper-amine complex (Cu-TEPA) was designed as a novel and efficient template for the one-pot synthesis of Cu-SSZ-13 zeolites (Cu-ZJM-1) with controllable Si/Al ratios. Cu-TEPA was a good template for the synthesis. It had the proper geometry and appropriate size to fit well in the CHA cages. Compared with the conventional ion exchange route, the products of the one-pot synthesis of the Cu-ZJM-1 zeolites had extremely high and controllable copper content and a high dispersion of the copper species. This provides a new route for synthesizing zeolites. The Cu-ZJM-1 zeolites exhibited superior catalytic performance in the NH_3 -SCR reaction, which is important for the abatement of environmentally harmful NO_x compounds.

Full-text paper available online at Elsevier ScienceDirect
<http://www.sciencedirect.com/science/journal/18722067>