Effect of Pore Structure on the activity of Cu/ZSM-5 Catalyst in NH_3-SCR: Studies of Simulated Exhaust and Engine Bench Testing

Zhenguo Li[1,2], Junhua Li[1], Xiaoyin Chen[2], Johannes W. Schwank[2]
[1]Tsinghua University, [2]University of Michigan

2015 DOE

CLEERS Workshop

April 27-29, 2015
University of Michigan - Dearborn

Outlines

1、 Background
2、 Research Status
3、 Experiments
4、 Results and discussion
5、 Conclusions

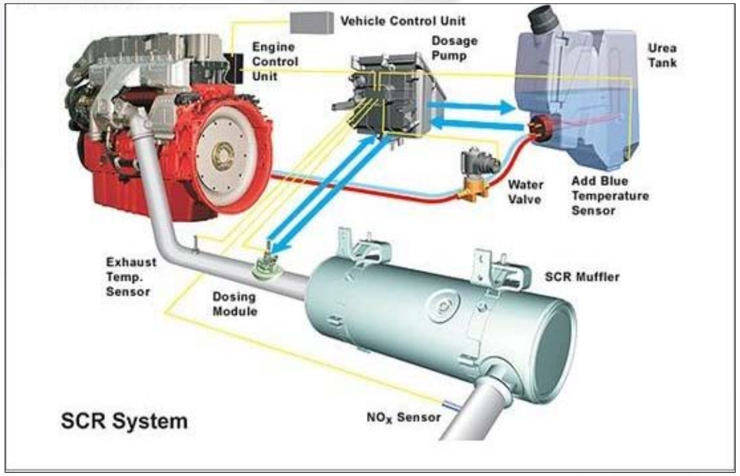
Background

Air pollution → **Automotives**

NO_x emissions

- A real threat in China
- Sources of acid rain and photochemical smog
- Half of NO_x emissions from automotives (especially **diesels**).

NO_x Removal Solution



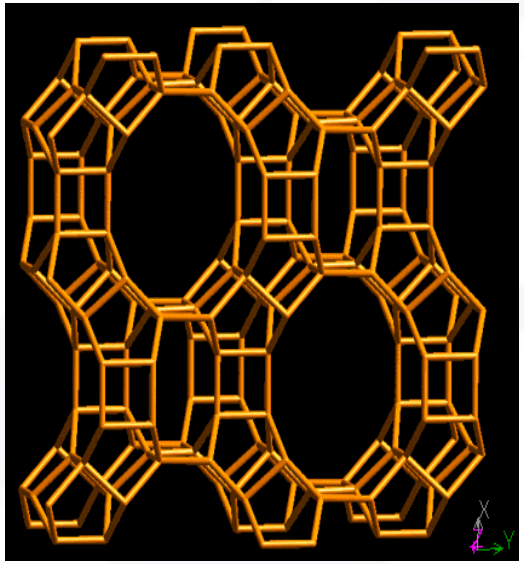
SCR System

- NH_3-SCR system (NO_x conversion > 90%)
- SCR catalyst is most critical

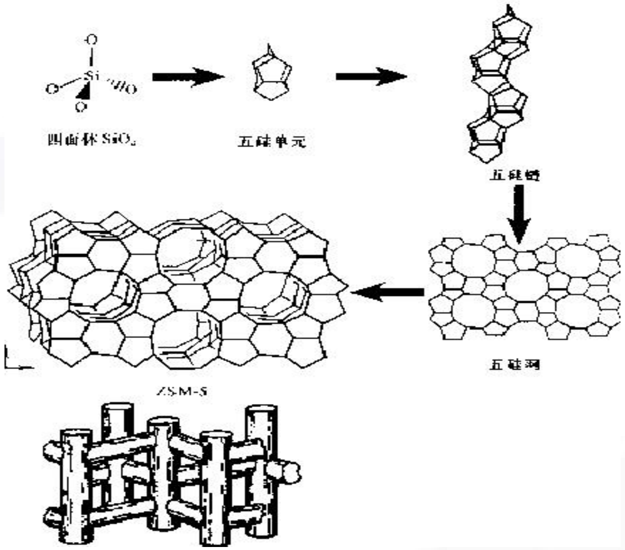
Research Status

To meet stringent standard, zeolite-based catalysts are promising for diesel emission control.

The most important issues for real applications include higher thermal stability and durability at high temperatures.



CHA (SAPO-34, SSZ-13)



MFI (ZSM-5)

- **<u>Fe-ZSM-5,</u>**
- **<u>Cu-ZSM-5,</u>**
- **<u>Mn-Ce-ZSM-5,</u>**
- **<u>Ce-ZSM-5,</u>**
- **<u>Fe-Mo-ZSM-5,</u>**
- **<u>Cu/Fe-ZSM-5</u>**

Yeom, Y. H. et al.*J. Catal.* **2005**, *231*, 181–193.
Sjovall, H. et al. *Appl. Catal., B* **2006**, *64*, 180–188.

Carja, G.et al.Appl. Catal., B 2007, 73, 60–64.
Qi, G. S.et al T. Appl. Catal.,B 2005, 60, 13–22.
Yeom, Y. H. et al J. Phys. Chem. B 2004, 108, 5386–5392.

ZSM-5-based Catalysts

Focuses of current research

- Reaction mechanism and active site
- Acid site
- Deactivation (HC & Sulfur, hydrothermal)

Active site vs Acid site:

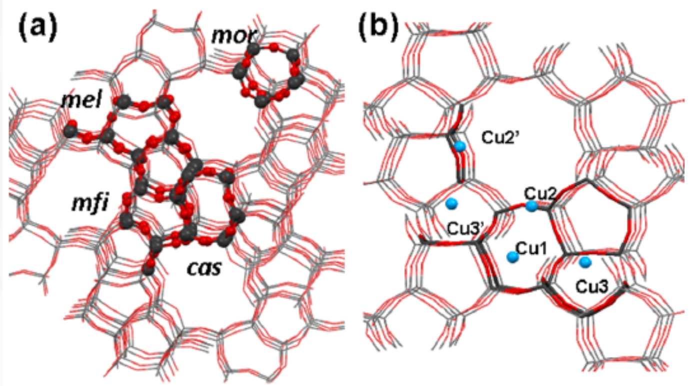
The active sites are related to acid sites (amount and strength) of ZSM-5, which can be adjusted by cations

Table 2. Physicochemical Properties of the Three MFI Zeolites

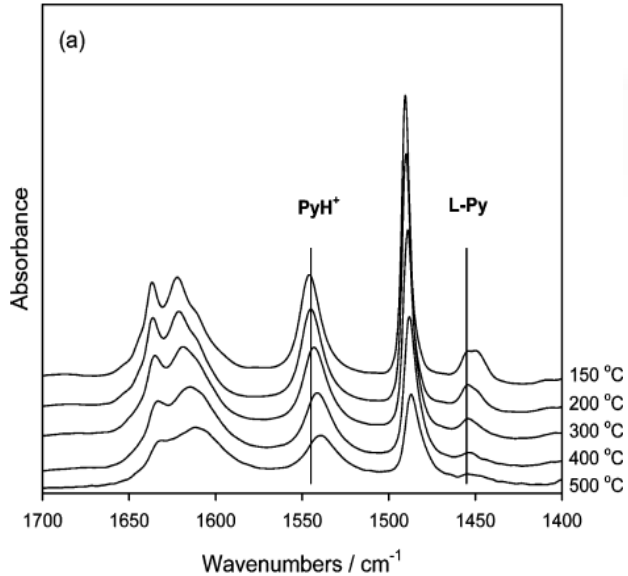
	H-[Al]-ZSM-5	H-[Al,Fe]-ZSM-5	H-[Fe]-ZSM-5
BET surface area (m^2/g)	451	467	487
pore volume (cm^3/g)	0.25	0.24	0.25
(micropore/mesopore volume ratio)	(0.16/0.09)	(0.16/0.08)	(0.16/0.09)
crystal size[a] (μm)	1.5−2	2−3	2−2.5
total acid amount[b] (μmol/g)	50.4	51.0	49.1
acid content[c] (μmol/g)	49.9	50.2	48.7
(Bronsted/Lewis acid site ratio)	(41.6/8.3)	(41.0/9.2)	(37.1/11.6)
TPD peak temperature (°C)	350	315	280

[a]Estimated from SEM images. [b]From NH_3 TPD measurements. [c]From pyridine IR analysis at 150 °C.

Reaction mechanism and active sites:



*Deka, U., I. Lezcano-Gonzalez, et al. ACS Catalysis 2013,**3**(3): 413-427.*



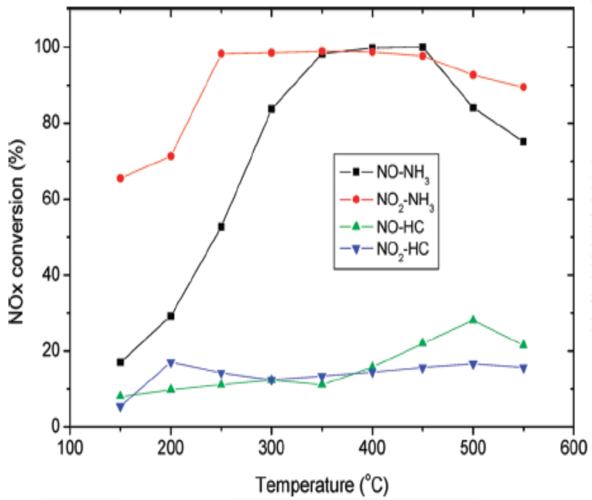
*Lee, K.-Y., S.-W. Lee, et al. Industrial & Engineering Chemistry Research 2014,**53**(24): 10072-10079.*

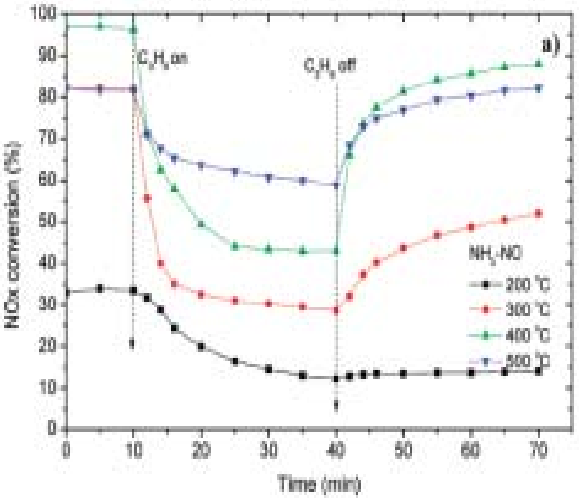
ZSM-5-based Catalysts

Focuses of current researches

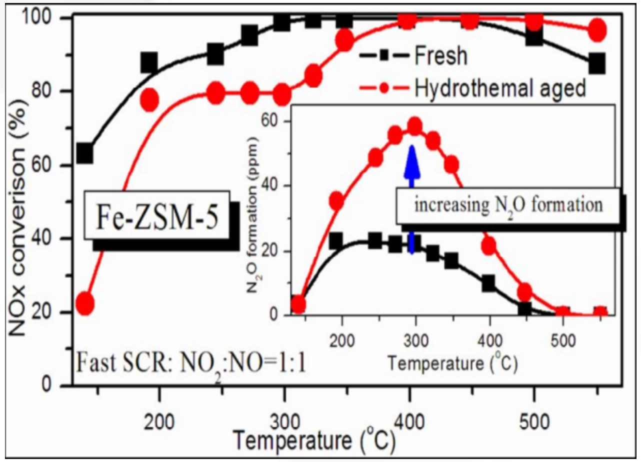
- Reaction mechanism and active site
- Acid site
- Deactivation (HC & Sulfur, hydrothermal)

Poisoning and hydrothermal aging:





Li J.H.et al.Environ. Sci. Technol. **2010,** *44,* 1799–1805



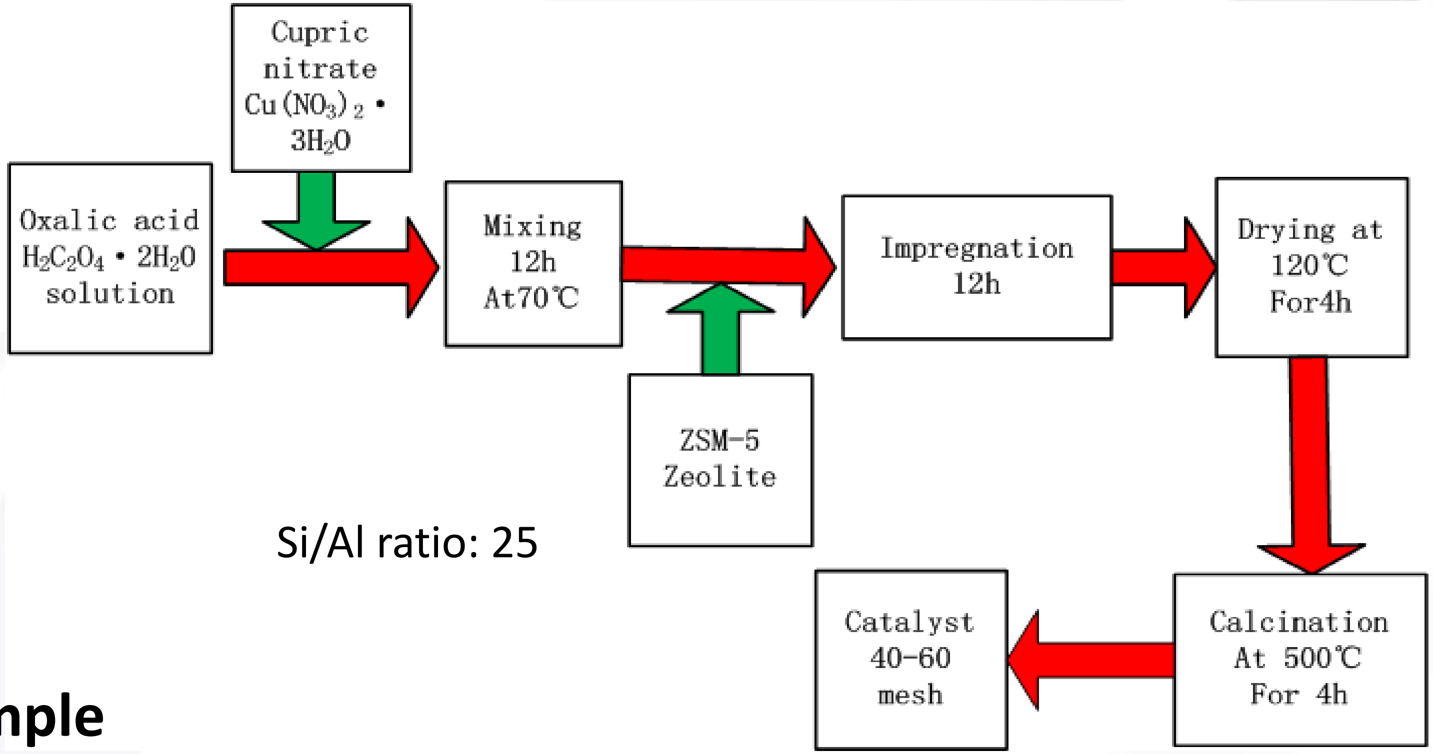
*Shi, X., F. Liu, et al. al.Environ. Sci. Technol. 2013,**47**: 3293-–3298.*

Engine bench testing data on the influence of pore structure on NOx activity of ZSM-5 catalysts are scarce.

In our study, the performance of 3%Cu-ZSM-5 powder and cordierite catalysts (with two types of commercial ZSM-5-A and ZSM-5-B) was investigated with simulated automobile exhaust gas and engine bench testing.

Experimental Approach

Catalyst preparation



Powder sample

- **Two types of commercial ZSM-5**
- **Cu/ZSM-5: Cu loading 3wt.% (noted CuZ-A and CuZ-B)**
- **<u>Impregnation</u>**

Monolith sample

- Monolith: 400 cpsi, Corning
- Wash Coating

Powder Activity and Characterization

Powder Activity



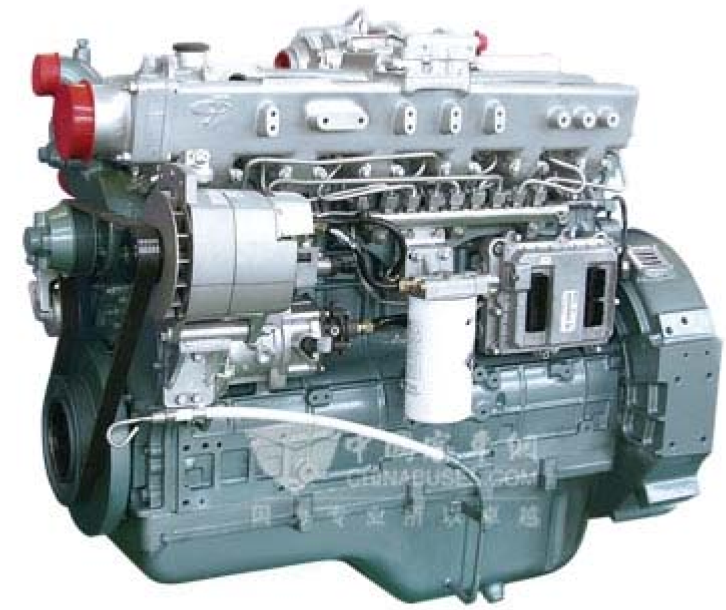
500 ppm NO, 500 ppm NH_3, 5% O_2 5%H_2O,N_2 balance,1000mL/min, 30,000 h^{-1}.
Thermo IS10 FTIR gas analyzer.

Characterization

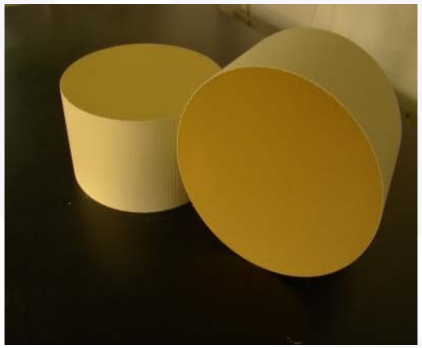
- BET
- XRD
- XPS
- TPR
- TPD

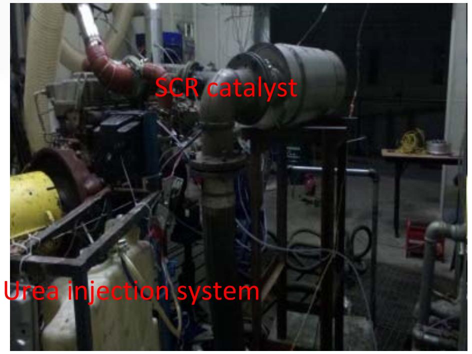
Engine Bench Test

Engine	YC6L-280-40
Type	Vertical , in-line , water-cooled , four-stroke, turbocharged , intercooled and 6-cylinders
Total displacement	8.42L
Compression ratio	17.5： 1
Rated speed	2200 r/min
Rated power	206 kW
Maximum torque speed	1200-1700 r/min
Maximum torque	1100 N.m
Emission	EURO IV
Exhaust after-treatment system	SCR，10.5×（6+3+6）/inch



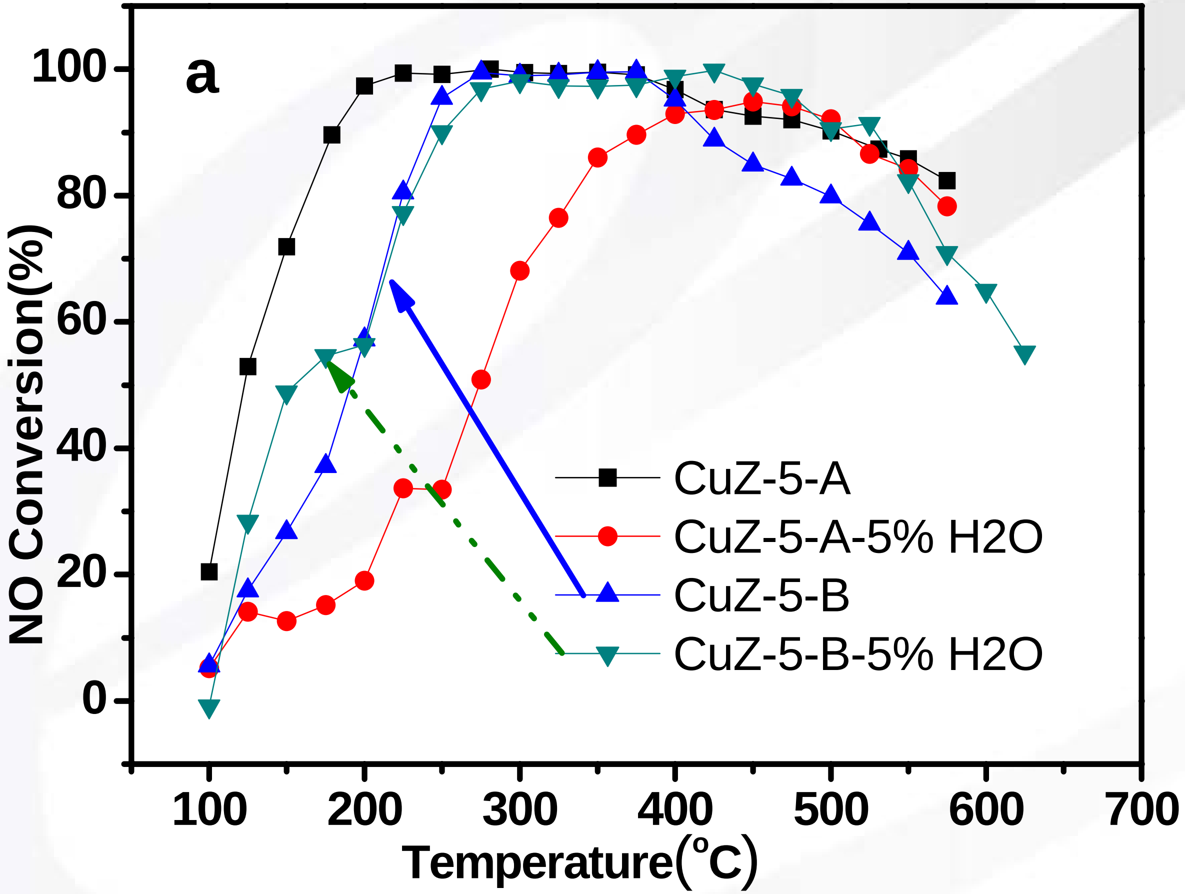
YC6L-280-40





Results and Discussion

Performance of powder catalysts with simulated exhaust gas

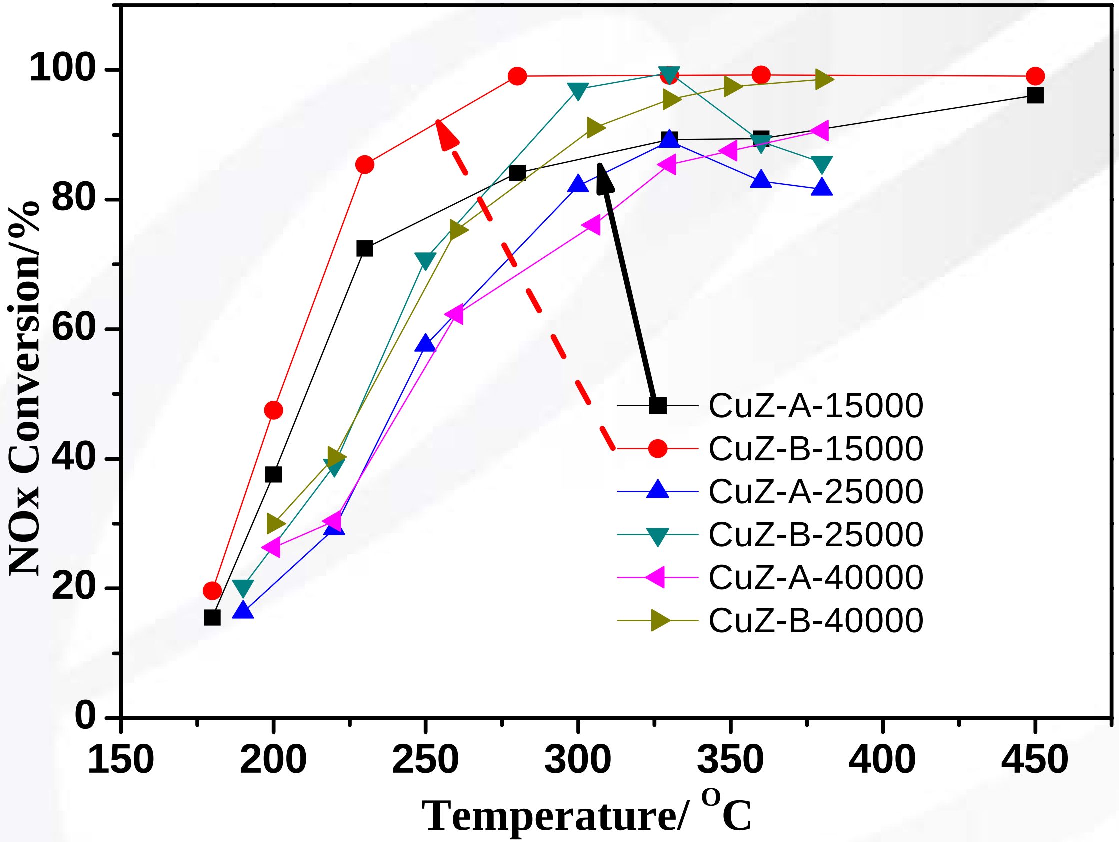


NO conversion vs. temperature

- $DeNO_x$ catalytic activity: CuZ-B did not significantly change in presence of water vapor compared to $DeNO_x$ catalytic activity of CuZ-A.

Performance in Engine Bench Test

Performance of light-off



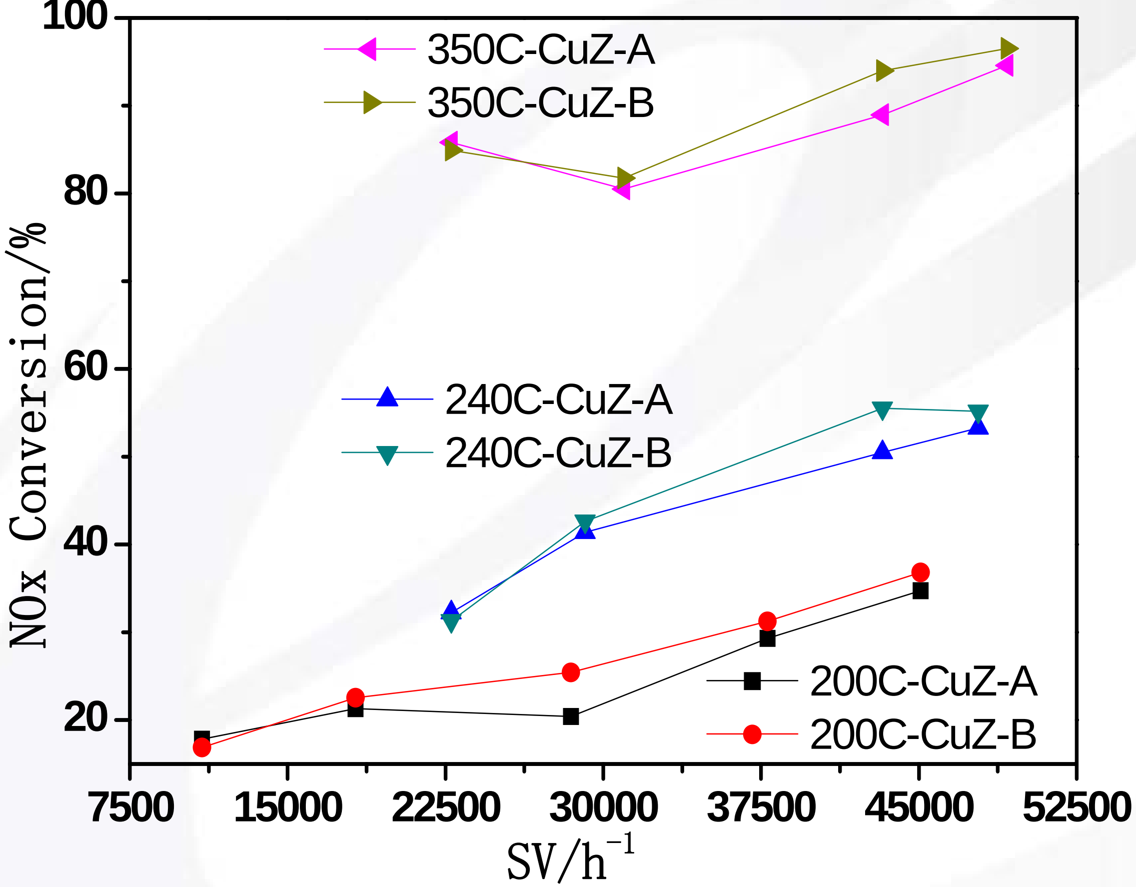
NO_x conversion vs temperature (NH_3/NO=1.2)

Key Results:

- Light-off temperature of CuZ-B: 215 ˚C at 15,000 h^{-1}.
- CuZ-B shows higher NO_x conversion than CuZ-A at GPSV = 15,000-45,000 h^{-1}.

Performance in Engine Bench Test

Performance under different space velocities

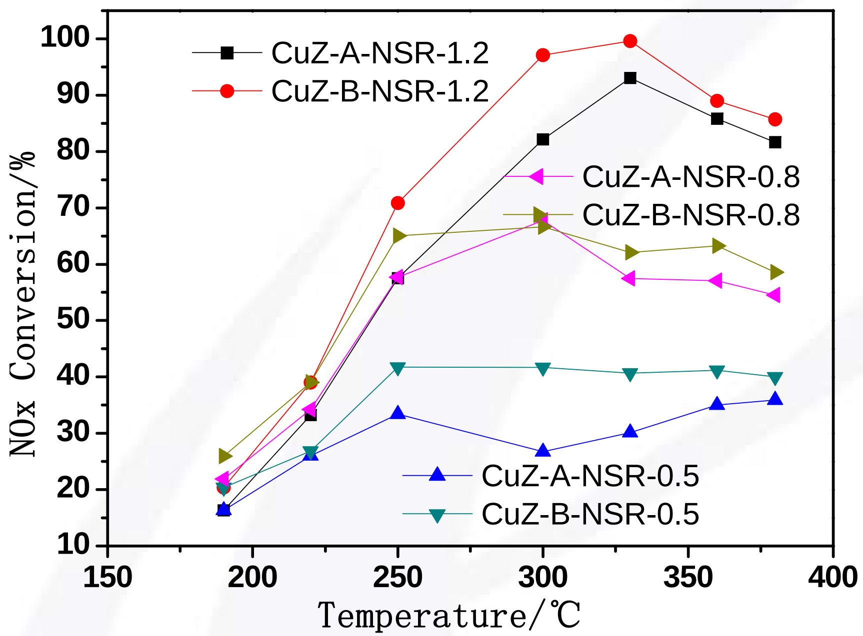


NO_x Conversion vs velocity (NH_3/NO=1.2) at 200, 240 and 350 ˚C.

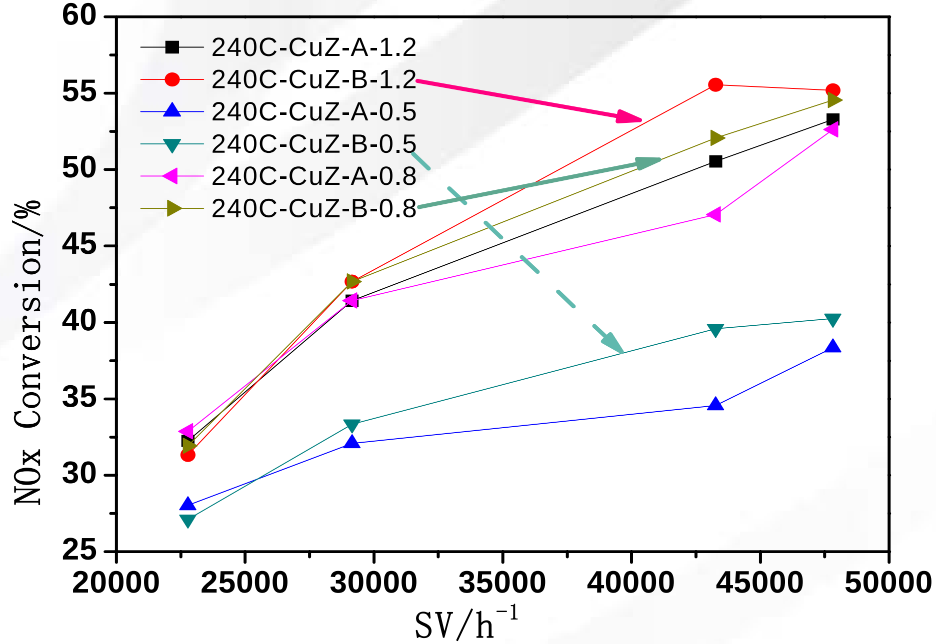
Key Results:

- When GPSV < 30,000 h^{-1}, similar NOx conversion for CuZ-A and CuZ-B at 240 and 350 ˚C
- When GPSV ≥ 30,000 h^{-1}, CuZ-B exhibits higher NO_x activity.

Performance under different NH_3/NO_x Ratios



Effect of NH_3/NO_x ratio on NO_x conversion



Effect of space velocity at 240℃.

Key Results:

- CuZ-B shows higher NO_x conversion than CuZ-A at NH_3/NO_x=0.5, 0.8, and 1.2.
- CuZ-B shows less dependence on NH_3/NO_x ratio than CuZ-A.

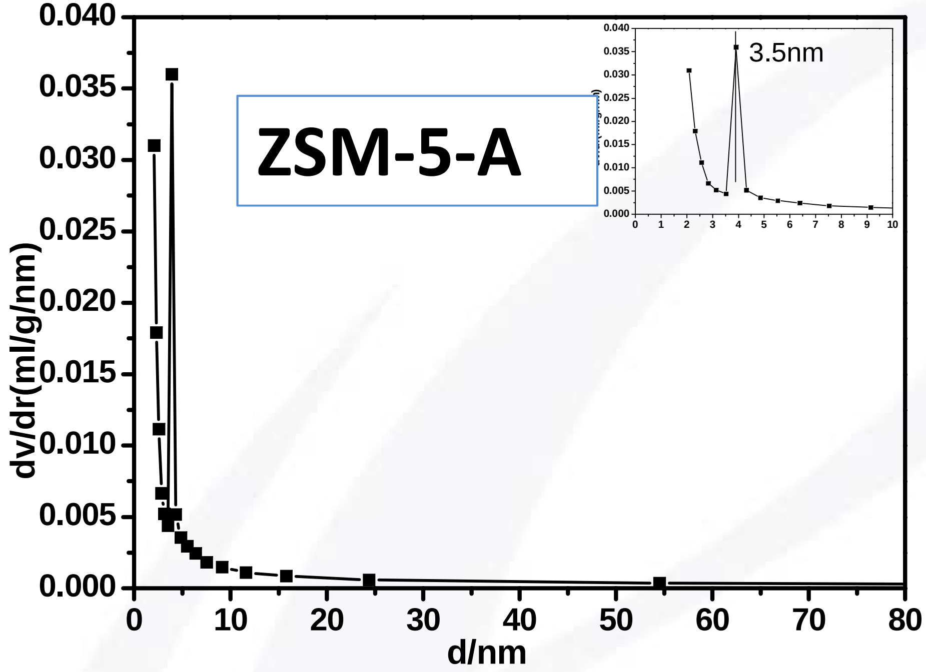
Catalyst Characterization

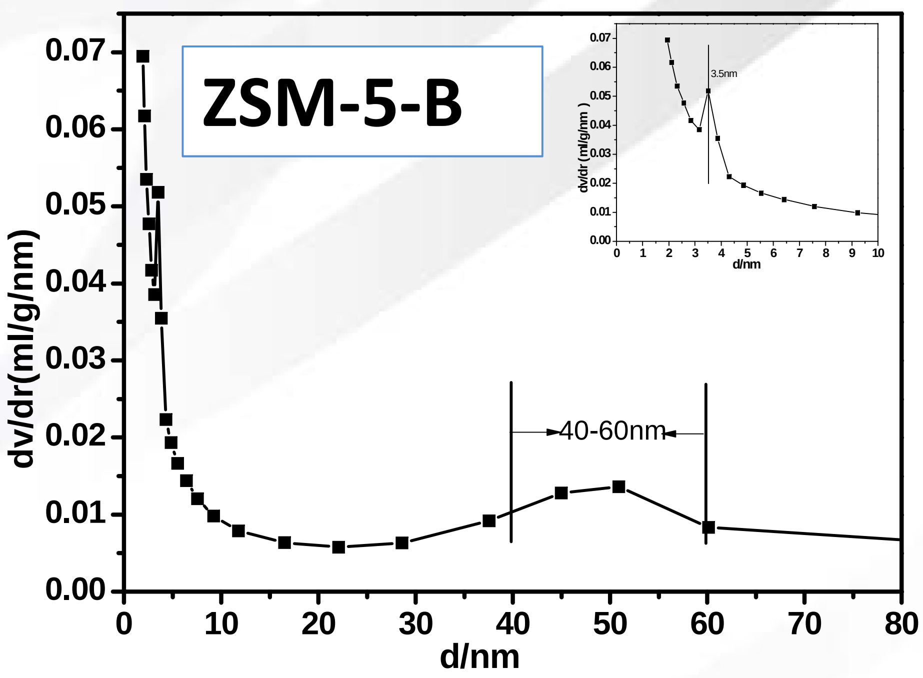
BET and Pore Distribution

Sample	S_{BET} (m^2/g)	[a]V(Total) $cm^3\ g^{-1}$	[b]V(Micro) $cm^3\ g^{-1}$	[c]Average pore size nm	[d]V(Meso) $cm^3\ g^{-1}$	Crystallinity (%)
ZSM-5-A	415	0.2510	0.1458	2.42	0.1052	100
ZSM-5-B	608	0.8880	0.1957	5.58	0.6923	84.1

- BET: ZSM-5-B is higher than ZSM-5-A sample.
- Total pore volume: ZSM-5-B is about 3.5 times higher than ZSM-5-A .
- Mesopores beneficial for improving pore volume of ZSM-5 material.

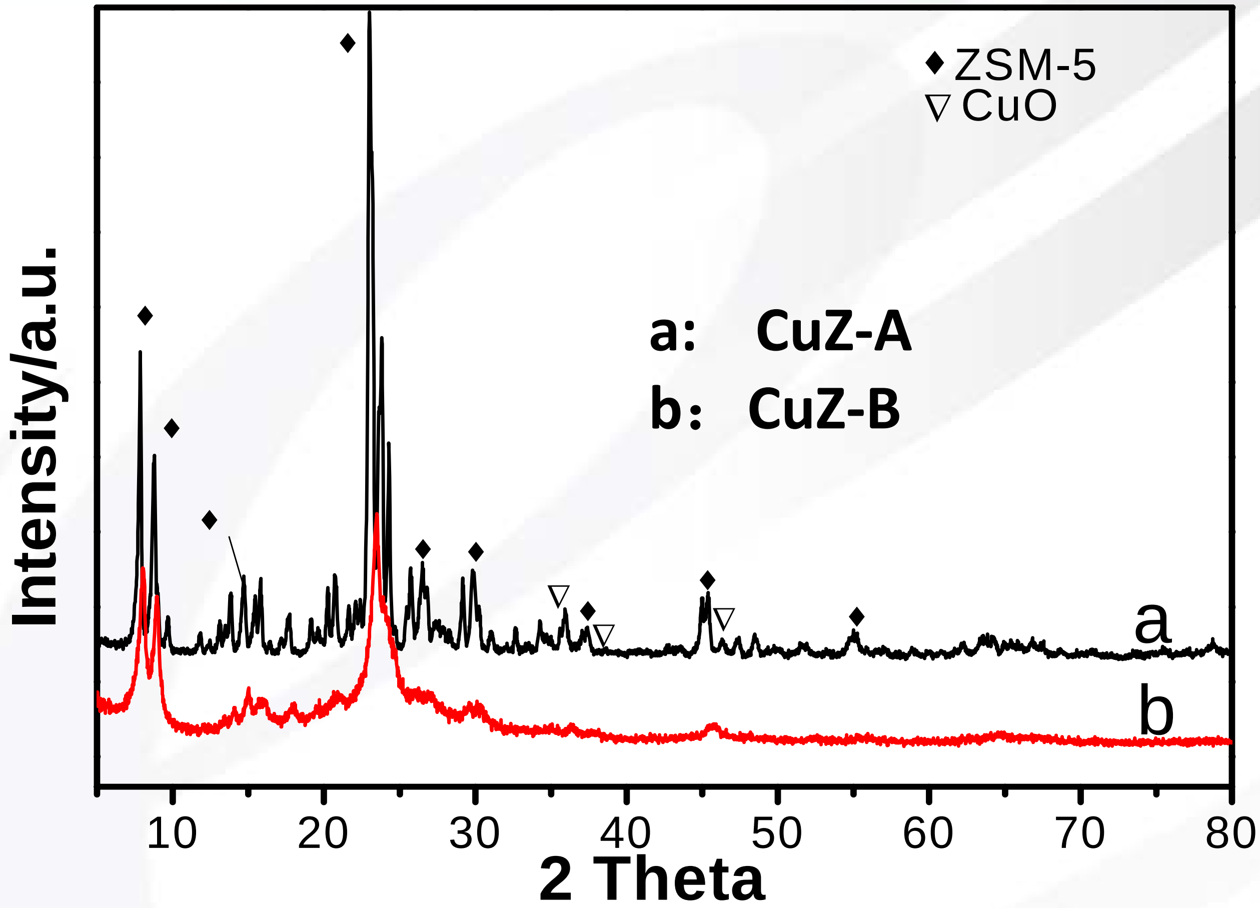
Pore Size Distribution





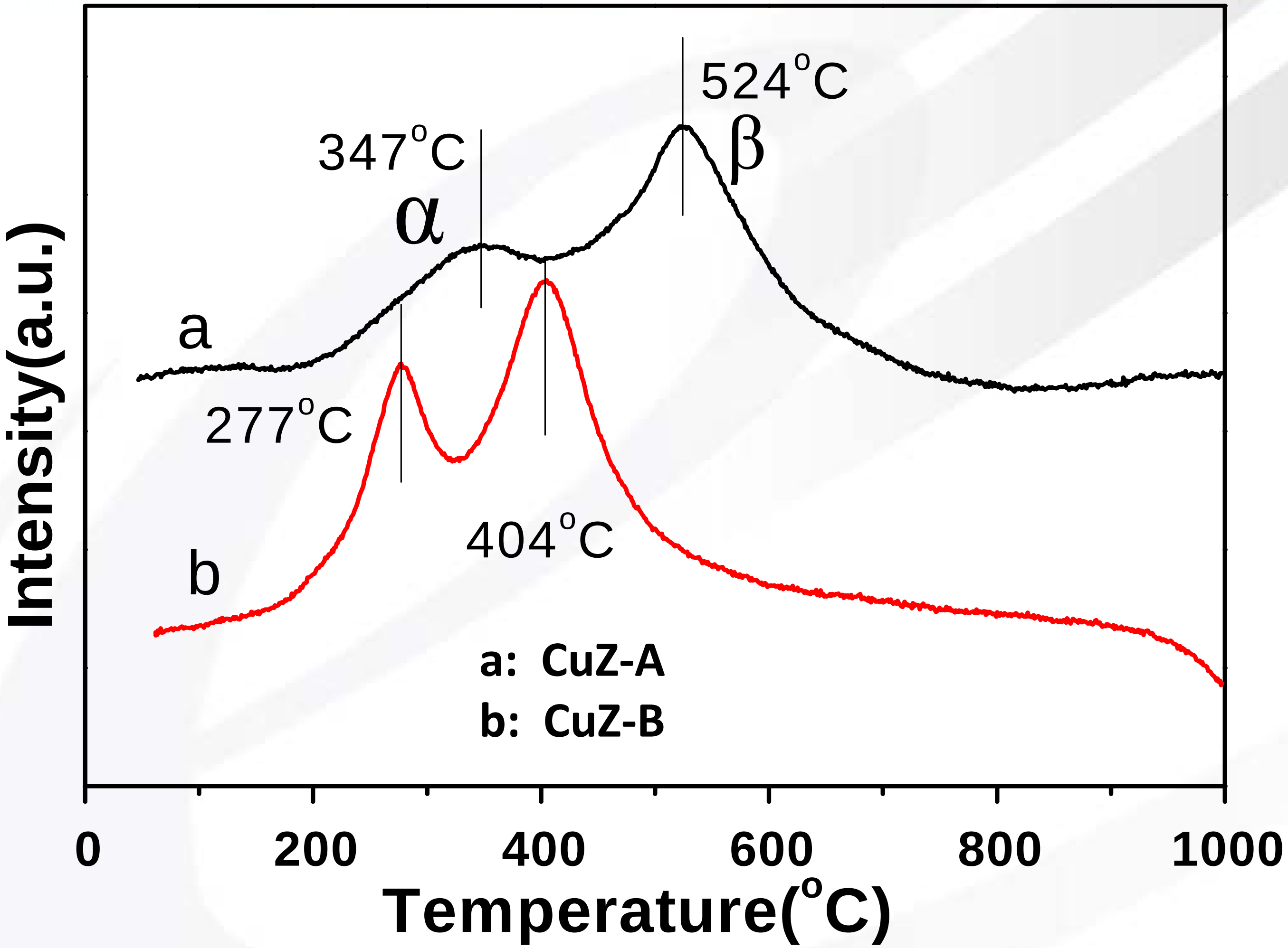
ZSM-5-B： Mesopores in the range of 35-60 nm

XRD



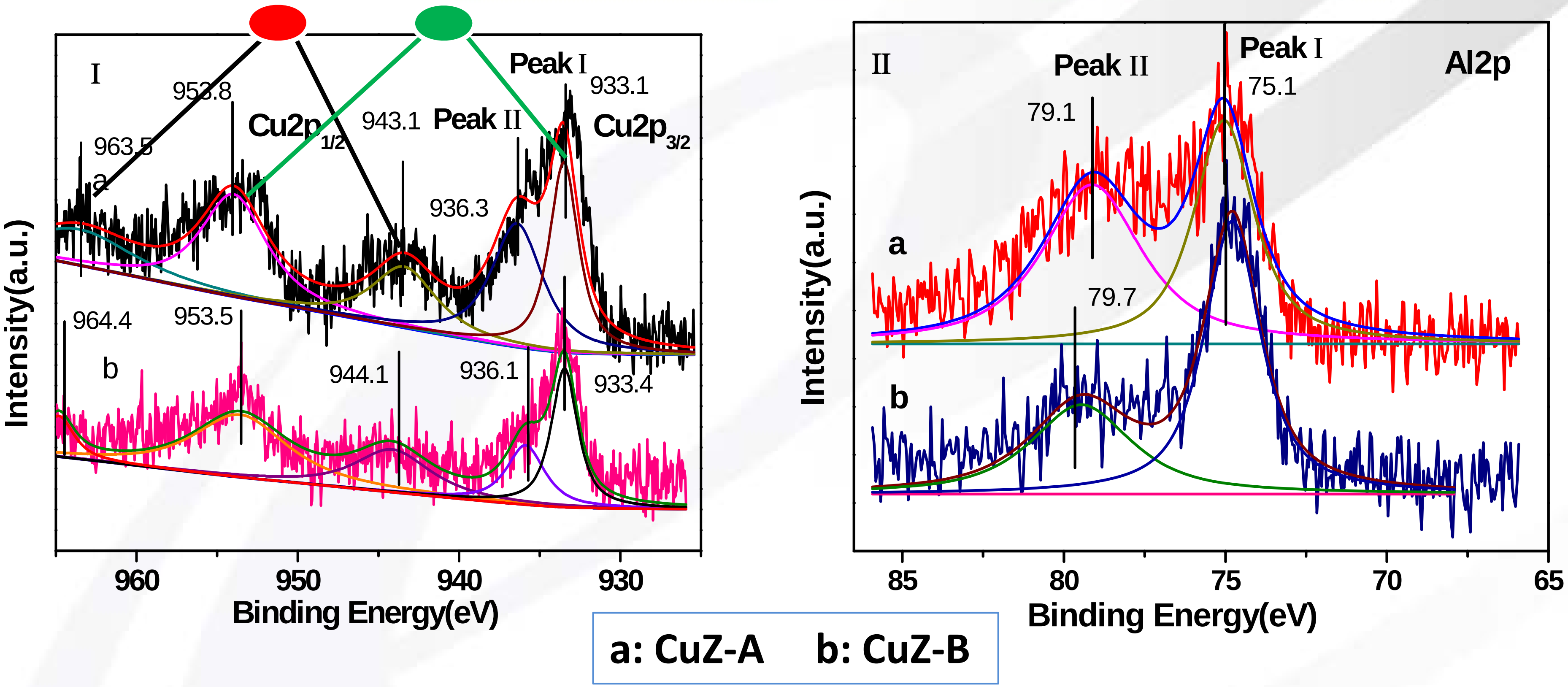
- More CuO in CuZ-A observed by XRD;
- Cu species have been well dispersed in the surface and bulk of ZSM-5-B zeolite
- The crystallinity of CuZ-B is 84%, compared to 100% of CuZ-A

TPR



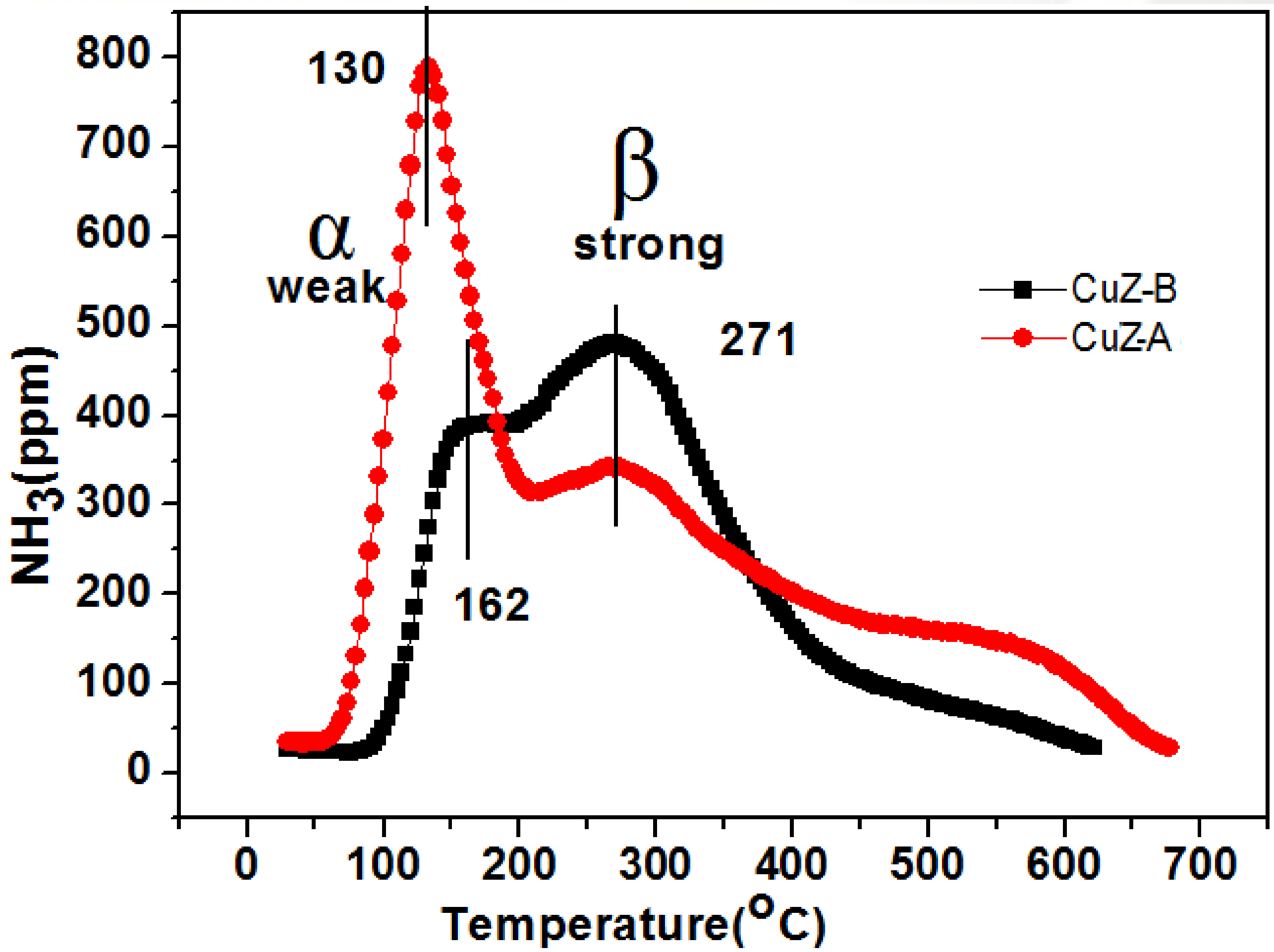
- Peak(α)： Surface CuO_x reduced to Cu metal, and isolated Cu^{2+} ions to Cu^{+} at 200–400˚C.
- Peak(β)： Cu^{2+} （Ion exchanged site） and Cu^{+} reduced to Cu metal at 400–600˚C.

XPS



- CuO（Cu species）: Two shake-up satellite peaks at 943.1 and 963.5 eV
- $Cu_{2p3/2}$: 933.1 eV (with a shoulder peak at 935.4 eV)
- $Cu_{2p1/2}$: 952.8 eV
- $Cu_{2p3/2}$: peak I 933-934 eV - tetrahedral Cu^{2+} site
  peak II 935-936eV - octahedral Cu^{2+} site

NH_3-TPD



- Weak acid sites (α)： Non-framework Lewis acid sites of ZSM-5 and surface copper cations
- Strong Brönsted acid sites (β)： On Si−O−Al groups and bulk copper cations

Conclusions

1. Higher porosity facilitates the NO_x conversion of CuZ-B catalyst. The high BET area, total pore volume and lower crystallinity provide more Cu active sites and acid sites.

2. The surface CuO_x species and ion-exchanged sites of Cu species in CuZ-B catalyst have higher redox property, higher Cu ion mobility, and strong interaction with Al and Si.

3. CuZ-B has higher number of strong Brönsted acid sites based on Si−OH−Al groups and Cu^{2+} ions located at the ion-exchanged sites. The Brönsted acid sites might be the main active sites in NH_3-SCR reaction.

4. Engine-bench testing results show that CuZ-B catalyst has higher $DeNO_x$ activity than CuZ-A and it is not sensitive to the NH_3/NO_x ratio and space velocity .

5. Stringent emission standards can possibly be met with CuZ-B catalyst by slightly over-dosing urea without exceeding NH_3 slip targets.

THANK YOU FOR YOUR ATTENTION!