

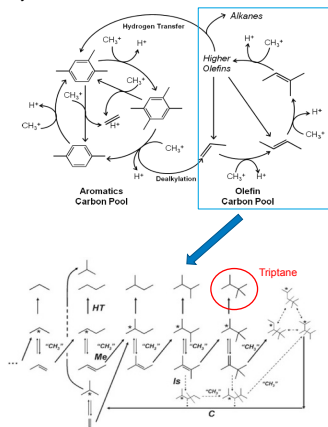
# Conversion of Dimethyl Ether to Branched Hydrocarbons Over Cu/BEA: the Roles of Lewis Acidic and Metallic Sites in H<sub>2</sub> Incorporation

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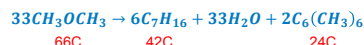
## Introduction

Dimethyl ether (DME) can be produced selectively from synthesis gas (CO and H<sub>2</sub>), which can be generated from renewable biomass feedstocks via gasification. Previous studies have reported that DME can be converted to a mixture of C<sub>4</sub>-C<sub>7</sub> hydrocarbons with high methanol/aromatic-free selectivity (~95%) over H-BEA zeolite catalysts at low temperatures (~200°C).<sup>1-3</sup> The primary C<sub>7</sub> hydrocarbon produced is 2,2,3-trimethylbutane (triptane), which is a valuable fuel additive having a research octane number of 112. The C<sub>5+</sub> product mixture is also of interest as a high-octane fuel itself; further, C<sub>4+</sub> olefin products hold potential for coupling to distillate-range fuels. There are two proposed catalytic cycles for DME homologation, olefin and aromatic, which govern the selectivity for this reaction.<sup>4,5</sup>



(1) Ahn, J. H.; Tomel, B.; Iglesia, E. *Angew Chem Int Ed* 2009, 48, 3814.  
(2) Simonetti, D. A.; Ahn, J. H.; Iglesia, E. *J. Catal* 2011, 277, 173.  
(3) Hazari, N.; Iglesia, E.; Labinger, J. A.; Simonetti, D. A. *Acc Chem Res* 2012, 45, 653.  
(4) Hsu, S.; Shan, A. *J. Catal* 2012, 290, 186.  
(5) Hsu, S.; Shan, A. *ACS Catal* 2012, 2, 18.

**Challenge #1:** DME homology to form alkanes is a hydrogen-deficient process, resulting in the formation of alkylated aromatic residues such as hexamethylbenzene (HMB). These byproducts reduce yield, may cause catalyst deactivation, and limit catalyst lifetime.<sup>1-3</sup> Consider the stoichiometric homology of DME to triptane, which forces a 36% loss in C yield to HMB:



**Challenge #2:** Catalytic dehydrogenation of cracked products like isobutane is not observed over HBEA at reaction conditions (180-220 °C) and alkanes are generally inactive in the catalytic cycle at these temperatures, leading to significant production of C<sub>4</sub> terminal products.

## Goals and Hypotheses

The **goals** of this work are to:

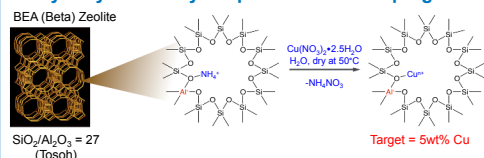
- Investigate H-atom management during DME homology
- Develop a multi-functional metal-modified BEA zeolite catalyst capable of:
  - Activating H<sub>2</sub>
  - Incorporating hydrogen into the desired products
  - Reducing deactivation
  - Increasing selectivity to C<sub>7</sub> products

Our **hypotheses** are:

- The addition of a Lewis-acidic metal center will lower the energetic barrier for H<sub>2</sub> activation and/or hydrogen abstraction from alkanes
- The addition of a metal hydrogenation center will facilitate dissociation of H<sub>2</sub> to H<sub>ads</sub> making it locally 'available' for reaction

## Experimental Details

### Catalyst Synthesis by Incipient Wetness Impregnation

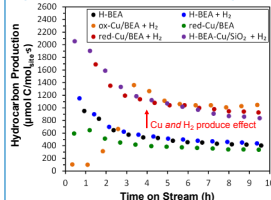


### Catalytic Testing

- Activation:
  - H-BEA: 500°C in dry air
  - Cu/BEA: 500°C in dry air (ox-Cu/BEA) followed by 300°C in H<sub>2</sub> (red-Cu/BEA)
  - H-BEA mixed with Cu/SiO<sub>2</sub>: oxidized in air and reduced in H<sub>2</sub> as above
- Fixed-bed, 0.69 g<sub>cat</sub>, 200°C, 1atm, 24h TOS, X<sub>DME</sub> < 15%
- Reaction feed:
  - No H<sub>2</sub>: 7.1sccm DME, 4.9sccm Ar
  - H<sub>2</sub>: 7.1sccm DME, 7.1sccm H<sub>2</sub>, 1sccm Ar

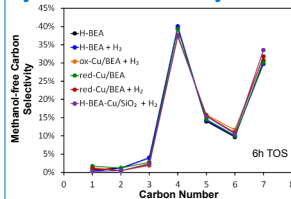
## Catalytic Testing

### Hydrocarbon Productivity

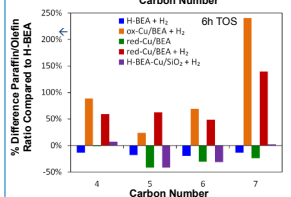


- Similar induction profiles observed
- Cu addition increased rate per acid site by 1.5-2 times when H<sub>2</sub> present
- Independent of whether Cu on zeolite or separated

### Hydrocarbon Selectivity

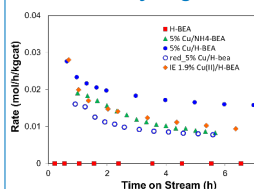


- Carbon number distribution was similar for all experiments
- Addition of Cu caused a significant increase in the paraffin/olefin ratios for C<sub>4</sub>-C<sub>7</sub>, but only when on BEA and H<sub>2</sub> present
- Paraffin/Olefin decreases when Cu present and H<sub>2</sub> absent or when Cu separate from BEA
- Cu/BEA shifted preference toward the olefin catalytic cycle
- Cu may remove ethylene as ethane, preventing it from entering the aromatization pathway



Formation rate ratio	$r_{C_7}$	$r_{C_6}$	$r_{C_{HMB}}$
	6h TOS	X <sub>CuBE</sub> = 11%	Total
Experiment			
H-BEA	0.23	0.16	0.12
H-BEA + H <sub>2</sub>	0.21	0.15	0.07
ox-Cu/BEA + H <sub>2</sub>	0.08	0.07	0.03
red-Cu/BEA + H <sub>2</sub>	0.24	0.24	0.14
red-Cu/BEA + H <sub>2</sub>	0.08	0.08	0.04
H-BEA-Cu/SiO <sub>2</sub> + H <sub>2</sub>	0.08	0.09	0.03

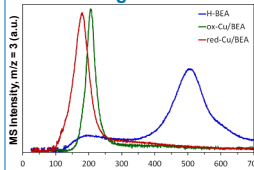
### Isobutane Dehydrogenation at 300°C



- 1% isobutane in He feed
- H-BEA inactive for recombinative H<sub>2</sub> abstraction
- Cu-containing catalysts produced H<sub>2</sub>
- Cu loading and chemical state impact activity

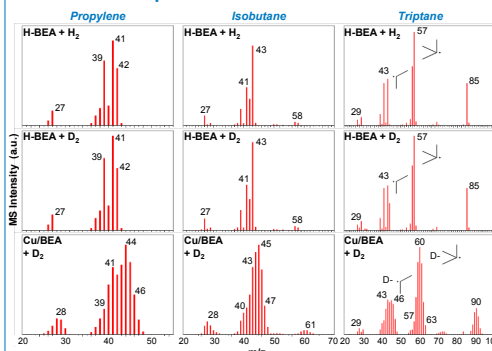
## Isotopic Experiments

### H-D Exchange



- Red-Cu/BEA and ox-Cu/BEA activated D<sub>2</sub> and evolved HD at a significantly lower temperature than H-BEA
- Total amount of HD evolved was nearly identical for all catalysts suggesting exchange of only -O-D for -O-H at Brønsted sites

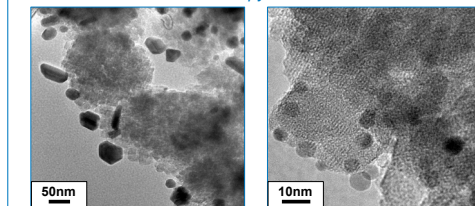
### Deuterium Incorporation



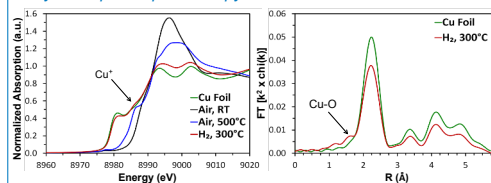
## Catalyst Characterization

### Structural and Chemical Characterization

#### Transmission Electron Microscopy



#### X-ray Absorption Spectroscopy

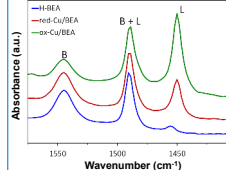


Treatment	Components	Ratio (%)
Air, 500°C	Cu(II)-zeolite	55
	CuO	45
H <sub>2</sub> , 300°C	Cu(0)	86
	Cu(II)-zeolite	10
	Cu(I)-zeolite	4

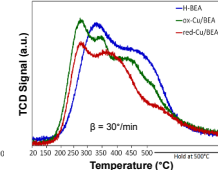
Treatment	Scatter	CN	R (Å)	DWF (Δσ <sup>2</sup> )	ΔE <sub>0</sub> (eV)
Air, 500°C	Cu-O	3.6	1.93	0.001	-1.70
H <sub>2</sub> , 300°C	Cu-Cu	9.5	2.54	0.001	0.92
	Cu-O	1.3	1.92	0.001	0.32

### Surface Analysis

#### Pyridine-DRIFTS



#### Ammonia TPD



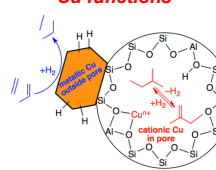
Catalyst	Total Acid Sites (μmol/g)	Brønsted Acid Sites (μmol/g)	Lewis Acid Sites (μmol/g)	Brønsted/Lewis Ratio
H-BEA	1642	1550	92	16.8
ox-Cu/BEA	2058	772	1286	0.6
red-Cu/BEA	1918	1337	581	2.3

- red-Cu/BEA possessed both metallic and cationic Cu sites
- Cationic Cu species introduced significant Lewis acidity and modified the distribution of weak and strong acid sites
- Metallic Cu was present on the outside of the BEA while cationic Cu was present within the pores

## Summary and Conclusions

- Cu/BEA achieved a two-fold increase in HC productivity when H<sub>2</sub> cofed to reactor
- Cu/BEA shifted preference toward products formed by the olefin catalytic cycle over the aromatic catalytic cycle
- The addition of Cu served to incorporate H<sub>2</sub> into reaction products without significantly impacting paraffin + olefin carbon selectivity

### Cu functions



- Metallic Cu on the H-BEA surface hydrogenated olefins, increasing paraffin selectivity
- H<sub>2</sub> activated on metallic Cu replenished protons
- Lewis acid cationic Cu within the zeolite pores promoted hydrogen abstraction from alkane products, creating a pathway for incorporation into the chain growth pool

More information: Schaidle, J.A.; Ruddy, D.A.; Habas, S.E.; Pan, M.; Zhang, G.; Miller, J.T.; Hensley, J.E. *ACS Catal* 2015, 5, 1794