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Effects of Alkali and Alkaline Earth Cocations on the Activity and Hydrothermal Stability of Cu/SSZ-13 NH_3-SCR Catalysts

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CLEERS Workshop, 04/29/2015

Cu Loading Dilemma in Cu/CHA SCR Catalysts

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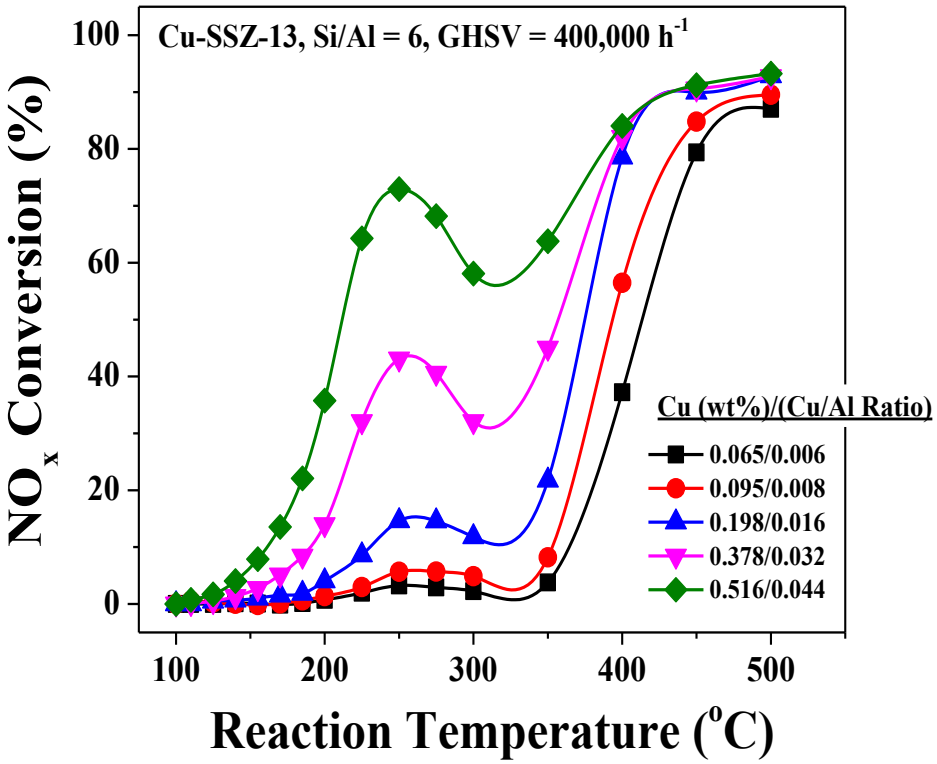
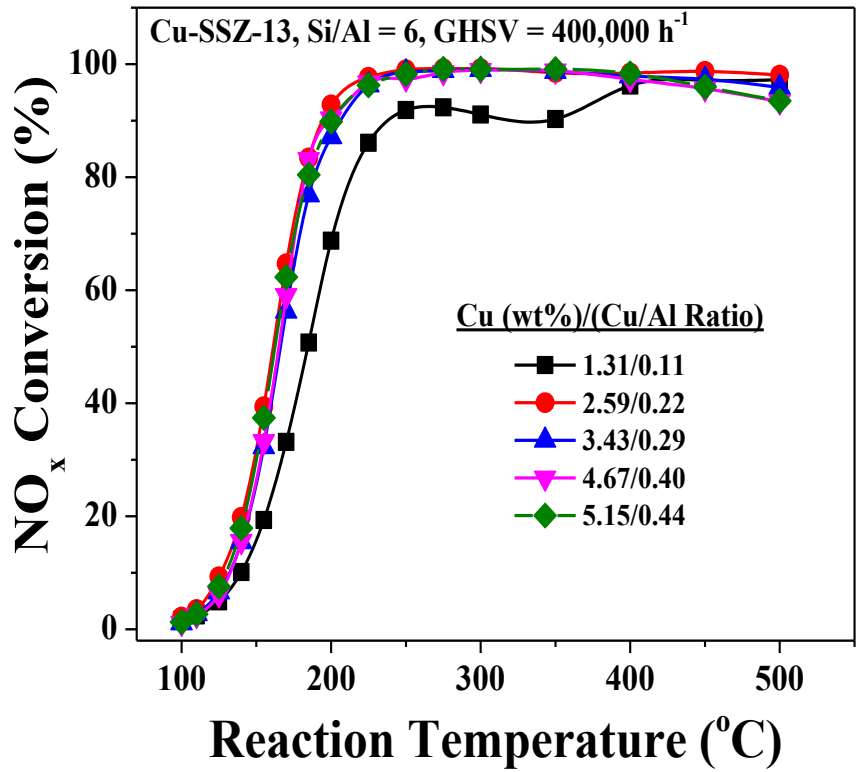
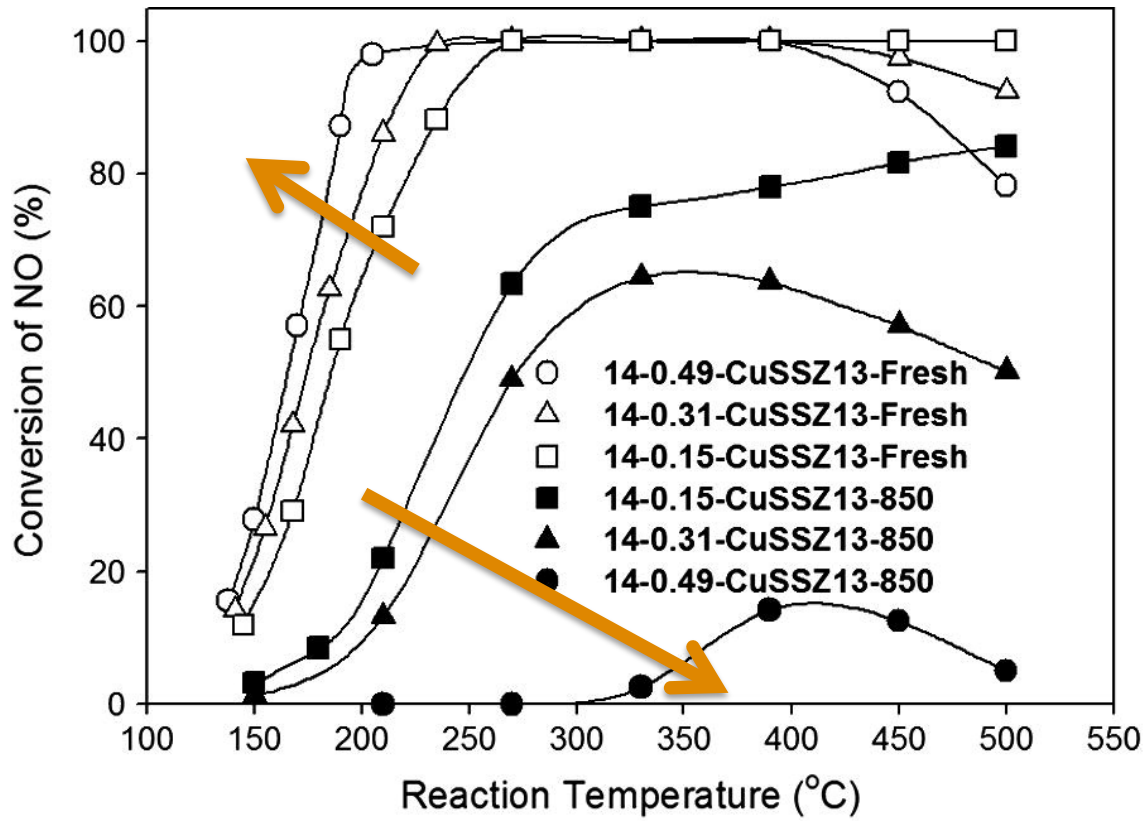




For good low-temperature activity, high Cu loadings (exchange levels) are required…

Cu Loading Dilemma in Cu/CHA SCR Catalysts



However, high Cu loading is detrimental to high-temperature hydrothermal stability…

Kim, et al., *Journal of Catalysis* **311** (2014) 447–457.

Origin on Cu Loading Effect to Hydrothermal Stability

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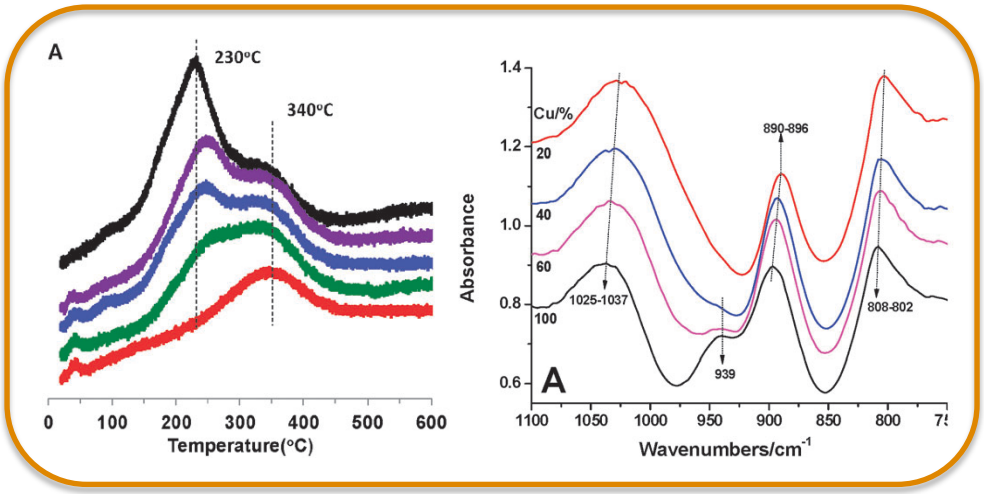
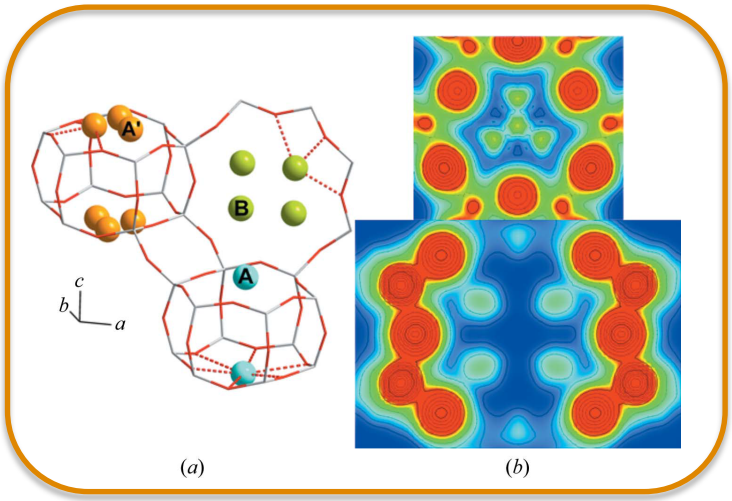
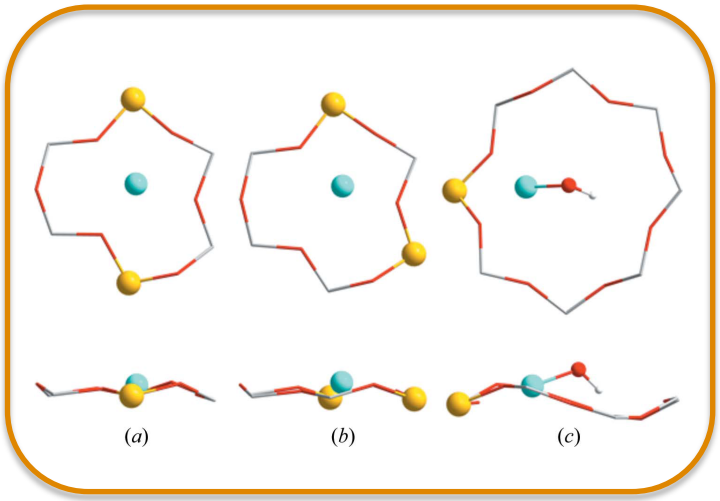


Kwak, et al., Chem. Commun., 48 (2012) 4758.

XRD/Maximum Entropy



DFT



Andersen, et al., *IUCrJ*, **1** (2014) 382-386.

Origin on Cu Loading Effect to Hydrothermal Stability

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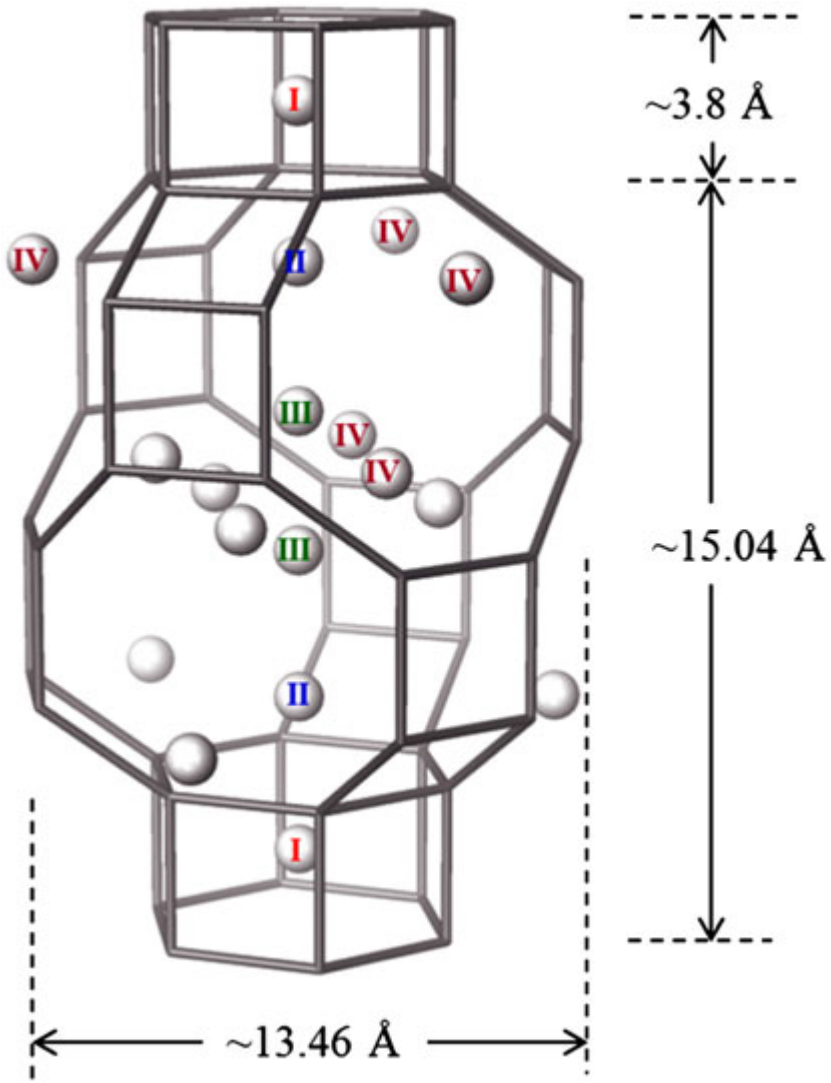
- $Cu(OH)^+$ species in CHA cage agglomerate to form CuO_x clusters more readily than Cu^{2+}-6MR during aging.
- **CuO_x clusters promote destruction of the CHA framework at high temperatures!**

- An easy solution to the Cu loading dilemma: synthesize and utilize Cu/CHA catalysts with intermediate Cu/Al ratios.

- Can we do even better?
  - Can we manipulate Cu ion positioning at a constant Cu loading?
  - Can we optimize both Cu loading and Brønsted acid site density?
  - Can we avoid dealumination during aging?

One Possible Solution…



Use cocations for:

- Space filling.
- Neutralize Brønsted acidity.
- Prevent dealumination.
- Lower redox barriers.
- …

Outline

1. Catalyst Synthesis.
2. Characterizations: H_2-TPR, NH_3-TPD, ^{27}Al NMR, DRIFTS, XRD, etc.
3. NH_3-SCR reactions.
4. Summary.

Catalyst Synthesis

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1. Na/SSZ-13 formation (Si/Al = 6) hydrothermally.
2. Solution ion-exchange to NH_4/SSZ-13.
3. Solution ion-exchange to M/SSZ-13 (M = Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}).
4. Solution ion-exchange to Cu,M/SSZ-13 (~1.0 wt% Cu if full exchange).
   - Wash, dry, calcine in air at 550 °C (**Fresh**);
   - Hydrothermal aging, 10% H_2O in zero air, 750 °C for 16 h (**HTA**).

Na/SSZ-13 → NH_4/SSZ-13 → M/SSZ-13 → Cu,M/SSZ-13

Catalyst Composition

Elemental analysis via ICP

Sample	Cu Content (wt%)	Cocation Content (wt %)	Ideal Stoichiometry
Cu,H/SSZ-13	0.87	-	$Cu_{0.3}H_{4.8}Al_{5.4}Si_{30.6}P_{72}$
Cu,Li/SSZ-13	0.98	0.40	$Cu_{0.33}Li_{1.25}H_{3.5}Al_{5.4}Si_{30.6}P_{72}$
Cu,Na/SSZ-13	0.98	1.78	$Cu_{0.33}Na_{1.67}H_{3.1}Al_{5.4}Si_{30.6}P_{72}$
Cu,K/SSZ-13	0.94	4.21	$Cu_{0.32}K_{2.33}H_{2.4}Al_{5.4}Si_{30.6}P_{72}$
Cu,Cs/SSZ-13	0.62	14.95	$Cu_{0.25}Cs_{2.86}H_{2.0}Al_{5.4}Si_{30.6}P_{72}$
Cu,Mg/SSZ-13	0.71	1.14	$Cu_{0.24}Mg_{1.0}H_{2.9}Al_{5.4}Si_{30.6}P_{72}$
Cu,Ca/SSZ-13	0.96	2.28	$Cu_{0.33}Ca_{1.23}H_{2.3}Al_{5.4}Si_{30.6}P_{72}$

NH_3-TPD on M/SSZ-13

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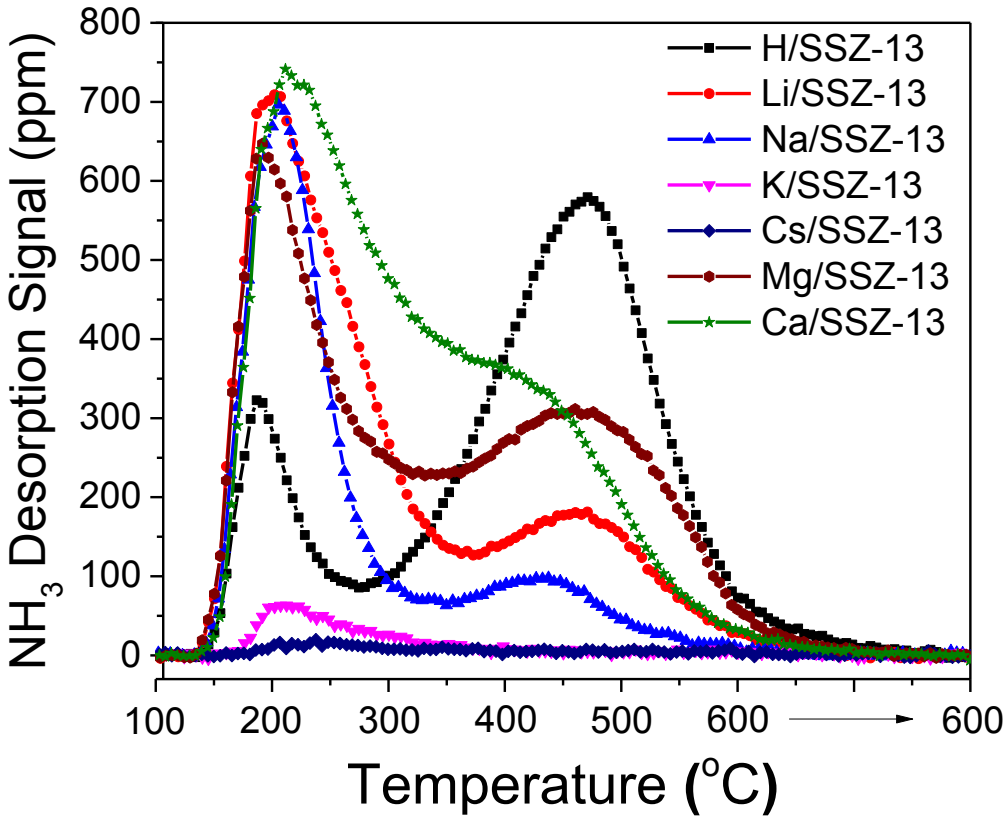
NH_4/SSZ-13 → M/SSZ-13



- K^+ and Cs^+ completely neutralize Brønsted acidity.
- Mg^{2+} and Ca^{2+} are the least efficient in removing Brønsted acid sites.

NH_3-TPD and DRIFTS on Cu,M/SSZ-13

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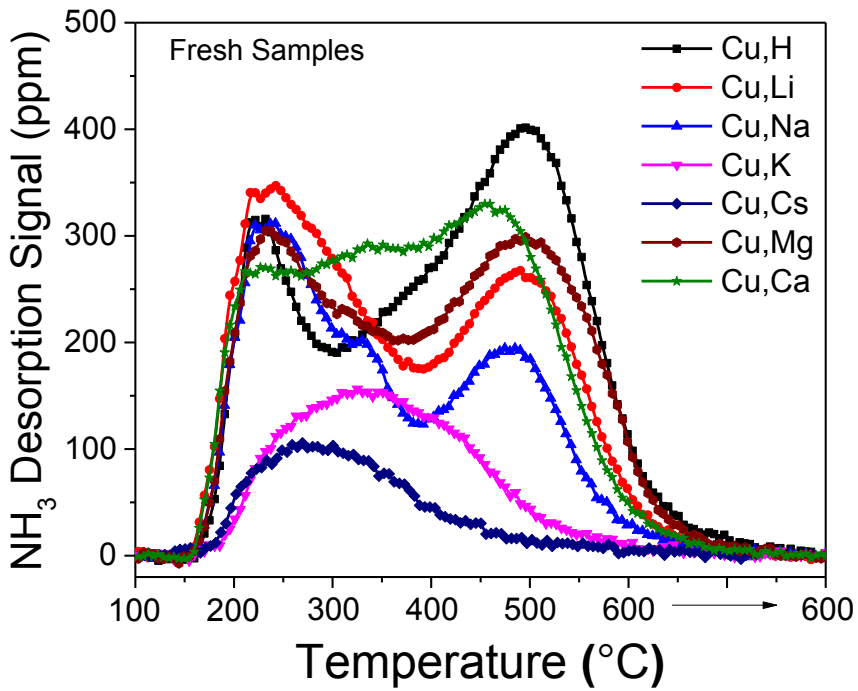
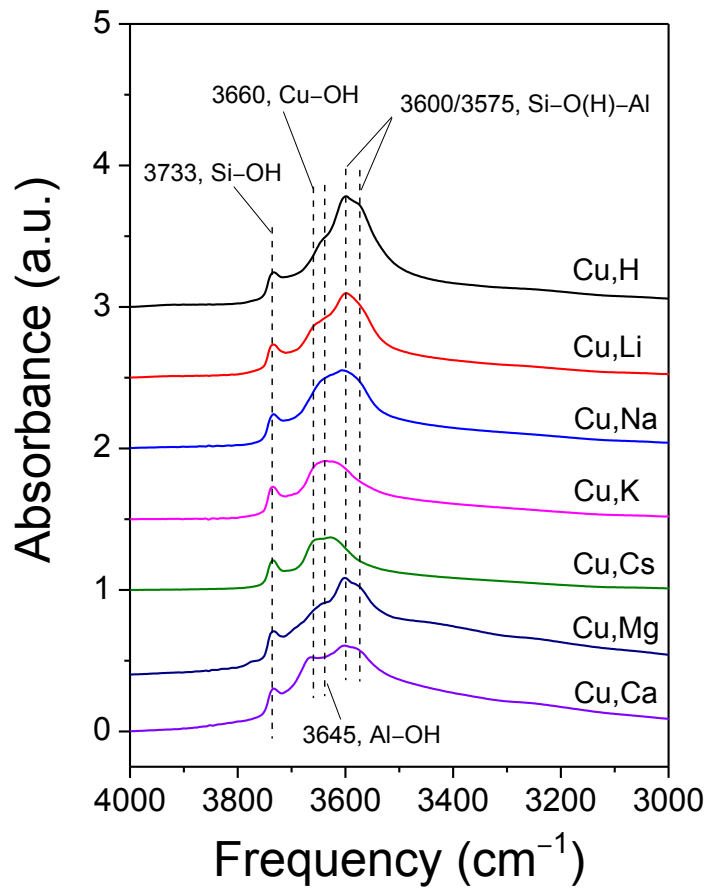
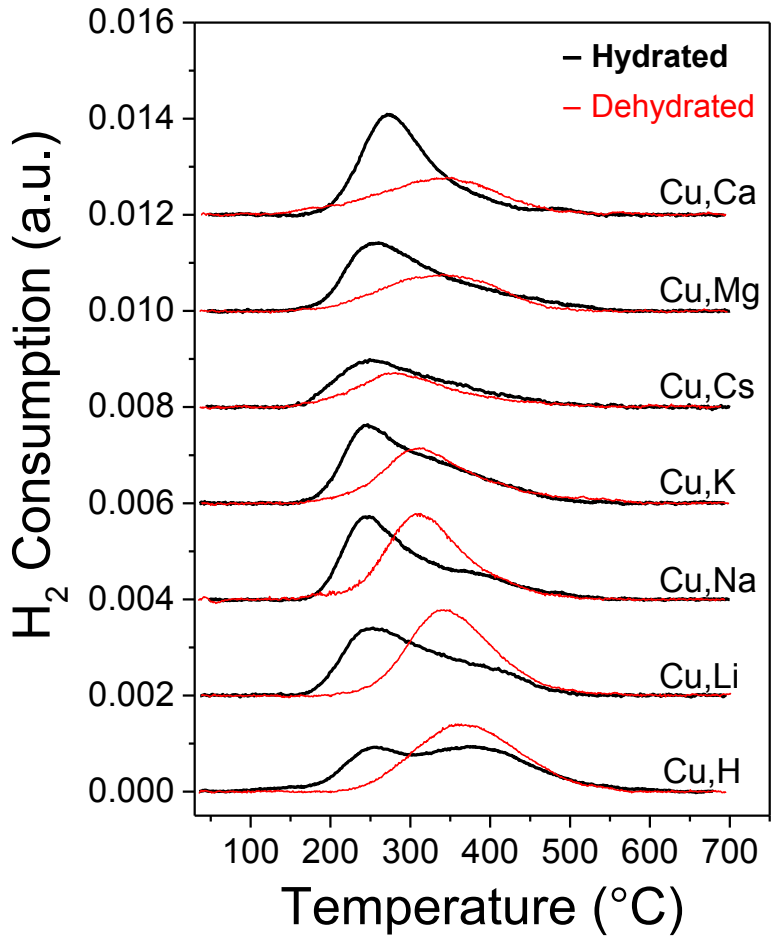
M/SSZ-13 → Cu,M/SSZ-13





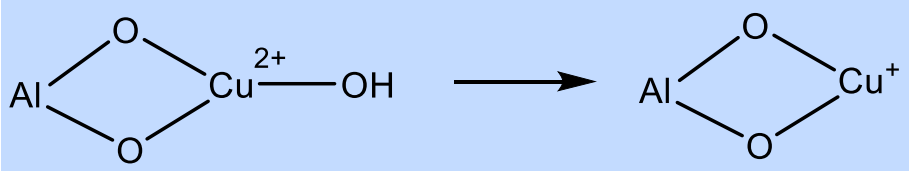
- Residual Brønsted acid site density: consistency between NH_3-TPD and ν_{OH}.
- NH_3 desorbs from Cu sites at ~320 °C.
- ν_{OH} in Cu-OH at ~3660 cm^{-1}.

H_2-TPR on Cu,M/SSZ-13



$Cu^{2+} + 1/2H_2 = Cu^{+} + H^{+}$

- Hydrated samples: samples exposed to air and saturated with moisture.
- Dehydrated samples: samples treated in an O_2/He flow at 550 °C and cooled to RT in the same flow.
- During dehydration, Cu^{2+} compete favorably against H^{+}, Li^{+} and Na^{+} for 6MR.
- However, K^{+}, Cs^{+}, Mg^{2+} and Ca^{2+} prevent all Cu^{2+} ions in finding the most favorable 6MR sites. Compete for the same sites and/or pore blocking?
- Cu^{2+} ions autoreduce if they cannot find the favorable sites.



Godiksen, et al., *J. Phys. Chem. C* 118 (2014) 23126–23138.

Effects from hydrothermal aging: ^{27}Al NMR and XRD

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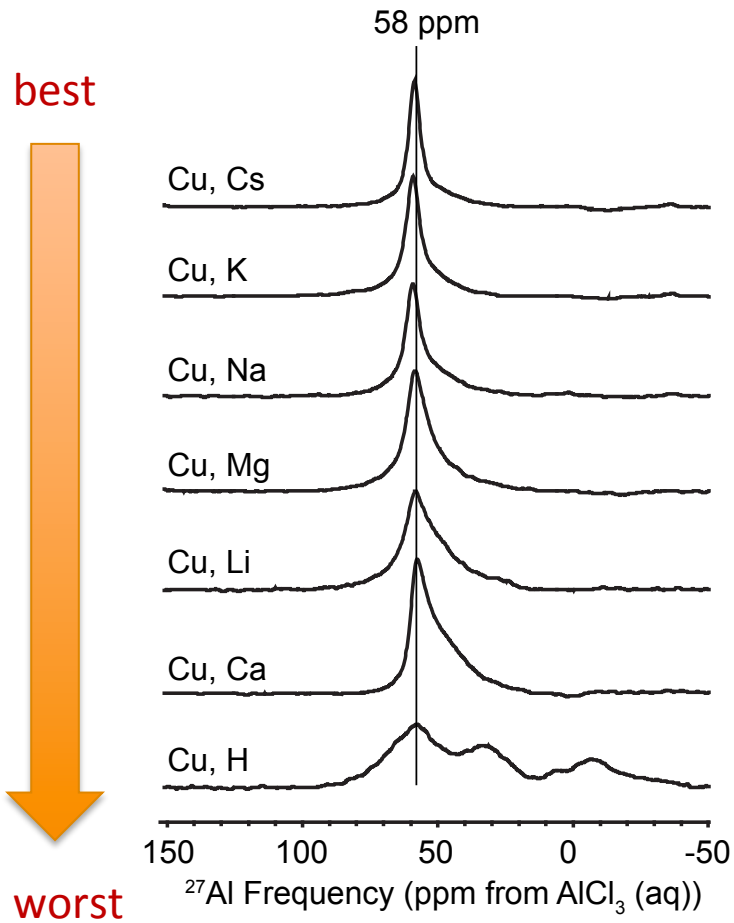

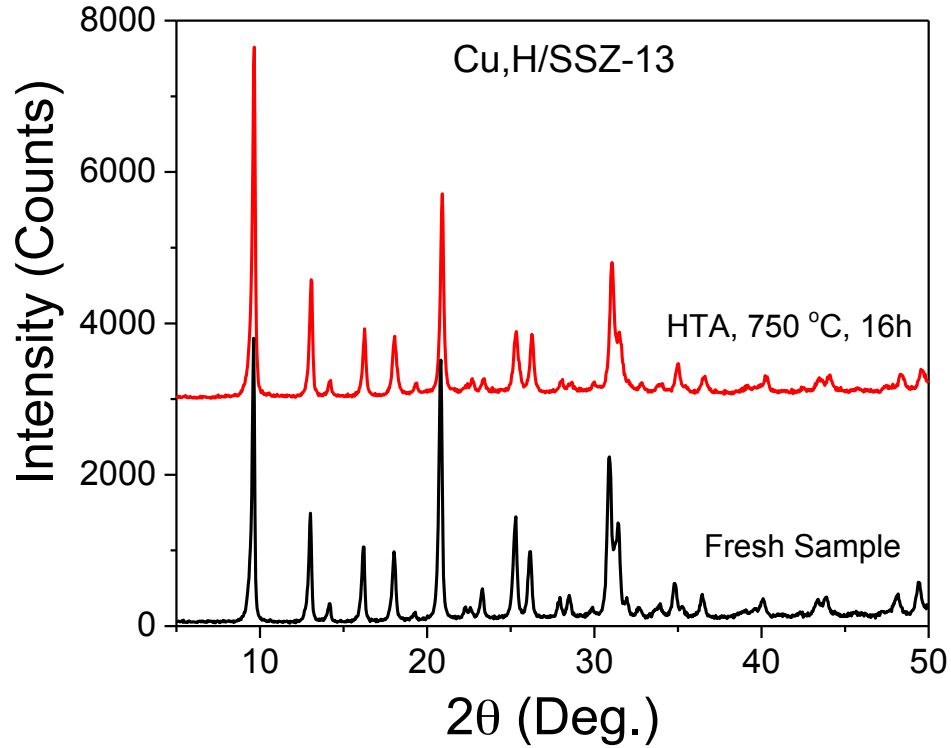

- All cocations prevent hydrolysis and dealumination of the Cu,M/SSZ-13 catalysts better than Cu,H/SSZ-13.
- Even for Cu,H/SSZ-13, no apparent degradation of the CHA framework in aging.

Effects from hydrothermal aging: NH_3-TPD

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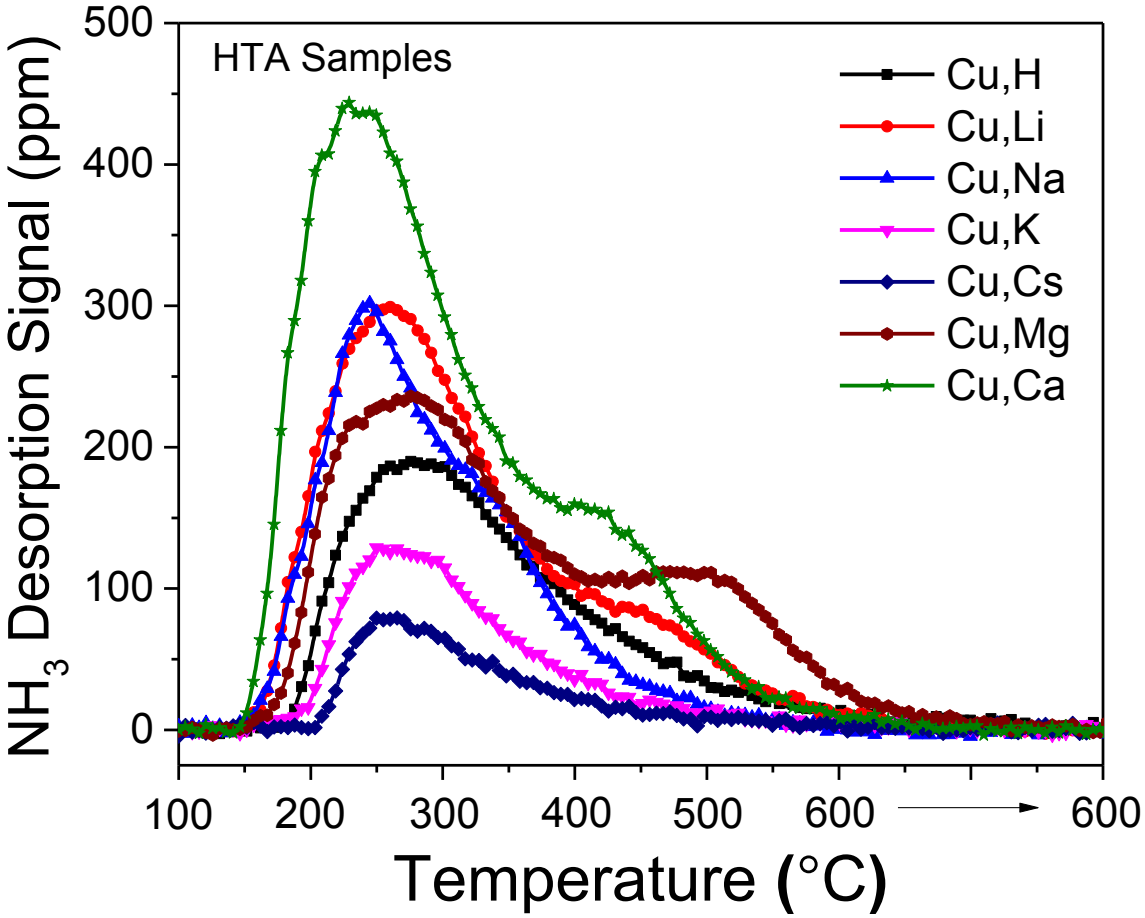
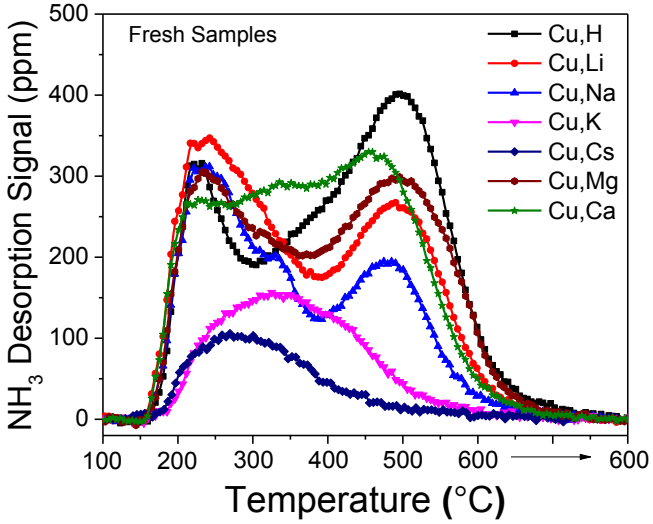
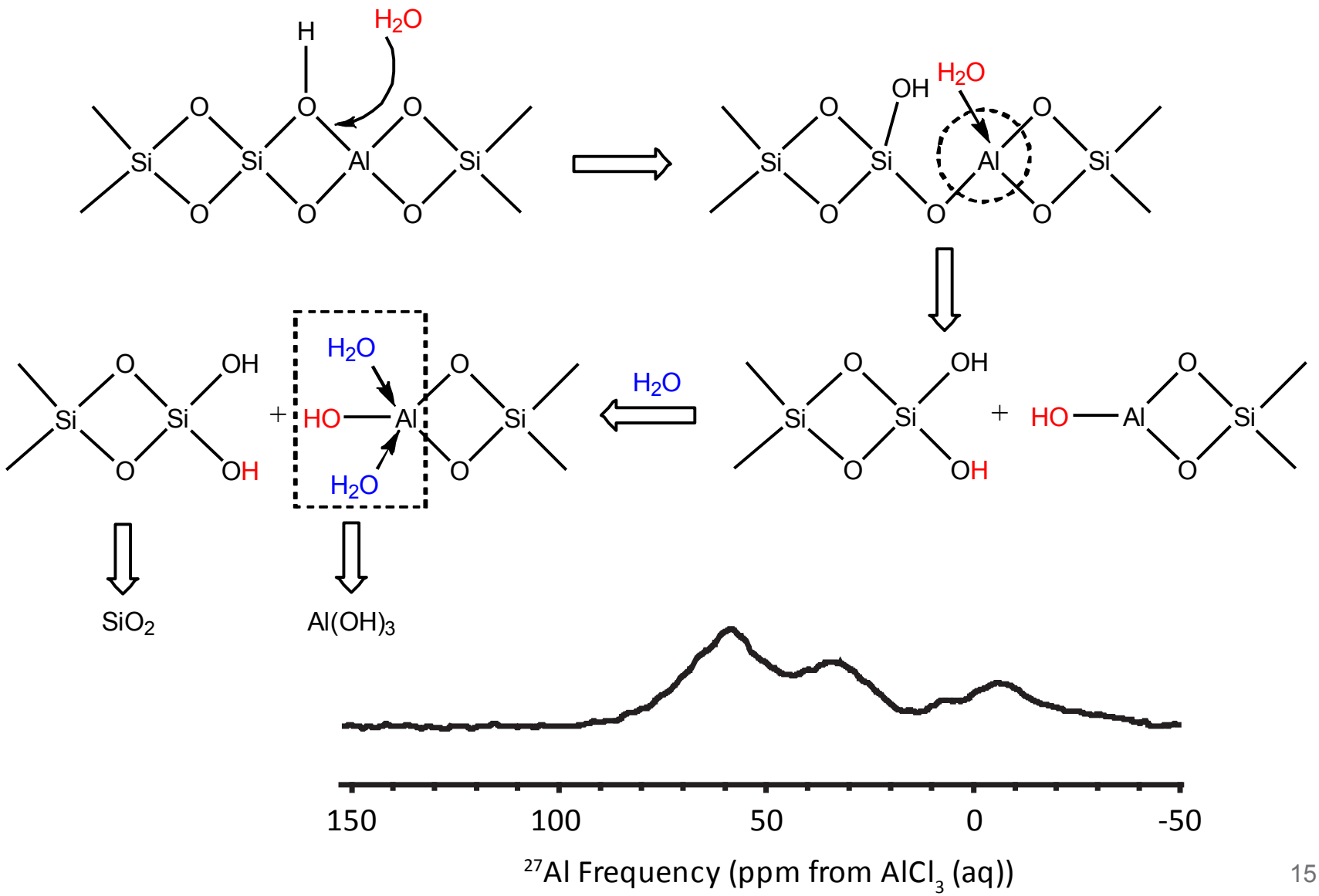




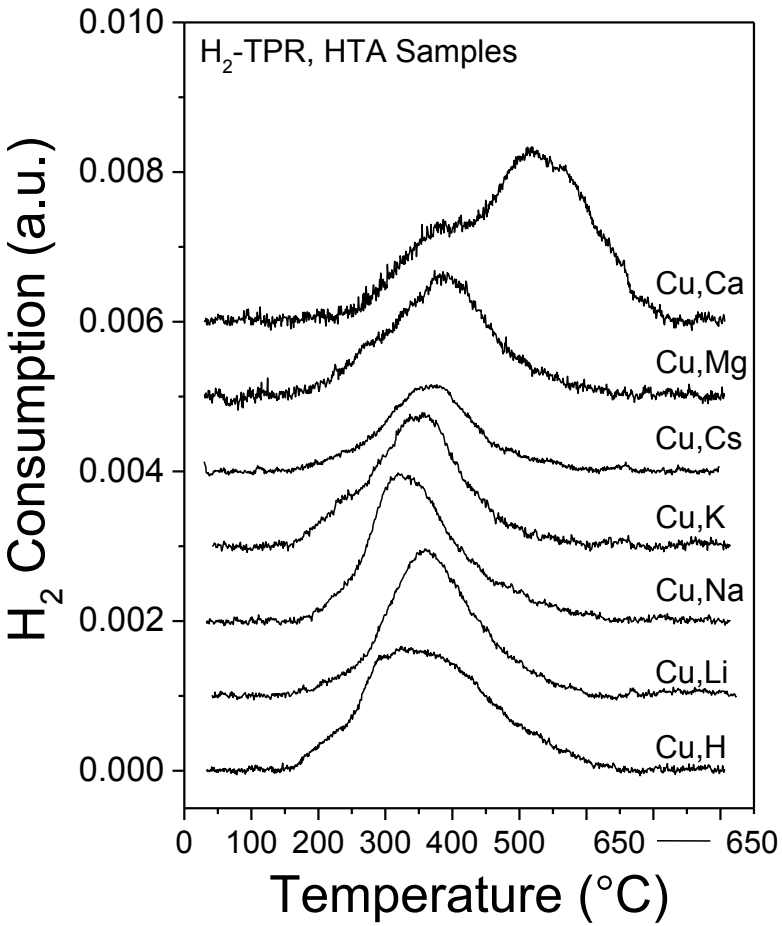
For all of the catalysts, loss of Brønsted acidity occurs during hydrothermal aging.

Loss of Brønsted acidity without apparent dealumination!

Effects from hydrothermal aging: hydrolysis pathways



Effects from hydrothermal aging: H_2-TPR



Sample	total Cu Content (wt%)	Cu^{2+} reduced to Cu^{+} before 650 °C (wt%)	Percentage (%)
Cu,H/SSZ-13	0.87	0.67	77
Cu,Li/SSZ-13	0.98	0.93	95
Cu,Na/SSZ-13	0.98	0.93	95
Cu,K/SSZ-13	0.94	0.92	98
Cu,Cs/SSZ-13	0.62	0.61	98
Cu,Mg/SSZ-13	0.71	0.56	79
Cu,Ca/SSZ-13	0.96	0.52	54

$Cu^{2+} + 1/2H_2 = Cu^{+} + H^{+}$

$Cu^{2+} + H_2 = Cu^{0} + 2H^{+}$

H_2-TPR consistent with ^{27}Al NMR.

Standard NH_3-SCR

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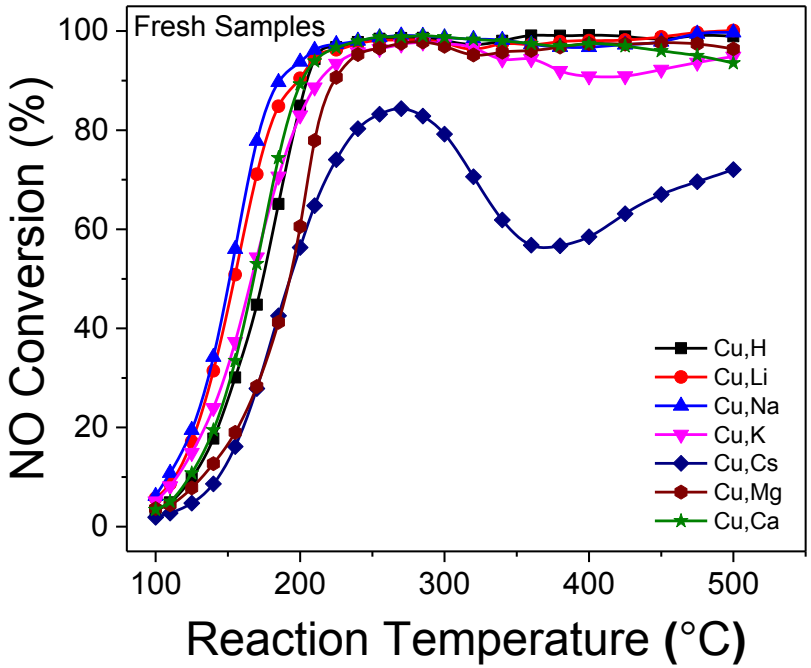
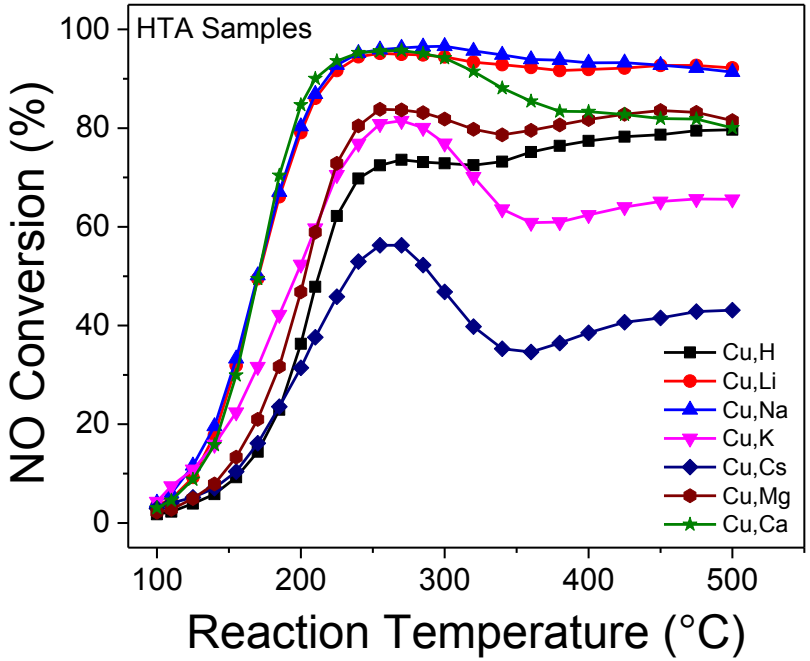
Fresh Catalysts



HTA Catalysts

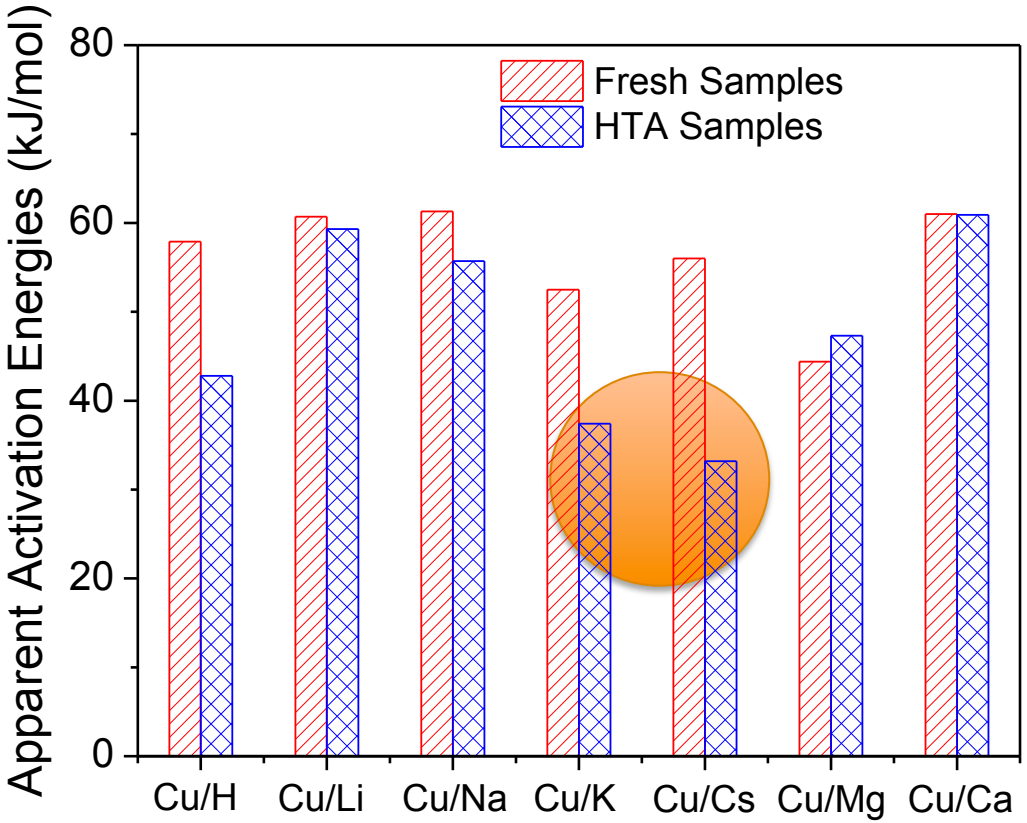


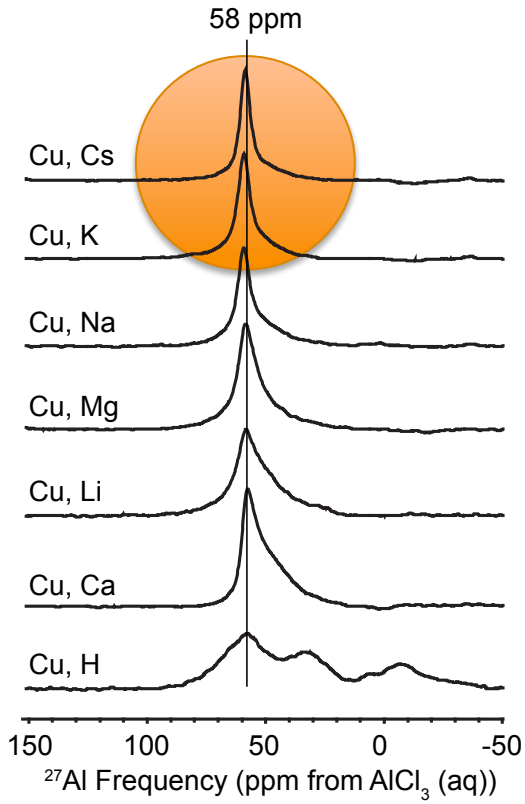
- NH_3 light-off curves mimic the NO light-off curves (i.e., excellent SCR selectivities).

T_{50}(°C)

Sample	Cu,H	Cu,Li	Cu,Na	Cu,K	Cu,Cs	Cu,Mg	Cu,Ca
Fresh	174	154	151	166	193	193	168
HTA	212	170	170	196	234	203	170

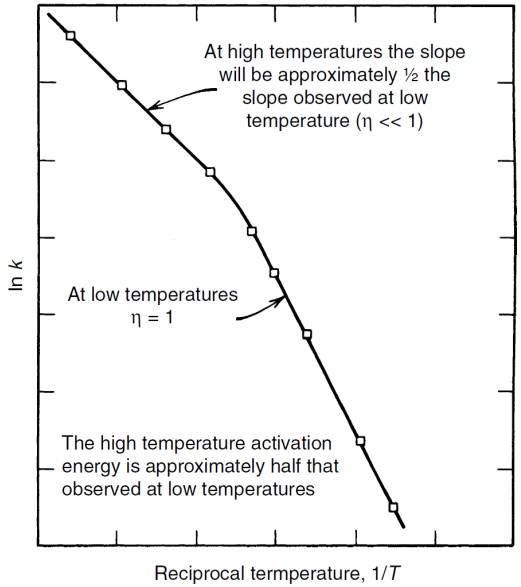
Standard NH_3-SCR



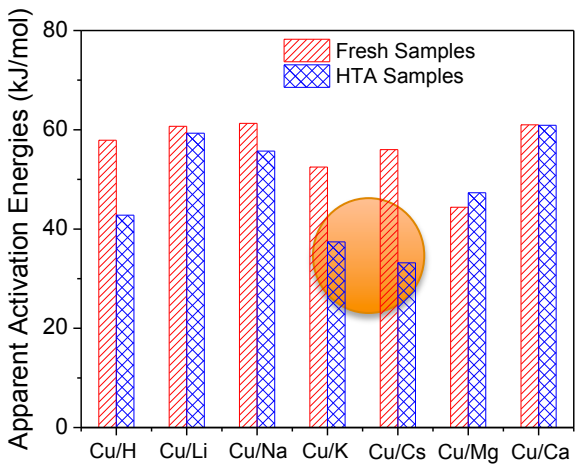


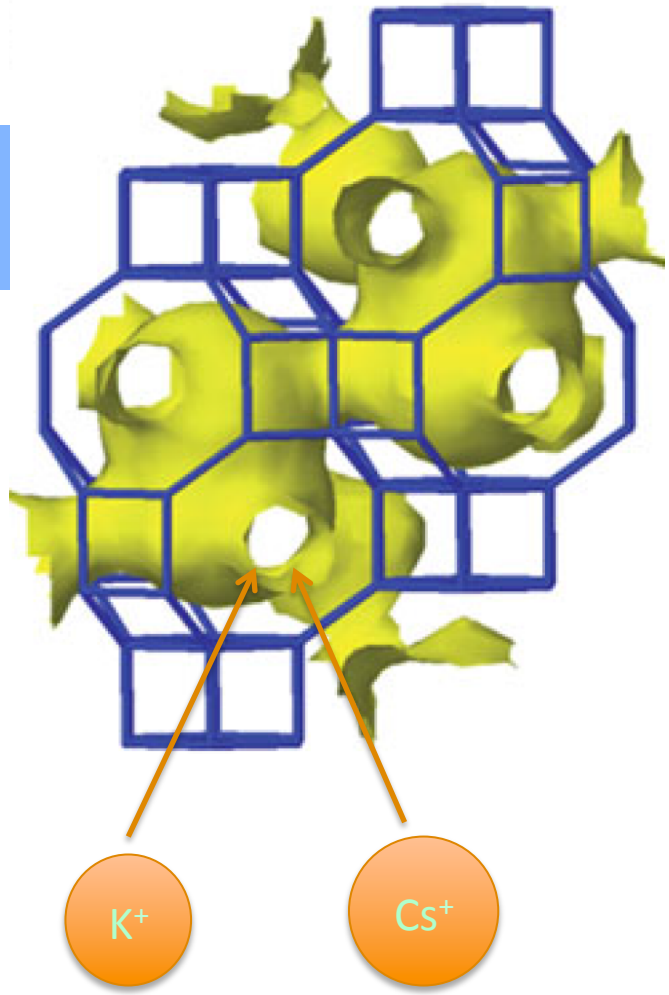
- For HTA samples, reaction results indicate redistribution of K^+ and Cs^+ cations in faces of 8MR to bring intracrystalline mass transfer limitations.

Intracrystalline mass transfer limitations



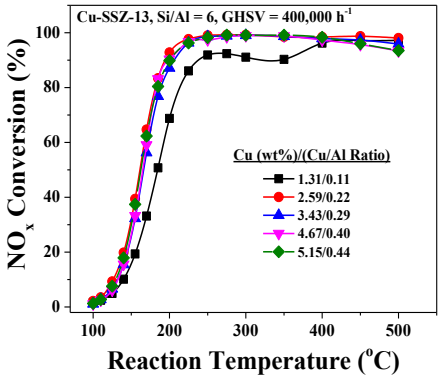
$$E_{ob} = E_a + E_D/2$$





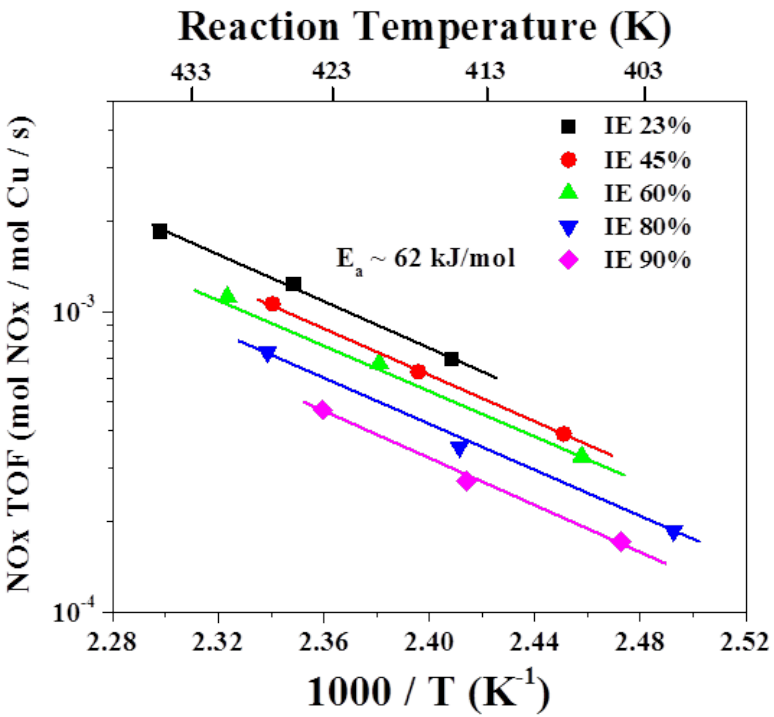
C. G. Hill, Jr., ''An Introduction to Chemical Engineering Kinetics and Reactor Design'', Wiley, NY, 1977.

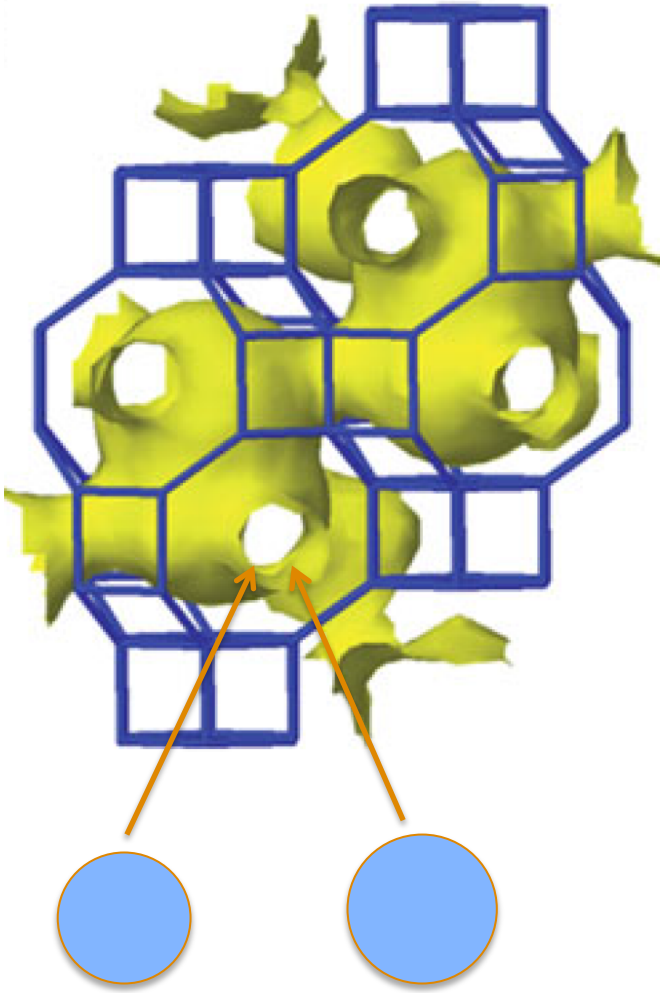
Intracrystalline mass transfer limitations



$$E_{ob} = E_a + E_D/2$$

E_D silent at high Cu loadings!

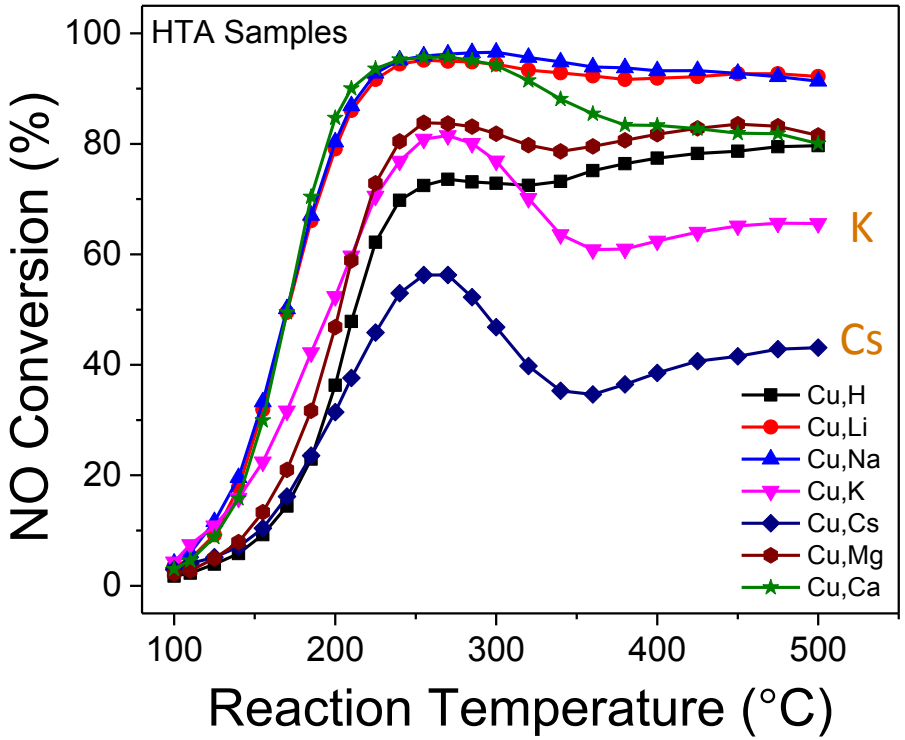


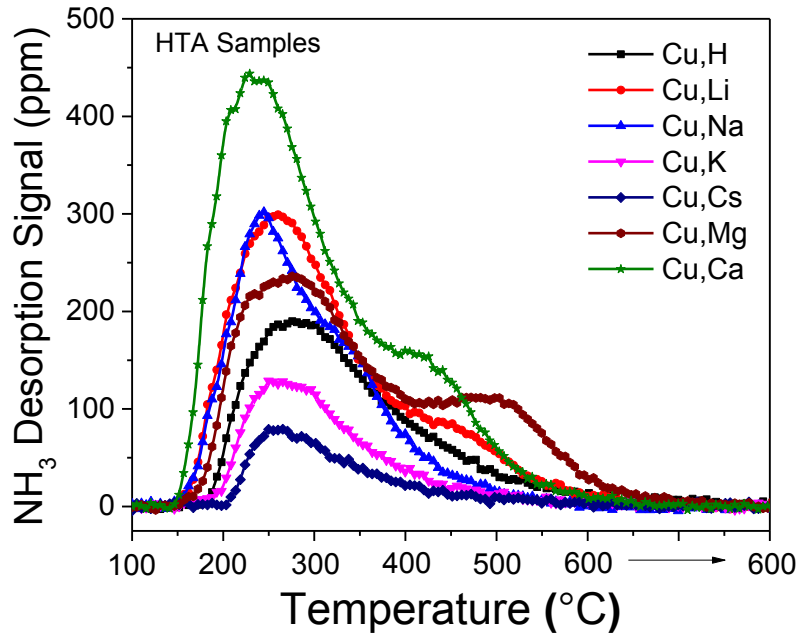


$Cu(OH)^+$ $[Cu\text{-}O\text{-}Cu]^{2+}$

Gao, et al., *Journal of Catalysis,* **300** (2013) 20–29; **319** (2014) 1–14.

NH_3 storage effects





NH_3 storage important to high-temperature SCR rates, less significant to low-temperature SCR rates.

Summary

(1) **Cocations weaken interactions between Cu-ions and the CHA framework.** This allows Cu-ions to be positioned deeper in the CHA cages and become more readily reducible. During dehydration of Cu,M/SSZ-13 samples, Li^+ and Na^+ do not prevent Cu^{2+} ions from migrating to energetically most favorable sites while other cocations, to various extents, do prevent all Cu^{2+} ions from residing in such sites. A portion of Cu^{2+} ions thus hydrolyze and even autoreduce to form Cu^+.

(2) **Cocations help to improve hydrothermal stability of Cu/SSZ-13.** This is mainly due to removal of Brønsted acid sites that are most vulnerable for hydrolysis during hydrothermal aging.

(3) **Li^+ and Na^+ cocations promote low-temperature SCR activity.** This is assigned to modifications to the redox and/or locations of Cu-ion active centers by the cocations. Large sized K^+ and Cs^+ cocations appear to decrease accessibility of Cu-ion active centers by blocking pore openings of the catalysts as evidenced from decrease in apparent activation energies, due likely to intracrystalline mass transfer limitations. At elevated reaction temperatures, catalysts with K^+ and Cs^+ cocations display decrease in NO conversion due to the lack of high-temperature NH_3 storage in these catalysts.

(4) From an application point of view, this study demonstrates that **introduction of a cocation is a useful strategy in manipulating Cu/CHA catalysts** for higher stability, higher selectivity and wider operational temperature window.

F. Gao, M. Kollár, Y. Wang, N.M. Washton, J. Szanyi, C.H.F. Peden, ACS Catalysis, submitted.

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