第十一届内燃机可靠性技术国际研讨会
山东，济南，2023-02-19

新型铜基小孔分子筛用于NH_3-SCR反应耐久性研究

Durability studies of New-type Cu-based small-pore zeolites for NH_3-SCR reaction

单玉龙，单文坡，余运波，贺泓

Yulong Shan, Wenpo Shan, Yunbo Yu, Hong He

中国科学院生态环境研究中心

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences

志存高远 | 励精图治 | 开拓进取 | 务实创新

Email: ylshan@rcees.ac.cn

目 录 Contents

1. NH_3-SCR反应与Cu基小孔分子筛催化剂

NH_3-SCR and Cu-based small-pore zeolites

中国科学院 CHINESE ACADEMY OF SCIENCES

1.1 NH_3-SCR反应常用催化剂 / Common Catalysts for NH_3-SCR Reaction

➢ **Stationary SCR**

低温活性，抗毒性

Low-T activity, poison resistance

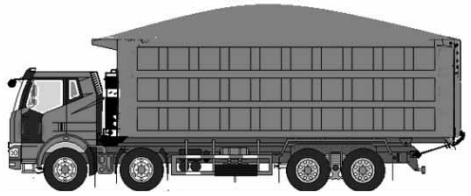
V-based Oxides	V_2O_5-$WO_3(MoO_3)/TiO_2$
Mn-based Oxides	MnO_x, Mn/TiO_2, $MnFeTiO_x$, Mn-Ce/TiO_2, Mn-Fe oxide, Mn-Ce oxide, Mn-W oxide
Carbon-supported Oxides	V_2O_5-Fe_2O_3/AC, Mn_2O_3/ACF, CuO/CNT, Fe_2O_3/ACF, V_2O_5/AC

Catal. Sci. Technol., 2015, 5, 4280; Appl. Catal. B, 2009, 93, 194; Catal. Commun., 2008, 9, 2217; Chem. Commun., 2003, 848; J. Catal., 2003, 217, 434; Catal. Sci. Technol., 2013, 3, 2699; Appl. Catal., B, 2010, 96, 157; Catal. Today, 2013, 201, 115; Ind. Eng. Chem. Res., 2016, 55, 2677

➢ **Mobile SCR:**

宽温度活性窗口，水热稳定性

Broad activity window, High HTS



V-based Oxides	V_2O_5/WO_3-TiO_2
V-free Oxides	$CeTiO_x$, $CeWTiO_x$, $CeWO_x$, $FeTiO_x$, WO_3/CeO_2-ZrO_2, Nb-Ce oxide
Zeolite Catalysts	**Fe-ZSM-5, Cu-ZSM-5, Fe-Beta, Cu-SSZ-13, Cu-SAPO-34**

Chem. Commun., 2014, 50, 8445; Chin. J. Catal., 2014, 35, 1251; Chin. J. Catal., 35, 1438; Chem. Commun., 2008, 1470; Catal. Commun., 2010, 11, 465; J. Am. Chem. Soc., 1999, 121, 5595; J. Catal., 2012, 287, 203; Chem. Commun., 2011, 47, 9789; Environ. Sci. Technol., 2014, 48, 566

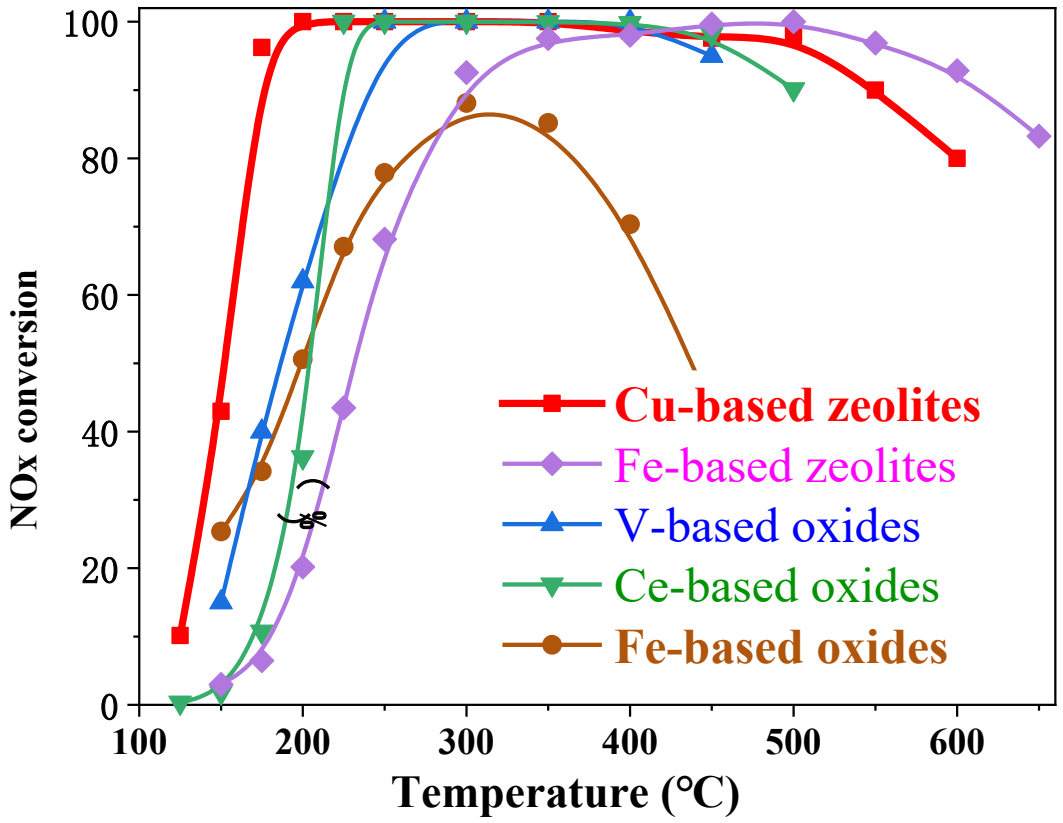
1. NH_3-SCR反应与Cu基小孔分子筛催化剂

NH_3-SCR and Cu-based small-pore zeolites

1.1 NH_3-SCR反应常用催化剂 / Common Catalysts for NH_3-SCR Reaction

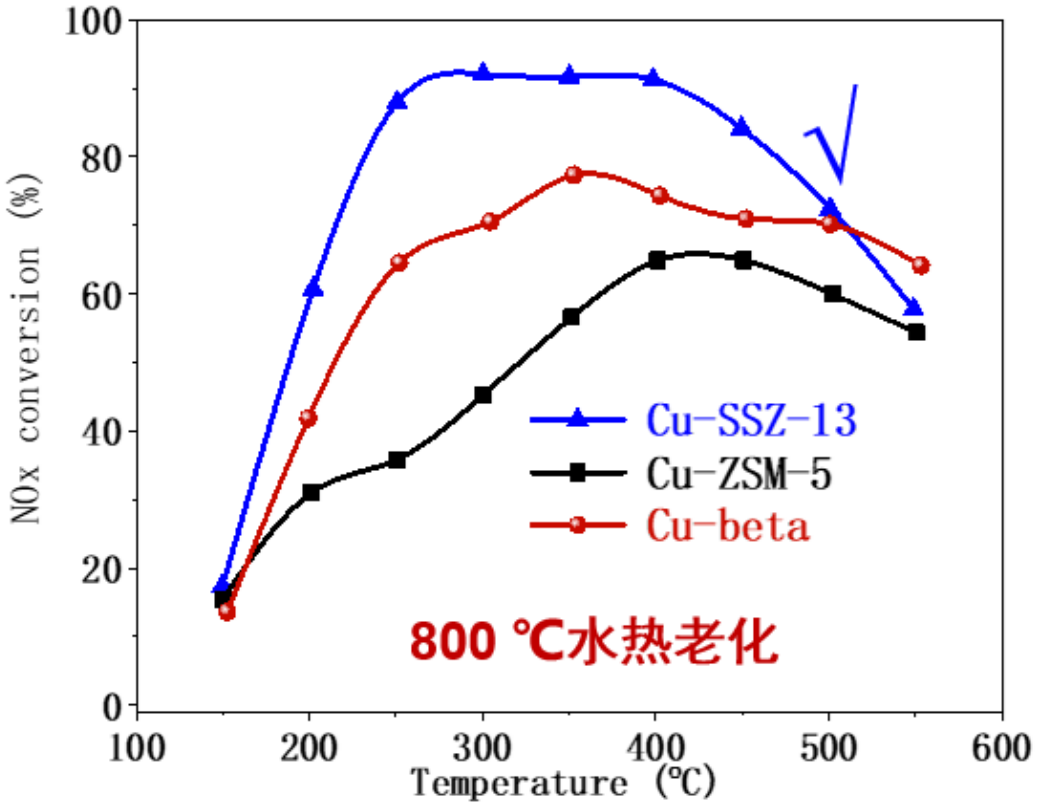
典型NH_3-SCR催化剂性能

NH_3-SCR activity of typical catalysts



Cu基分子筛水热稳定性

Hydrothermal stability (HTS) Cu-based zeolite



1.2 NH_3-SCR催化剂设计原则 / Design Principles of NH_3-SCR Catalysts

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$

科学原理:

NH_3-SCR反应需要**氧化还原位点**、**酸性位点**共同参与

The **redox sites** and **acid sites** must work together in NH_3-SCR

设计原则:

同种功能位点的**高度分散**

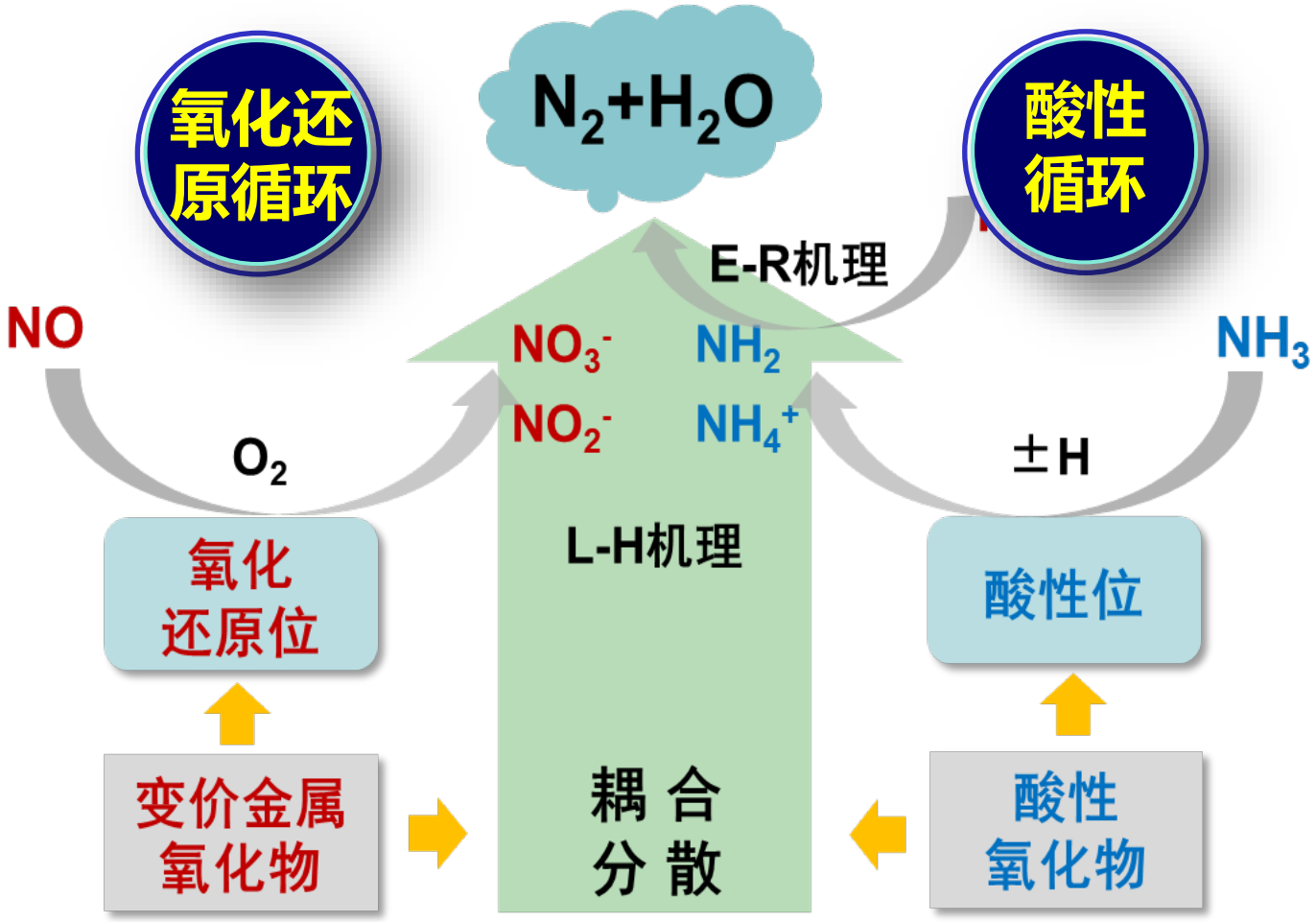
High dispersion of active sites

不同功能位点的**紧密耦合**

Tight coupling of redox-acid sites

所有功能位点的**充分暴露**

Adequate exposure of active sites

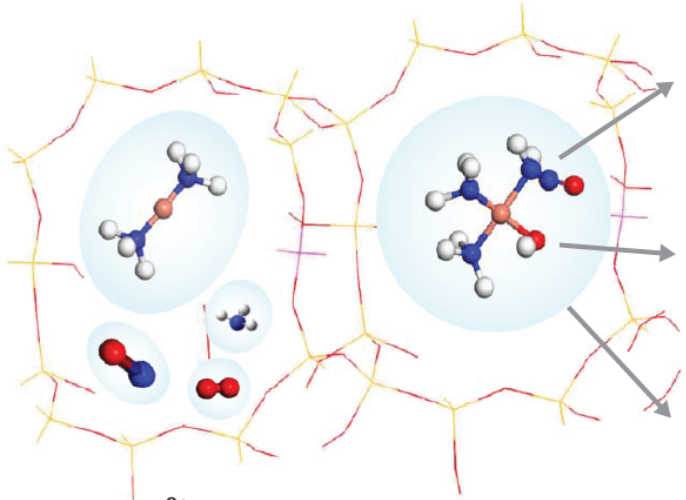


1. NH_3-SCR反应与Cu基小孔分子筛催化剂

NH_3-SCR and Cu-based small-pore zeolites

中国科学院 CHINESE ACADEMY OF SCIENCES

1.3 Cu基小孔分子筛的构效关系与设计/ Structure-activity and Design of Cu-based small-pore zeolites

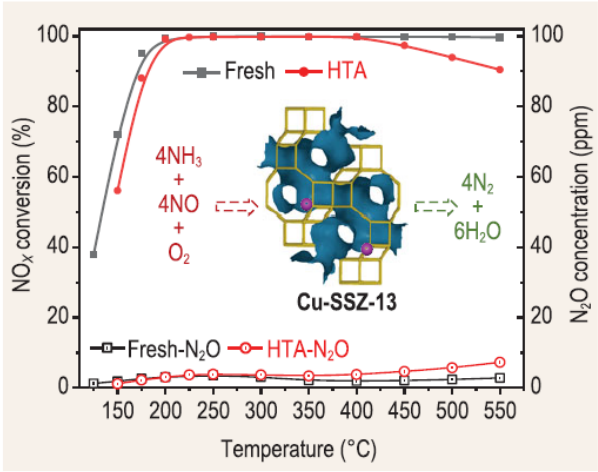


Cu^{2+}-exchanged zeolites

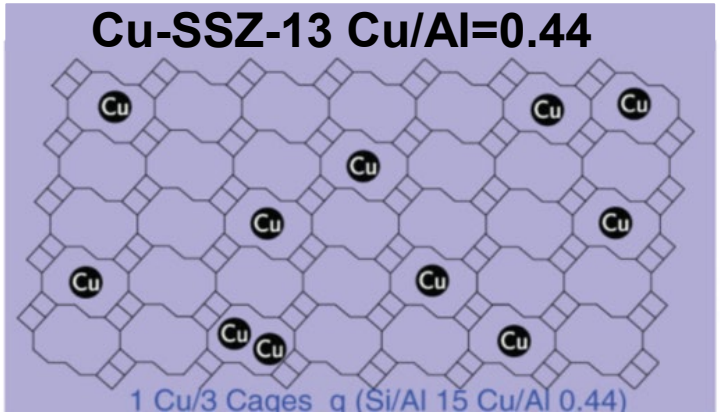
Dual-functional site of Cu^{2+} → Tight coupling of redox-acid sites

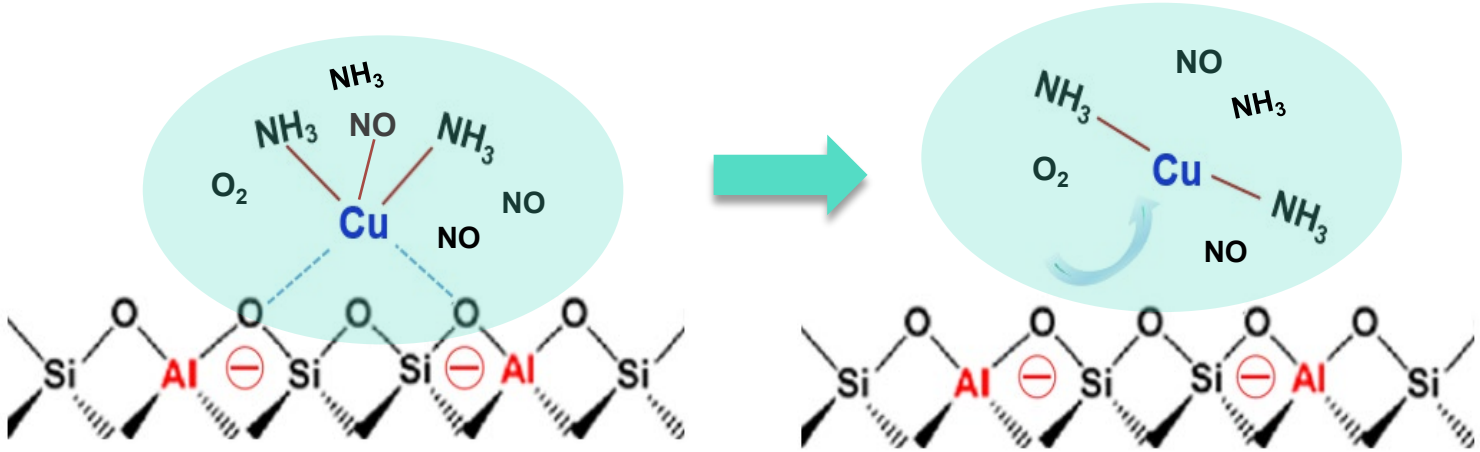
Atomic-level dispersion → High dispersion of active sites

Locally homogeneous reaction → Adequate exposure of active sites



Efficient SCR catalyst





Yulong Shan et al., Natil. Sci. Rev., 2021, 8, nwab010.

1. NH_3-SCR反应与Cu基小孔分子筛催化剂

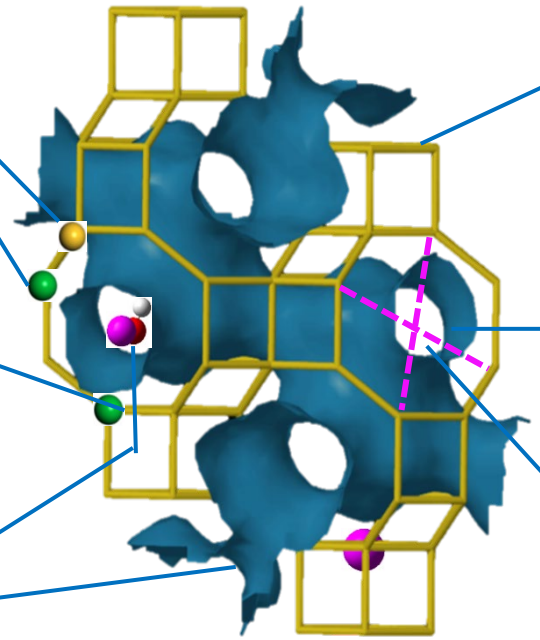
NH_3-SCR and Cu-based small-pore zeolites

1.3 Cu基小孔分子筛的构效关系与设计/ Structure-activity and Design of Cu-based small-pore zeolites

Cu-SSZ-13

组 成 Composition

- **Si/Al**
  - Si：骨架结构稳定性
  - Si：framework stability
  - Al：酸性位和离子交换位
  - Al：acid and ion-exchange sites
- **Al分布 Distribution**
  - 影响Cu物种分布及状态
  - Cu distribution and state
  - 酸性位分布 骨架Al稳定性
  - Acid distribution FAl stability
- **Cu物种 Cu species**
  - NH_3-SCR活性
  - NH3-SCR performance
  - 水热稳定性，抗硫性等
  - H_2O and SO_2 resistance



结构 Structure

- **结晶度 Crystallinity**
  - 骨架结构稳定性
  - Framework stability
  - 利于反应物扩散
  - Reaction diffusion
- **CHA笼 CHA cavity**
  - NH_3-SCR反应场所
  - Reaction zone for NH_3-SCR
  - 提供大量功能位点
  - Offering functional sites
- **孔径 Pore diameter**
  - 择形性, 抗毒(SO_2、HCs)
  - Shape selectivity Poison resistance
  - 选择性通过NH_3-SCR反应物
  - NH_3-SCR molecules selectivity

Yulong Shan et al., Natil. Sci. Rev., 2021, 8, nwab010.

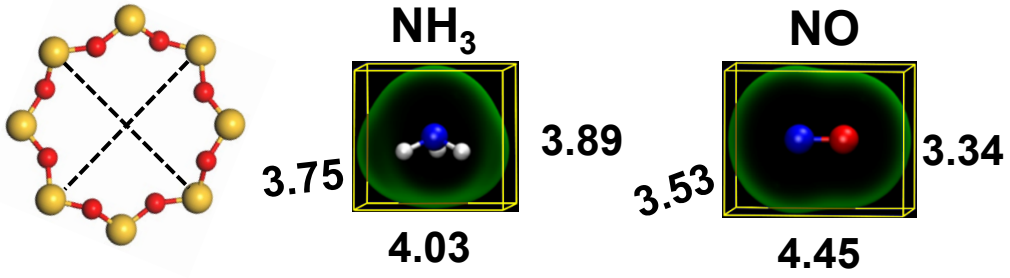
1. NH_3-SCR反应与Cu基小孔分子筛催化剂

NH_3-SCR and Cu-based small-pore zeolites

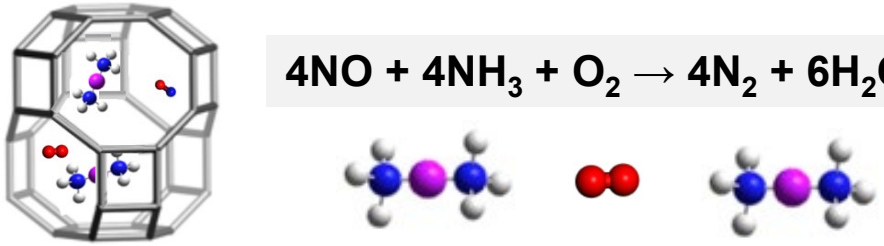
中国科学院 CHINESE ACADEMY OF SCIENCES

1.3 Cu基小孔分子筛的构效关系与设计/ Structure-activity and Design of Cu-based small-pore zeolites

➢ 8元环孔道 / 8MR channel：~4×4 Å



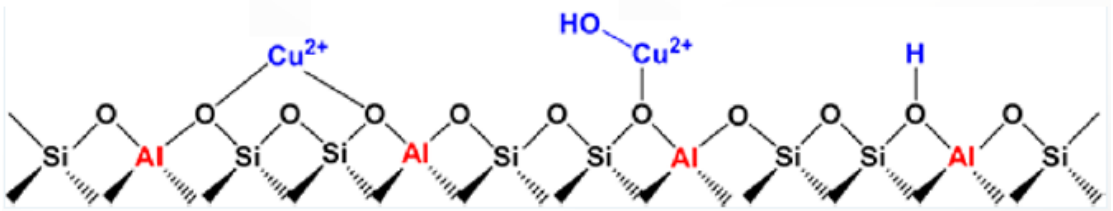
➢ 反应场所：笼状结构 / Reaction zone: Cavity



$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

➢ 元素组成：离子交换和酸性位

➢ Elemental composition: ion-exchange and acid sites



ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS	AFT	AFV	AFX
AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS	ATT	ATV	AVE	AVL	AWO
AWW	BCT	BEC	BIK	BOF	BOG	BOZ	BPH	BRE	BSV	CAN	CAS	CDO	CFI	CGF
CGS	CHA	-CHI	-CLO	CON	CSV	CZP	DAC	DDR	DFO	DFT	DOH	DON	EAB	EDI
EEI	EMT	EON	EPI	ERI	ESV	ETL	ETR	EUO	EWS	EZT	FAR	FAU	FER	FRA
GIS	GIU	GME	GON	GOO	HEU	IFO	IFR	-IFT	-IFU	IFW	IFY	IHW	IMF	IRN
IRR	-IRY	ISV	ITE	ITG	ITH	ITR	ITT	-ITV	ITW	IWR	IWS	IWV	IWW	JBW
JNT	JOZ	JRY	JSN	JSR	JST	JSW	KFI	LAU	LEV	LIO	-LIT	LOS	LOV	LTA
LTF	LTJ	LTL	LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI	MFS	MON	MOR	MOZ
MRT	MSE	MSO	MTF	MTN	MTT	MTW	MVY	MWF	MWW	NAB	NAT	NES	NON	NPO
NPT	NSI	OBW	OFF	OKO	OSI	OSO	OWE	-PAR	PAU	PCR	PHI	PON	POR	POS
PSI	PUN	PWN	PWO	PWW	RHO	-RON	RRO	RSN	RTE	RTH	RUT	RWR	RWY	SAF
SAO	SAS	SAT	SAV	SBE	SBN	SBS	SBT	SEW	SFE	SFF	SFG	SFH	SFN	SFO
SFS	SFW	SGT	SIV	SOD	SOF	SOR	SOS	SOV	SSF	SSY	STF	STI	STT	STW
-SVR	SVV	SWY	SZR	TER	THO	TOL	TON	TSC	TUN	UEI	UFI	UOS	UOV	UOZ
USI	UTL	UWY	VET	VFI	VNI	VSV	WEI	-WEN	YFI	YUG	ZON			

Moliner and Corma et al., Appl. Catal. B, 2017, 217, 125;

Corma et al. Chem. Commun., 2012, 48, 826;

Wang et al., Micropor. Mesopor. Mater., 2014, 183, 185;

Li et al., Chem. Eng. J., 2018, 348, 608;

He et al., Catal. Sci. Technol., 2019, 9, 106;

Kim et al., ACS Catal., 2017, 7, 6070;

Hong et al., Angew. Chem. Int. Ed., 2017, 56, 1;

Hong et al. ACS Catal., 2016, 6, 2443;

Wang et al., Ind. Eng. Chem. Res., 2018, 57, 16763;

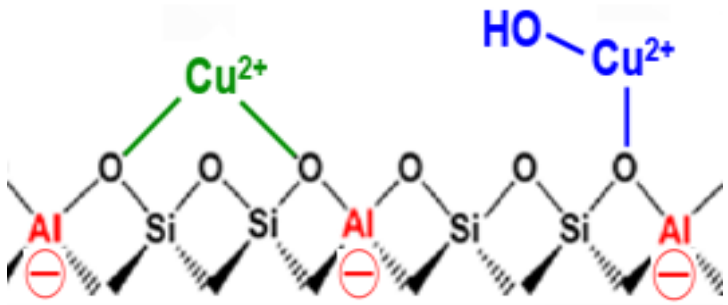
Can et al., Catal. 2018, 8, 3.

目 录 Contents

2. 铜基小孔分子筛用于NH_3-SCR

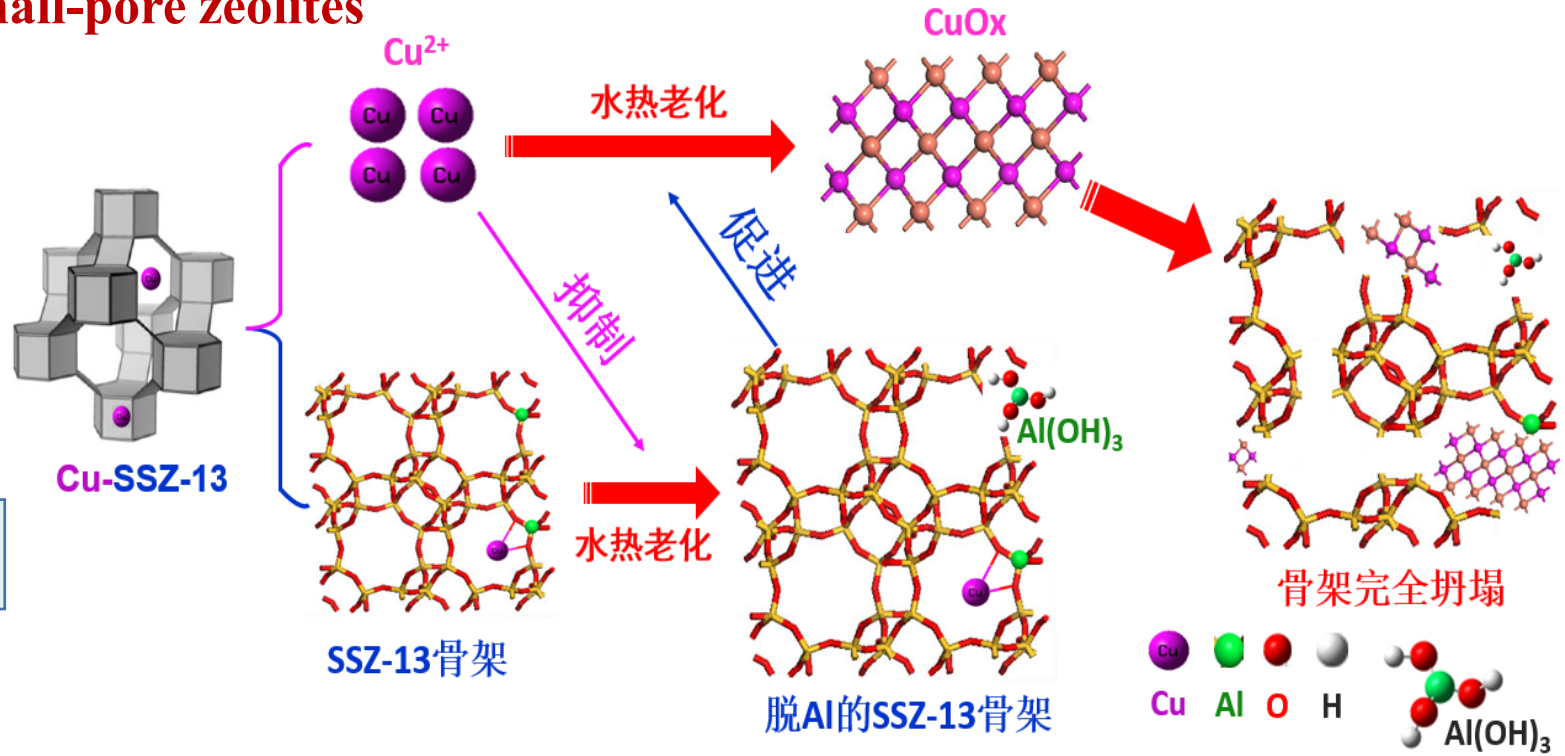
Cu-based small-pore zeolites for NH_3-SCR

2.1 Cu-CHA 小孔分子筛/ Cu-CHA small-pore zeolites



基于Cu-Al之间强烈的电荷相互作用

Yulong Shan et al., Appl. Catal. B, 2020, 264, 118511



- **水热脱铝：H_2O攻击分子筛Al位，形成$Al(OH)_3$，脱离骨架位，造成骨架破坏和酸性位丧失；**
- **Hydrothermal dealuminization:** H_2O attacks the Al site of the molecular sieve, forming Al(OH)3, which breaks away from the skeleton site, resulting in skeleton destruction and loss of acid site;
- **CuOx积聚：活性Cu^{2+}物种积聚，形成CuOx颗粒，造成活性位丧失并破坏八元环结构；**
- **CuOx accumulation:** The accumulation of active Cu^{2+} species, forming CuOx particles, resulting in loss of active site and destruction of eight-membered ring structure;

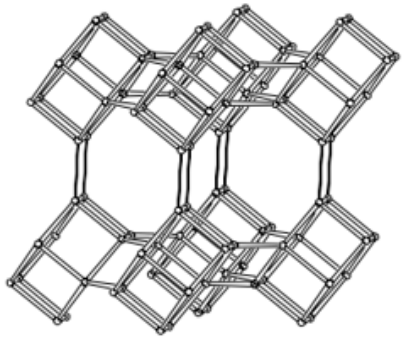
2. 铜基小孔分子筛用于NH_3-SCR

Cu-based small-pore zeolites for NH_3-SCR

2.2 Cu-AEI 小孔分子筛/ Cu-AEI small-pore zeolites

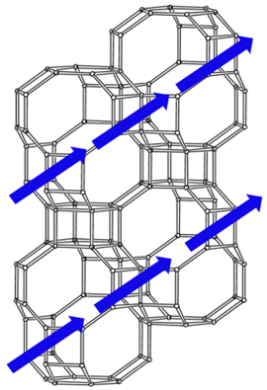
SSZ-13 zeolite

CHA structure

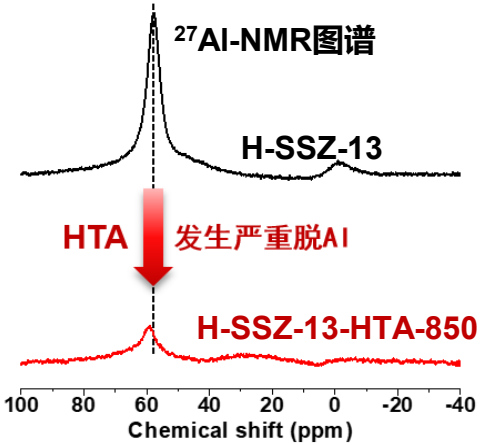


双六元环 平行分布

D6R: Parallel distribution

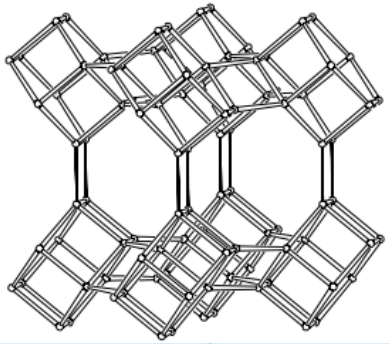


贯通的孔道结构 / well-connected pore channel



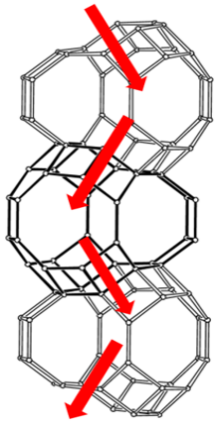
SSZ-39 zeolite

AEI structure

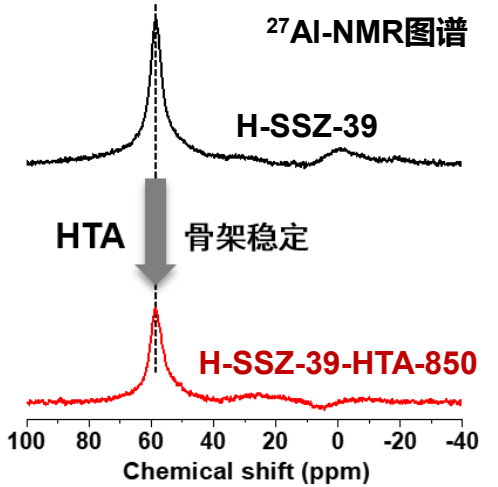


双六元环 对称分布

D6R: Symmetric distribution



弯曲的孔道结构 / tortuous pore channel



Yulong Shan et al., Appl. Catal. B, 2020, 264, 118511

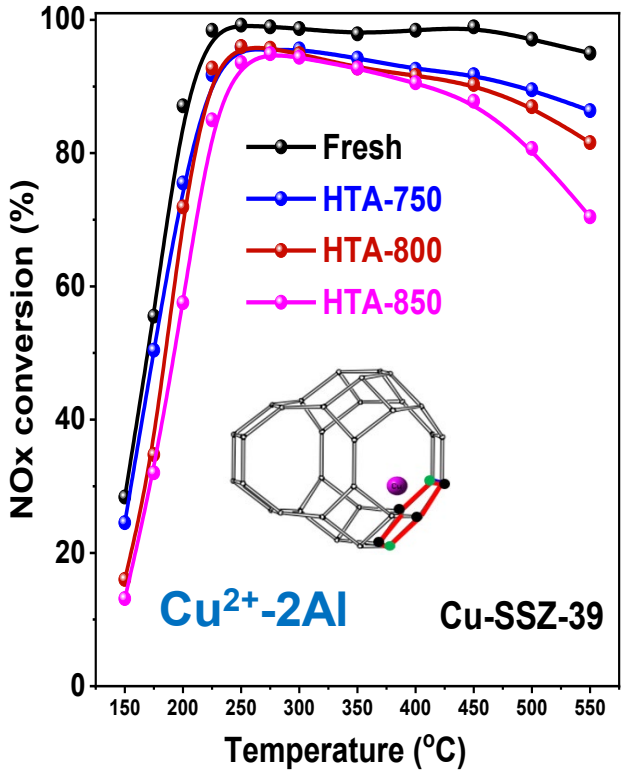
- SSZ-39（AEI）结构具有更弯曲的孔道结构，在水热老化过程中，结构不易损坏；
- SSZ-39 (AEI) structure has an excellent hydrothermal stability due to tortuous pore structure

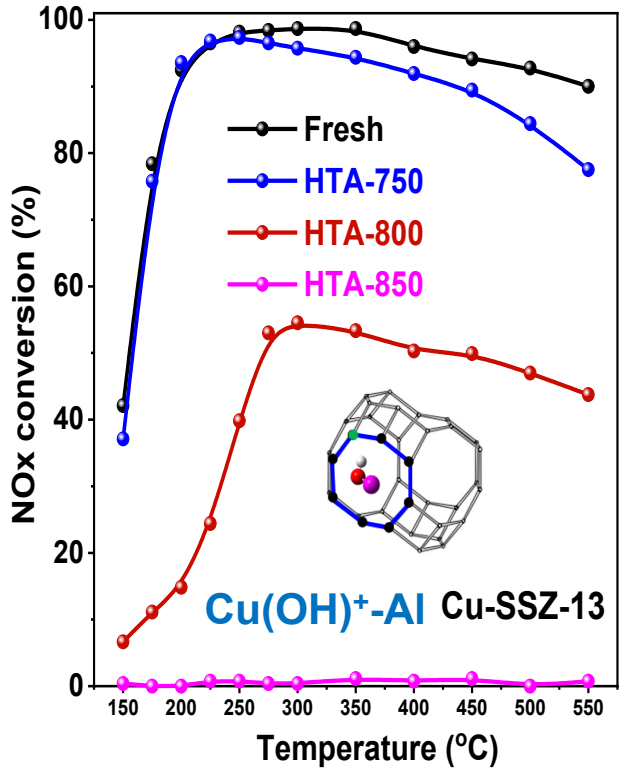
2. 铜基小孔分子筛用于NH_3-SCR

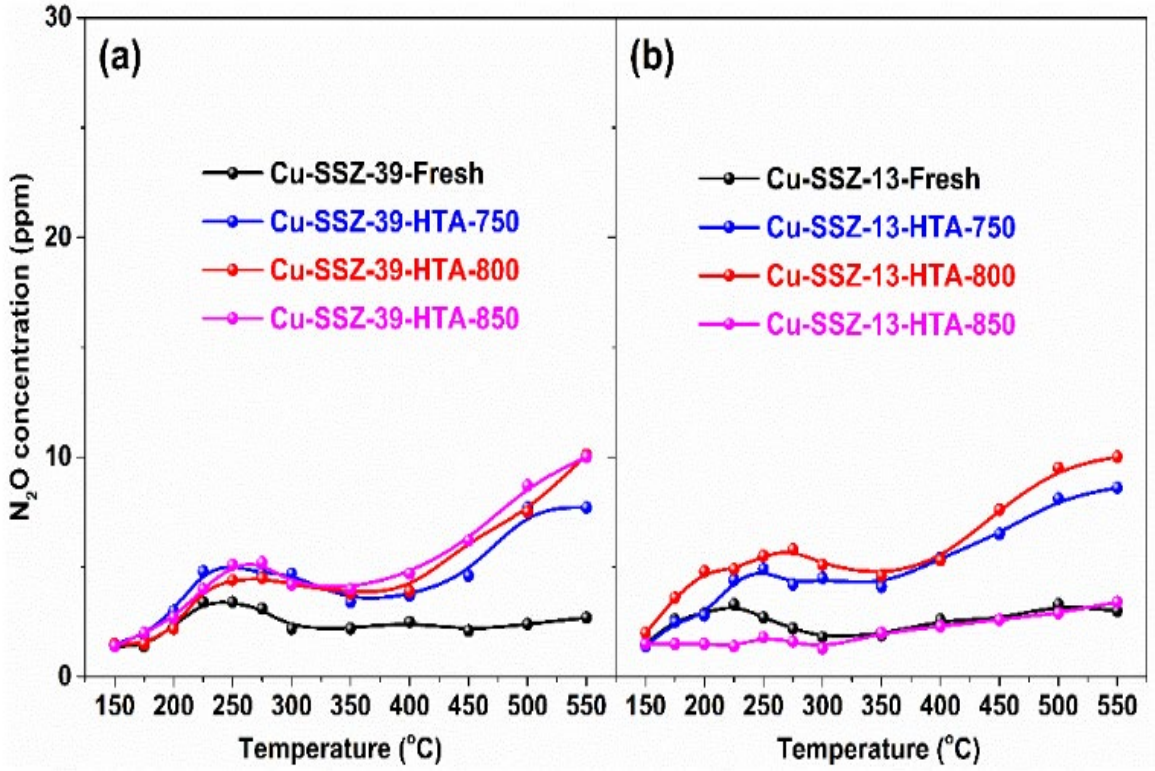
Cu-based small-pore zeolites for NH_3-SCR

中国科学院 CHINESE ACADEMY OF SCIENCES

2.2 Cu-AEI 小孔分子筛/ Cu-AEI small-pore zeolites







- Cu-SSZ-39具有较Cu-SSZ-13更优异的高温NH_3-SCR活性、水热稳定性和较低的N_2O生成。
- Cu-SSZ-39 possess superior high-temperature NH_3-SCR activity and hydrothermal stability to Cu-SSZ-13.

2. 铜基小孔分子筛用于NH_3-SCR

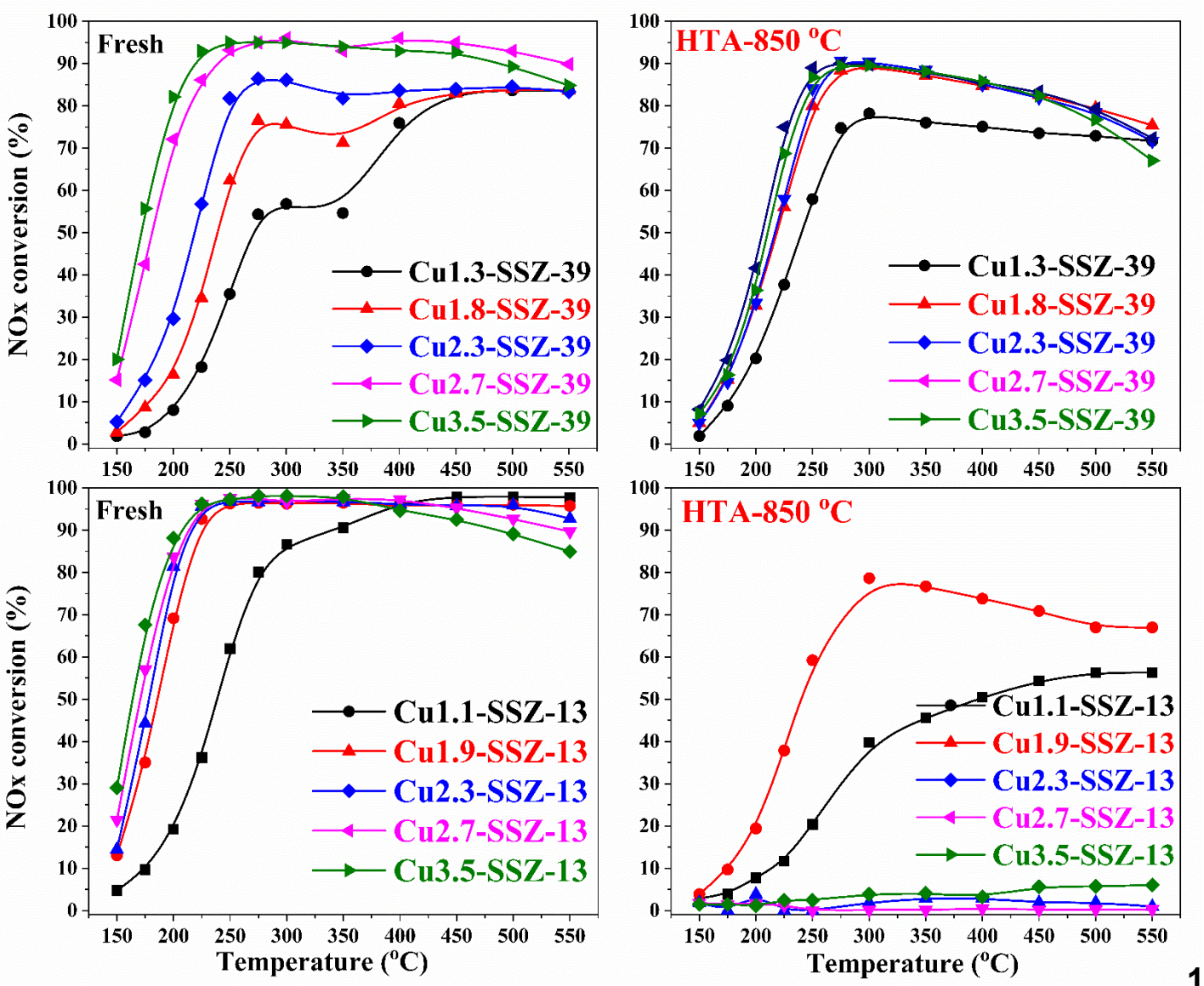
Cu-based small-pore zeolites for NH_3-SCR

中国科学院 CHINESE ACADEMY OF SCIENCES

2.2 Cu-AEI 小孔分子筛/ Cu-AEI small-pore zeolites

- 具有不同Cu含量梯度的Cu-SSZ-39都具有较Cu-SSZ-13更优异的水热稳定性。
- Cu-SSZ-39 with various Cu loadings showed higher hydrothermal stability than Cu-SSZ-13 with the same Cu loadings.

- 中低Cu含量的Cu-SSZ-39在水热老化后，其NH_3-SCR活性有一定程度的提升。
- The deNOx efficiency of Cu-SSZ-39 with medium and low Cu loadings increase after hydrothermal stability.



2. 铜基小孔分子筛用于NH_3-SCR

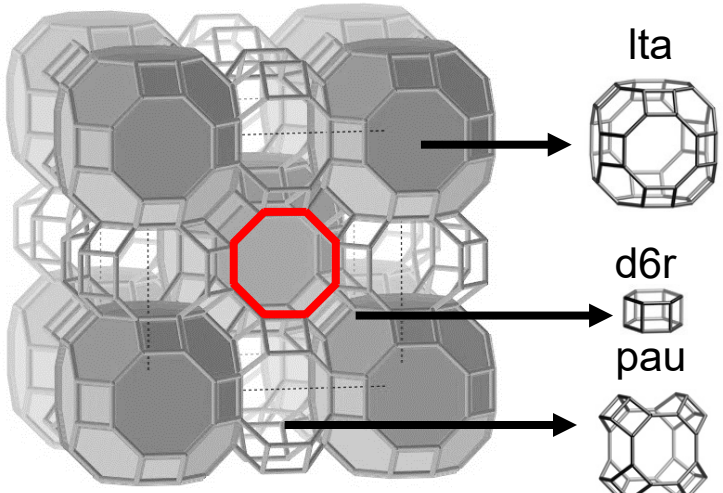
Cu-based small-pore zeolites for NH_3-SCR

中国科学院 CHINESE ACADEMY OF SCIENCES

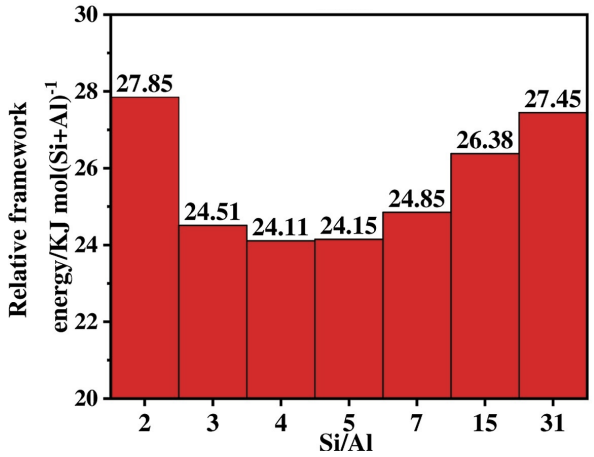
2.3 Cu-KFI 小孔分子筛/ Cu-KFI small-pore zeolites

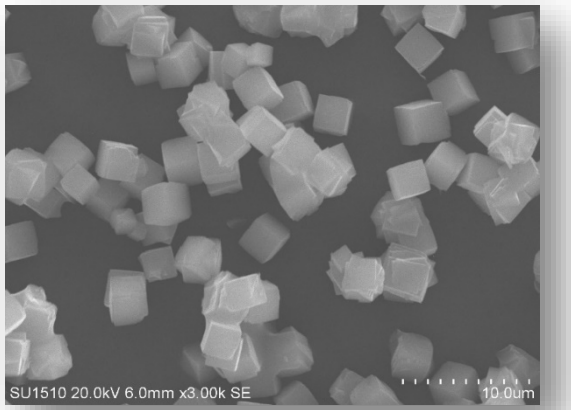
KFI zeolite：

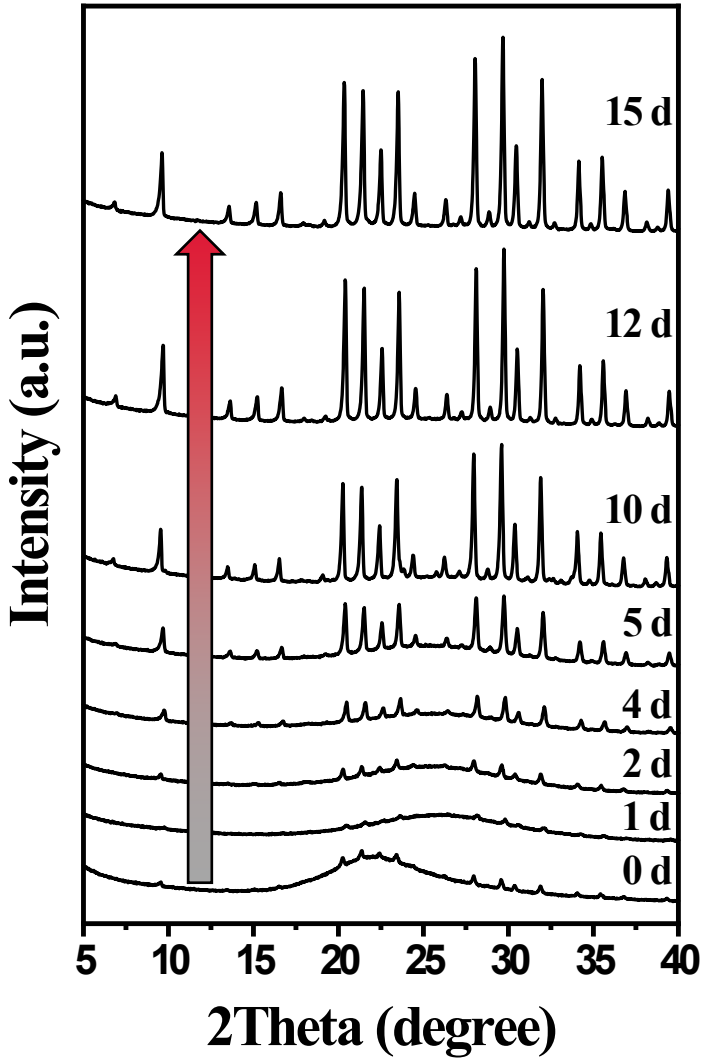
- 三维孔道结构
- Three-dimensional pore channel
- 由无模板剂法得到富铝型KFI分子筛
- Al-rich KFI zeolite was obtained by OSDAs-free method



0.39 × 0.39 nm





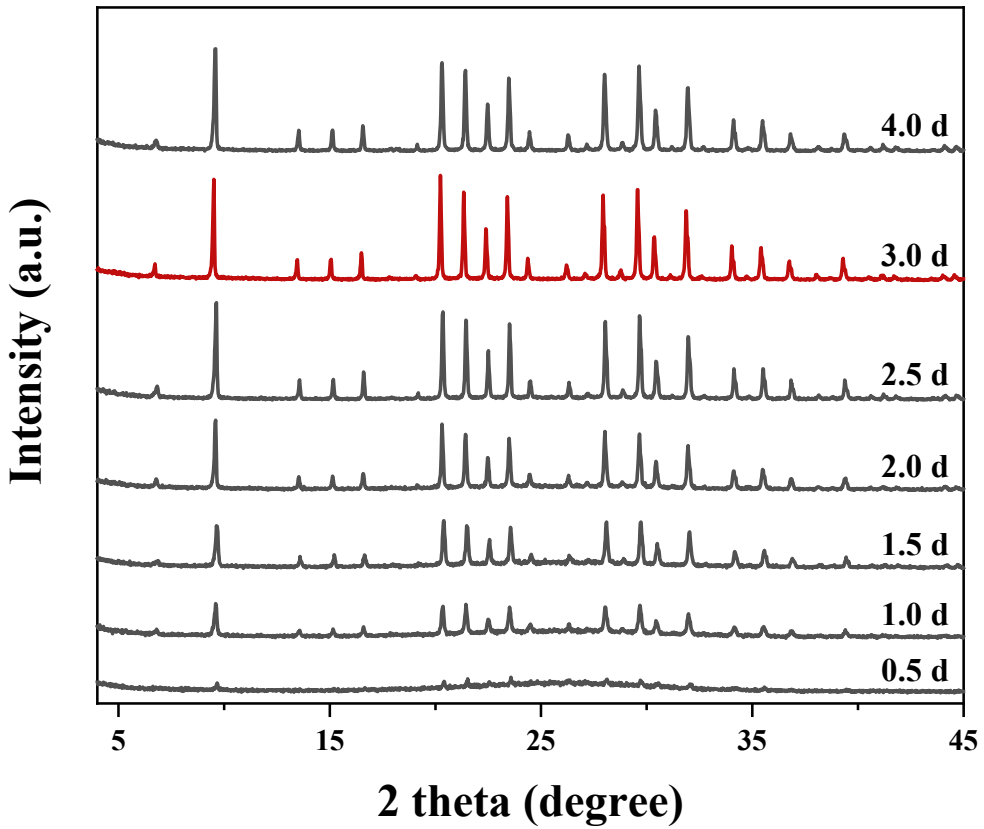


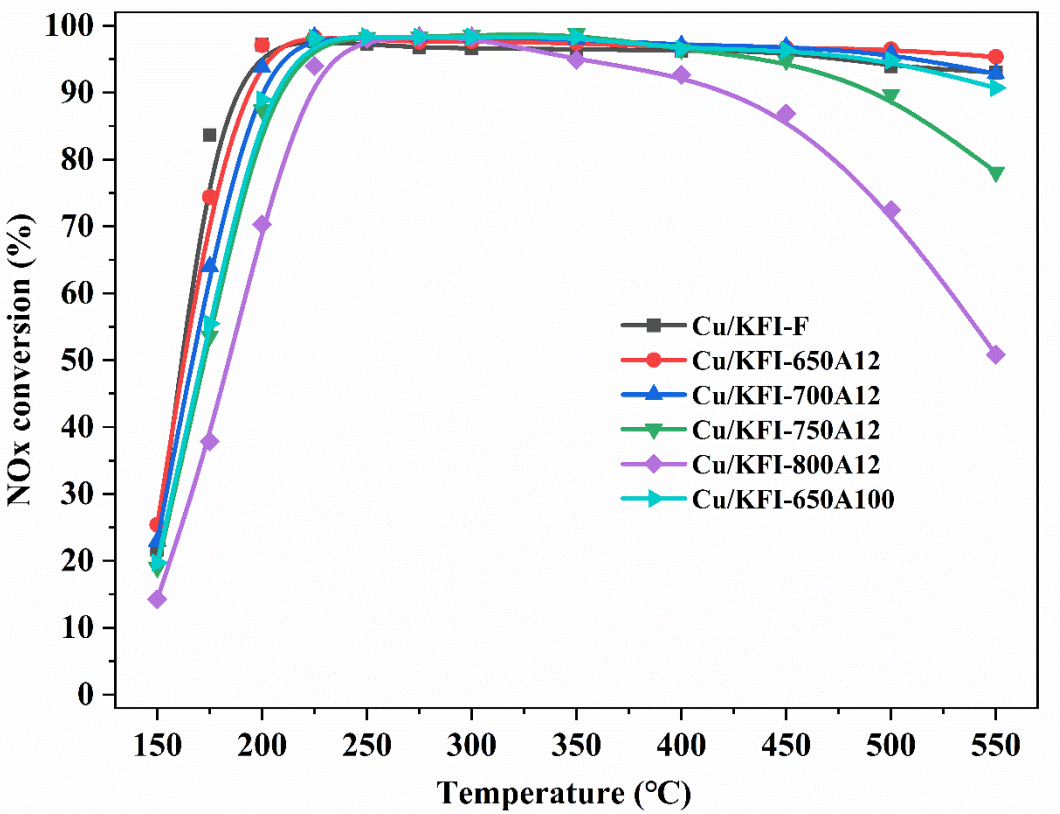
2. 铜基小孔分子筛用于NH_3-SCR

Cu-based small-pore zeolites for NH_3-SCR

中国科学院 CHINESE ACADEMY OF SCIENCES

2.3 Cu-KFI 小孔分子筛/ Cu-KFI small-pore zeolites





- 快速合成的Cu-KFI具有较好的水热稳定性和优异的NH_3-SCR活性。
- The rapid synthesized Cu-KFI exhibits good hydrothermal stability and excellent NH_3-SCR activity.

2. 铜基小孔分子筛用于NH_3-SCR

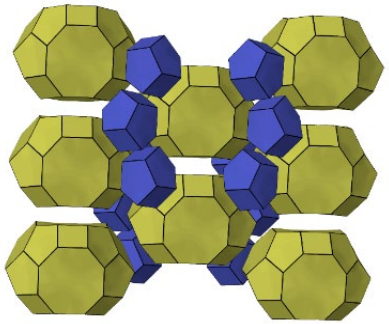
Cu-based small-pore zeolites for NH_3-SCR

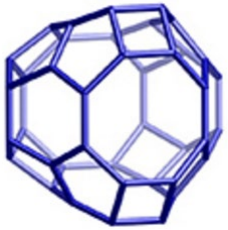
中国科学院 CHINESE ACADEMY OF SCIENCES

2.4 Cu-SSZ-50 (RTH构型) 小孔分子筛/ Cu-RTH small-pore zeolites

RTH zeolite:

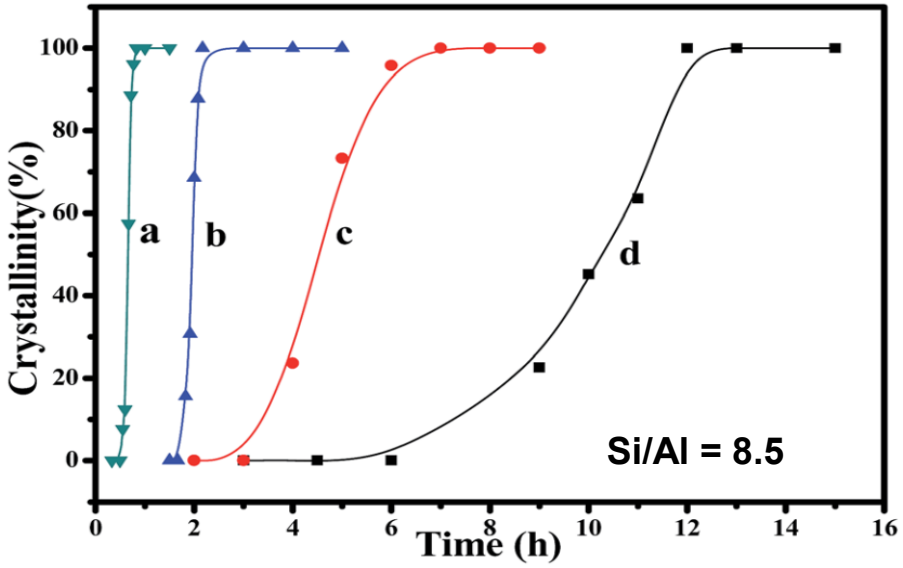
- 二维孔道结构 / 2-dimensional structure
- 包含两种8MR / Containing two types of 8MR
- 快速合成 / Efficient synthesis



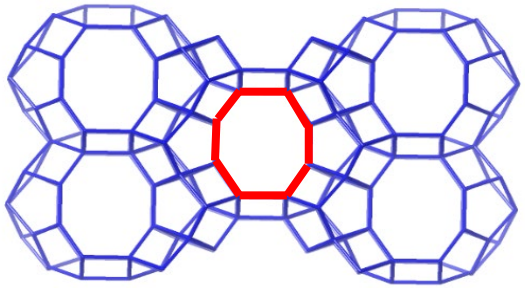


ite ($4^6 \cdot 5^8 \cdot 6^4 \cdot 8^4$)

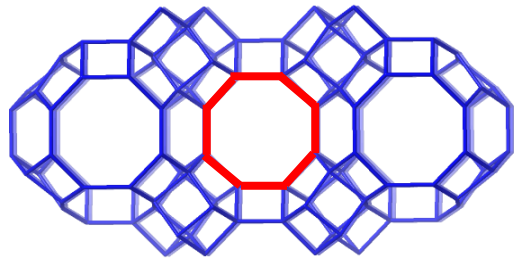
rth ($4^4 \cdot 5^4$)



Xu et al., J. Mater. Chem. A. 2018, 6, 8705-8711



0.56 × 0.25 nm



0.56 × 0.56 nm

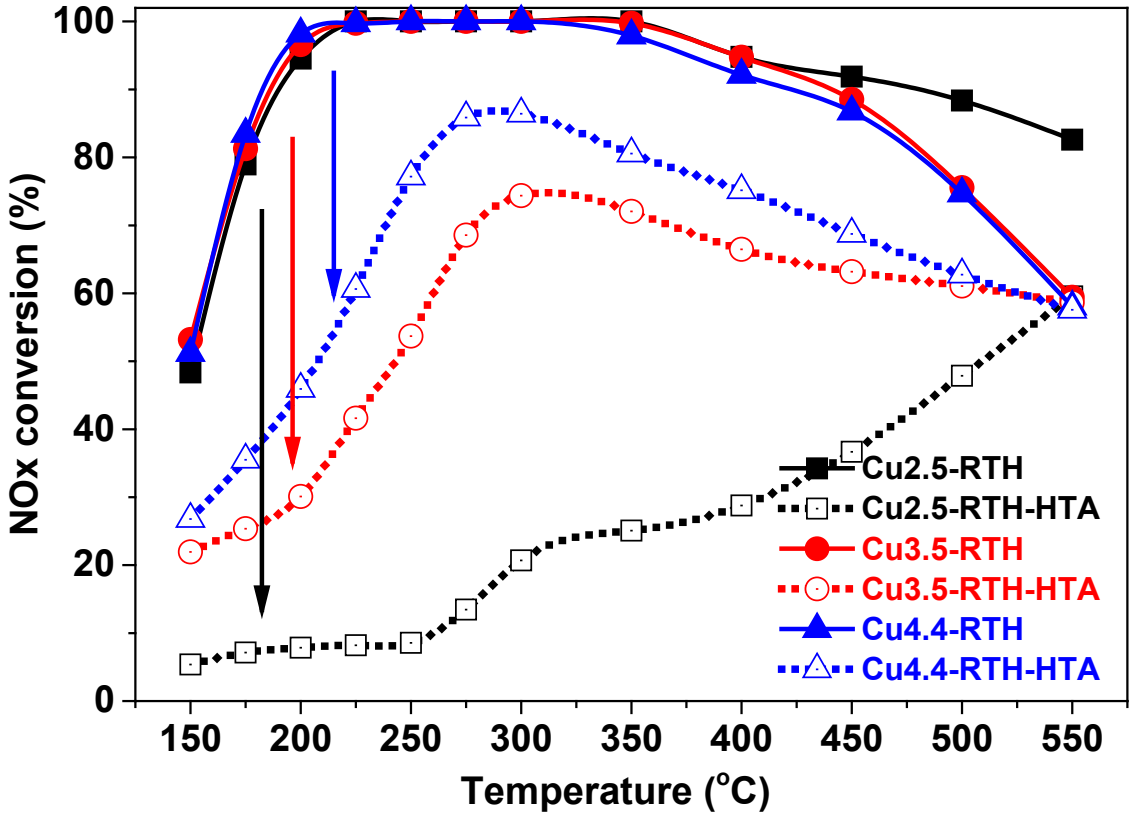
IZA: Data base of Zeolite structures, Http://www.Iza-Structure.Org/

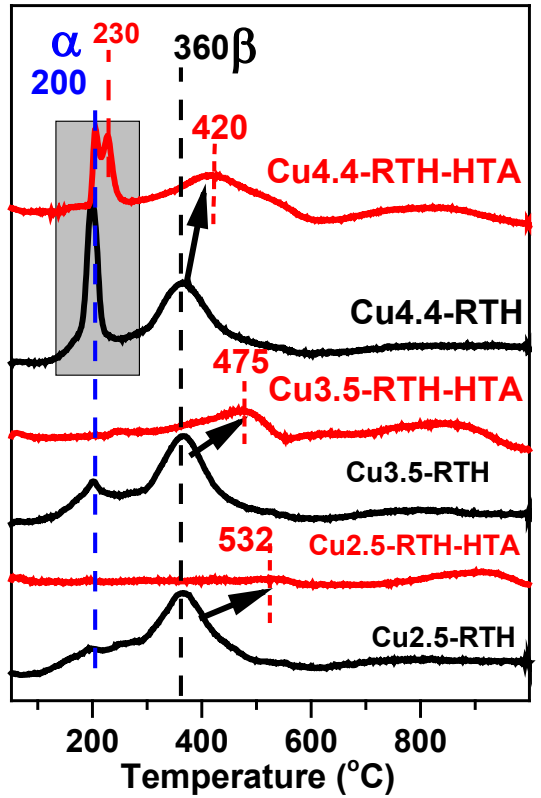
2. 铜基小孔分子筛用于NH_3-SCR

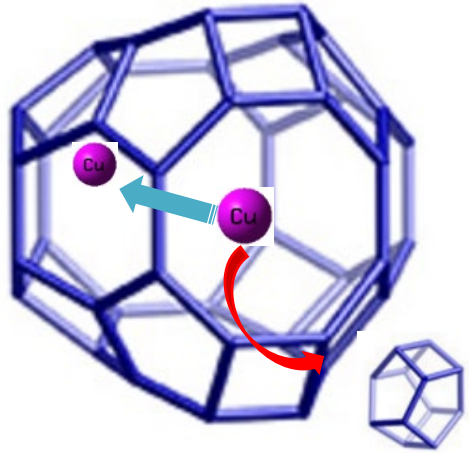
Cu-based small-pore zeolites for NH_3-SCR

中国科学院 CHINESE ACADEMY OF SCIENCES

2.4 Cu-SSZ-50 (RTH构型) 小孔分子筛/ Cu-RTH small-pore zeolites







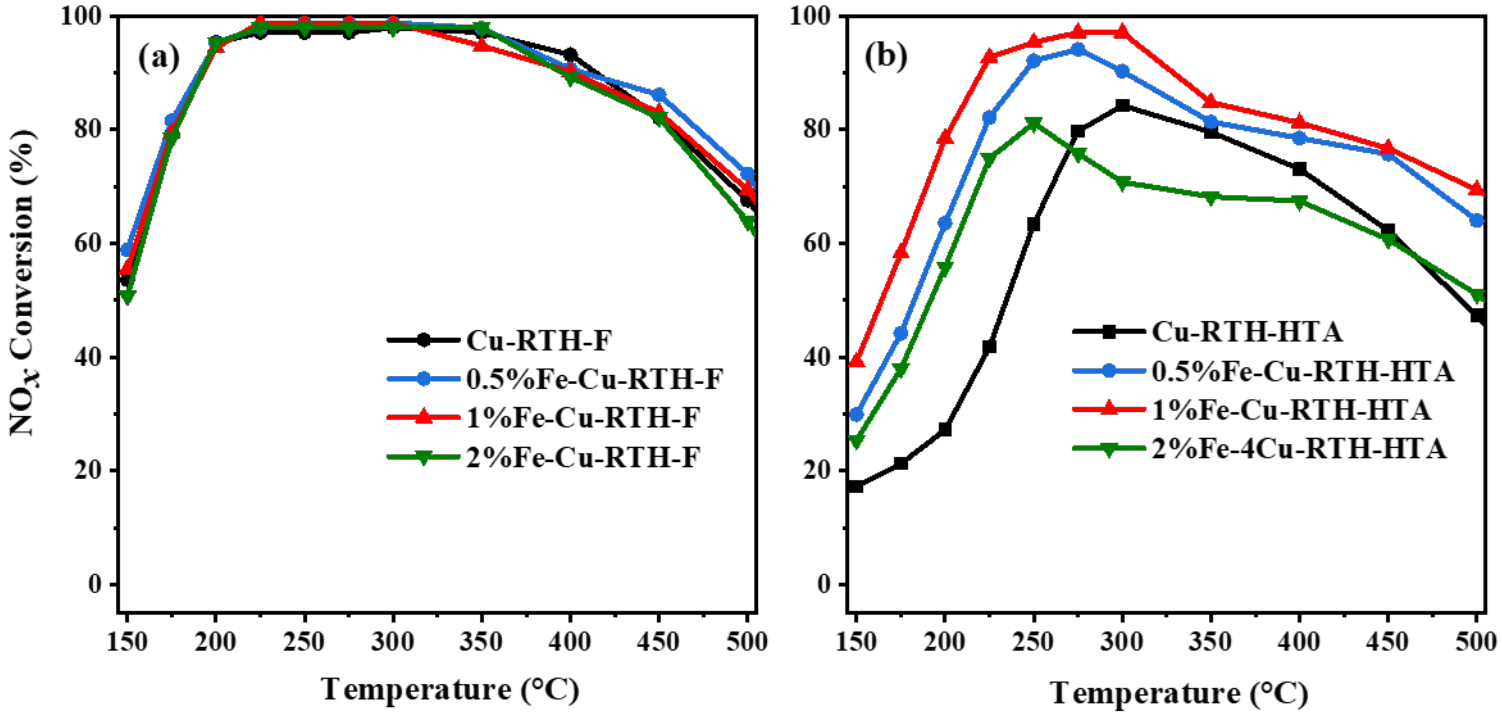
- Cu-RTH具有较好的NH_3-SCR活性，但稳定性较差，是由于活性Cu物种不稳定。
- Cu-RTH catalysts showed good NH_3-SCR performance but poor hydrothermal stability due to the instability of active Cu species.

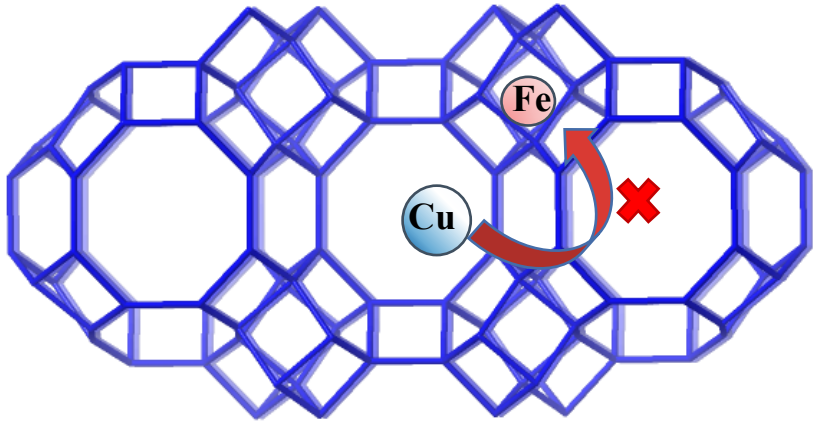
2. 铜基小孔分子筛用于NH_3-SCR

Cu-based small-pore zeolites for NH_3-SCR

中国科学院 CHINESE ACADEMY OF SCIENCES

2.4 Fe-Cu-SSZ-50 (RTH构型) 小孔分子筛/ Fe-Cu-RTH small-pore zeolites





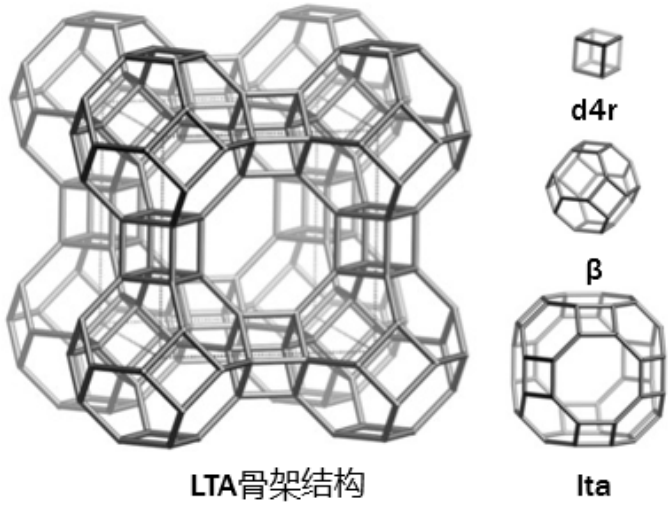
- Fe掺杂后新鲜NH_3-SCR活性不受影响
- The fresh NH_3-SCR activity of Cu-RTH was unaffected by Fe-doping.
- Fe掺杂极大提升了Cu-RTH水热老化后的脱硝活性
- Fe-doping greatly enhanced the deNOx conversion of Cu-RTH after hydrothermal aging (HTA).

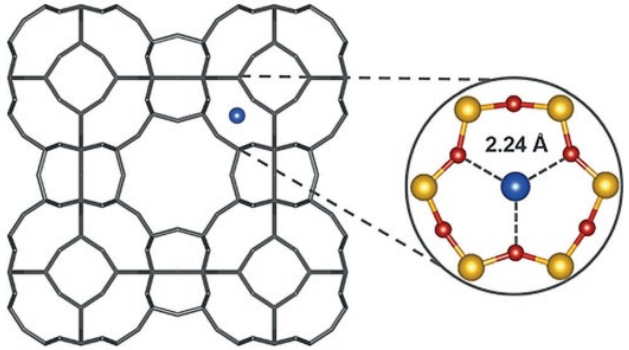
2. 铜基小孔分子筛用于NH_3-SCR

Cu-based small-pore zeolites for NH_3-SCR

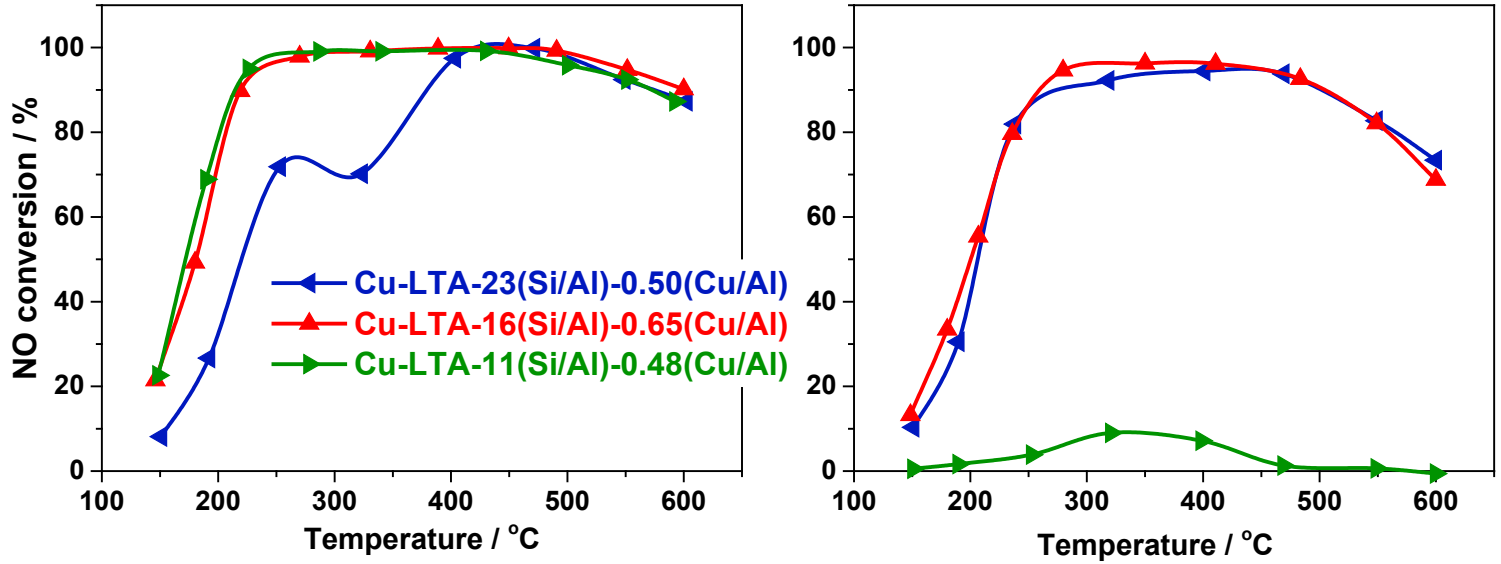
中国科学院 CHINESE ACADEMY OF SCIENCES

2.5 其他小孔分子筛材料-Cu-LTA





Cu^{2+}位于6MR中心，与3个O原子相连



S. K. Hong et al., ACS Catal., 2016, 6, 2443-2447. S. K. Hong et al. Angew. Chem. Int. Ed. 2017, 56,1-6.

- Cu-LTA即使经过900 ℃水热老化后，仍然可以保持较为优异的NH_3-SCR性能。
- Cu-LTA still maintained good NH_3-SCR performance despite hydrothermal aging at 900 ℃

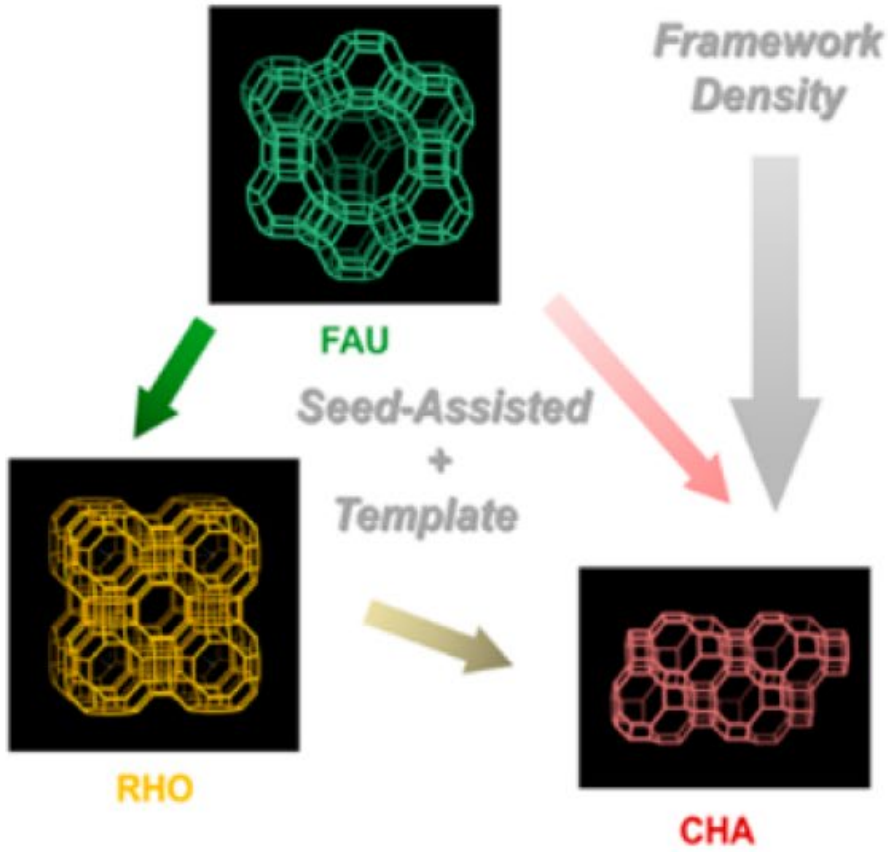
Taekyung Ryu, Suk Bong Hong* et al., 2017, Angew. Chem. Int. Ed., 2017, 56, 1

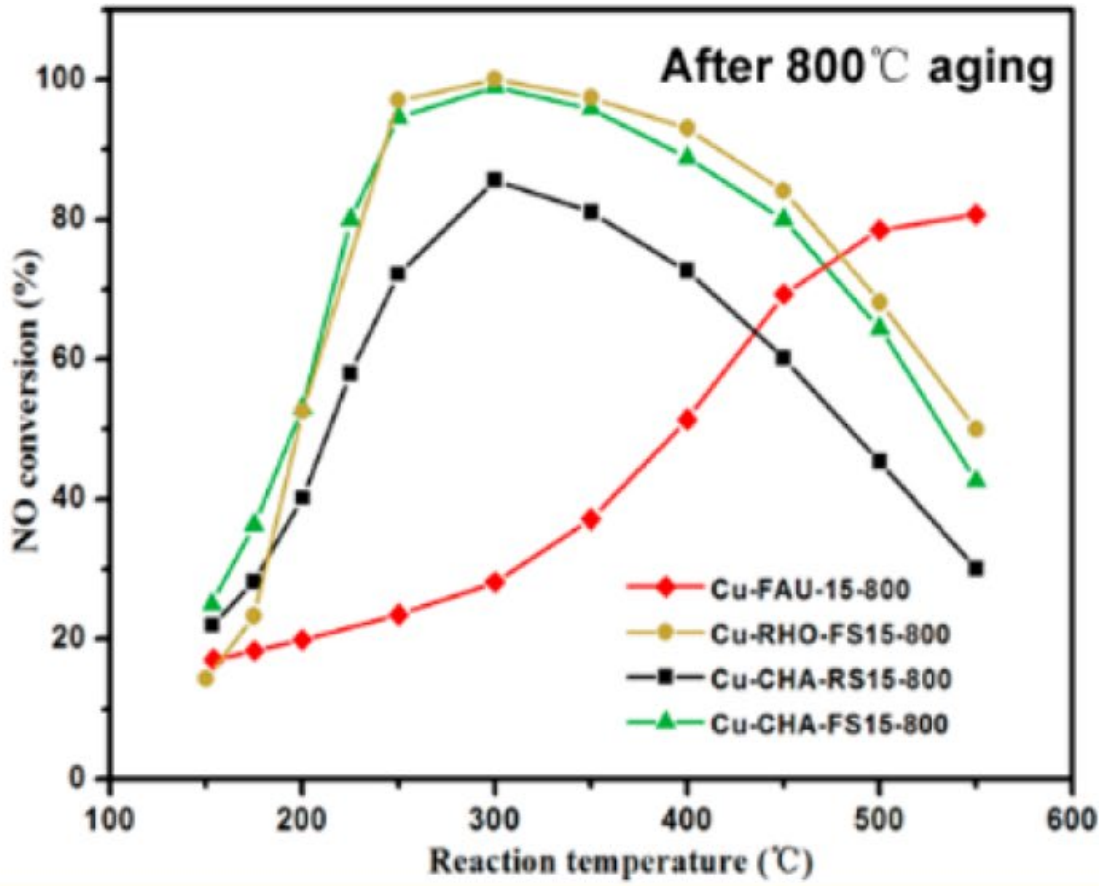
2. 铜基小孔分子筛用于NH_3-SCR

Cu-based small-pore zeolites for NH_3-SCR

中国科学院 CHINESE ACADEMY OF SCIENCES

2.5 其他小孔分子筛材料-Cu-RHO



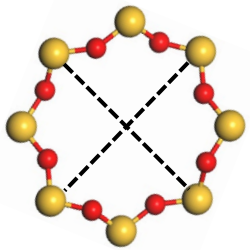


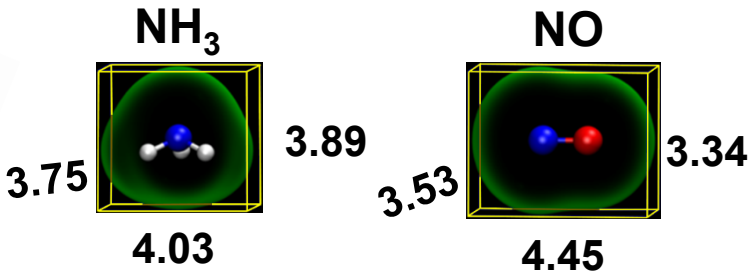
Quanli Ke, Shudong Wang et al., *Ind. Eng. Chem. Res.* 2018, 57, 16763−16771

目 录 Contents

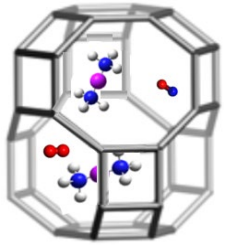
3. 机遇与挑战 / Opportunities and Challenges

➢ 8元环孔道 / 8MR channel：~4×4 Å





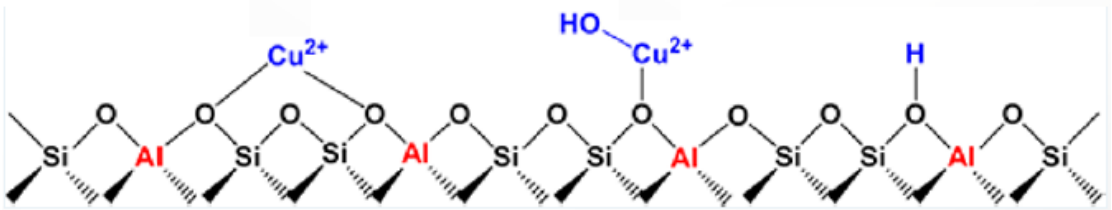
➢ 反应场所：笼状结构 / Reaction zone: Cavity



$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

➢ 元素组成：离子交换和酸性位

➢ Elemental composition: ion-exchange and acid sites

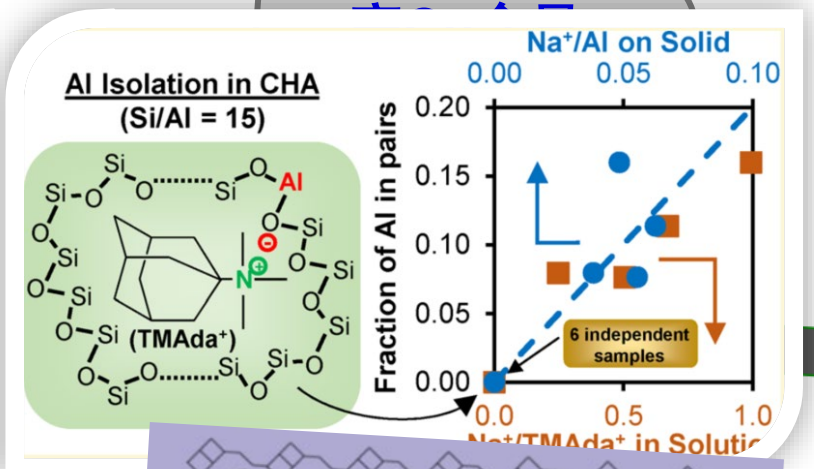


ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS	AFT	AFV
AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS	ATT	ATV	AVE
AVL	AWO	AWW	BCT	BEC	BIK	BOF	BOG	BOZ	BPH	BRE	BSV	CAN	CAS
CDO	CFI	CGF	CGS	CHA	-CHI	-CLO	CON	CSV	CZP	DAC	DDR	DFO	DFT
DOH	DON	EAB	EDI	EEI	EMT	EON	EPI	ERI	ESV	ETL	ETR	EUO	EWS
EZT	FAR	FAU	FER	FRA	GIS	GIU	GME	GON	GOO	HEU	IFO	IFR	-IFT
-IFU	IFW	IFY	IHW	IMF	IRN	IRR	-IRY	ISV	ITE	ITG	ITH	ITR	ITT
-ITV	ITW	IWR	IWS	IWV	IWW	JBW	JNT	JOZ	JRY	JSN	JSR	JST	JSW
KFI	LAU	LEV	LIO	-LIT	LOS	LOV	LTA	LTF	LTJ	LTL	LTN	MAR	MAZ
MEI	MEL	MEP	MER	MFI	MFS	MON	MOR	MOZ	MRT	MSE	MSO	MTF	MTN
MTT	MTW	MVY	MWF	MWW	NAB	NAT	NES	NON	NPO	NPT	NSI	OBW	OFF
OKO	OSI	OSO	OWE	-PAR	PAU	PCR	PHI	PON	POR	POS	PSI	PUN	PWN
PWO	PWW	RHO	-RON	RRO	RSN	RTE	RTH	RUT	RWR	RWY	SAF	SAO	SAS
SAT	SAV	SBE	SBN	SBS	SBT	SEW	SFE	SFF	SFG	SFH	SFN	SFO	SFS
SFW	SGT	SIV	SOD	SOF	SOR	SOS	SOV	SSF	SSY	STF	STI	STT	STW
-SVR	SVV	SWY	SZR	TER	THO	TOL	TON	TSC	TUN	UEI	UFI	UOS	UOV
UOZ	USI	UTL	UWY	VET	VFI	VNI	VSV	WEI	-WEN	YFI	YUG	ZON	

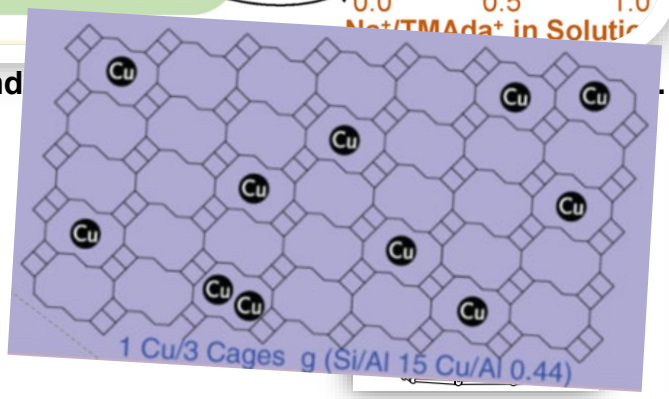
- 经济、绿色的工业化合成方法至关重要
- Economic, sustainable and industrialized method

基于活性Cu^{2+}物种的配位结构和动态效应，对其进行调控

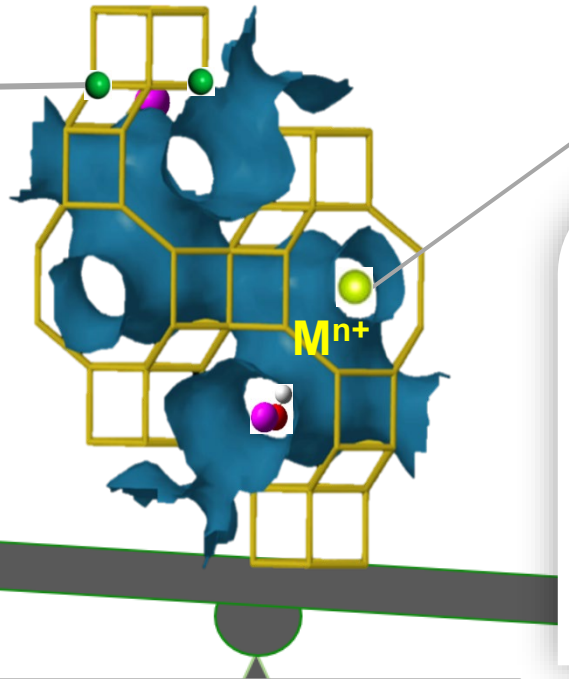
Al含量及分布调控



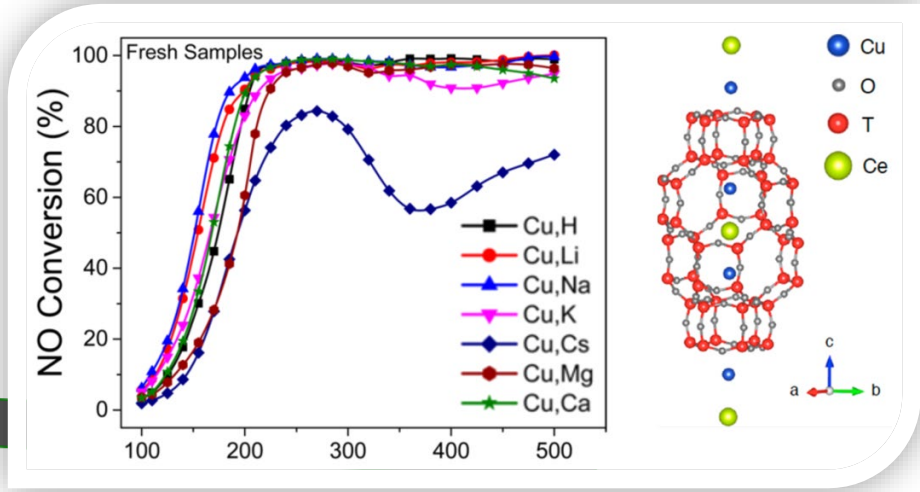
R. Gound



LTA

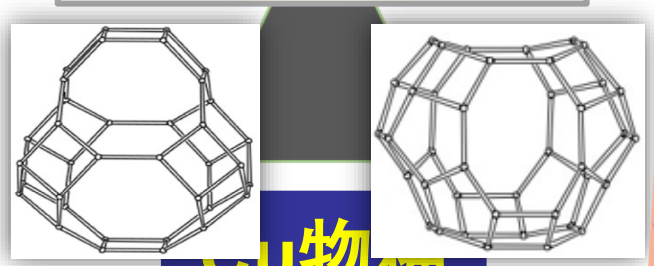


碱(土)/稀土金属调控



C. H. F. Peden et al., ACS catal, 2015, 5, 6780-6791.
ACS catal., 2018, 9, 9165-9173.

小孔分子筛的构型调控

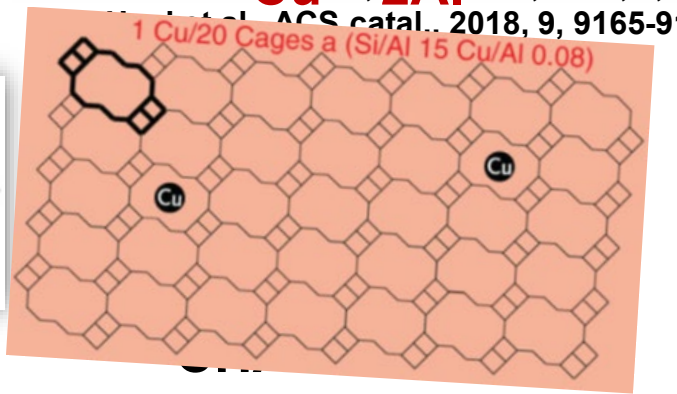


AEI

RTH

Cu物种

Cu^{2+}-2Al



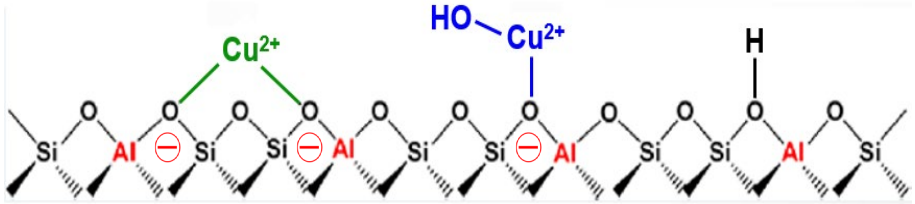
基于Cu/zeolites的基本特征，设计合成新型高效稳定的小孔分子筛

具有小孔八元环孔道结构

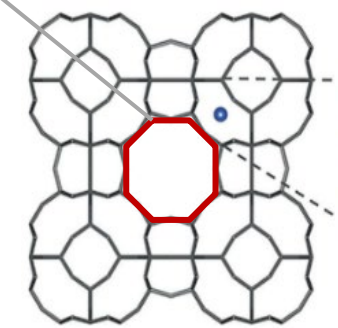
- 选择性通过反应物小分子；
- 高N_2选择性；
- 抗中毒能力等

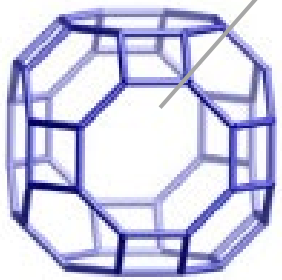
适中的Si/Al (3-20)

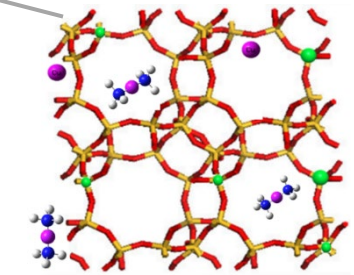
- 骨架稳定性；
- 酸性位/离子交换位

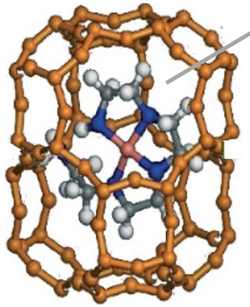


分子筛的结构与组成







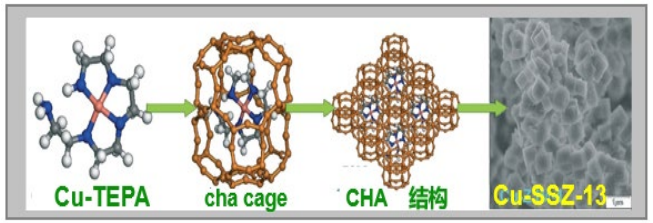


较大的笼状结构

- NH_3-SCR反应场所
- 丰富的氧化还原位和酸性位点

高效、廉价、绿色的合成方法

- 原位/一步合成
- 固相/快速合成等
- 无溶剂/模板剂/氟/钠合成



谢谢！ 敬请批评指正

- 感谢国家科技部、国家自然科学基金委、中国科学院等的项目支持；
- 感谢我的导师贺泓院士、余运波研究员、单文坡研究员及课题组所有成员；
- 感谢浙江大学肖丰收教授，孟祥举教授，吴勤明教授及其课题组所有成员；
- 感谢潍柴动力、东风商用车、艾可蓝环保、威孚环保催化剂等公司的支持！

单玉龙，单文坡，余运波，贺泓

中国科学院生态环境研究中心

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences

志存高远 | 励精图治 | 开拓进取 | 务实创新

Email: ylshan@rcees.ac.cn