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## **Synthesis of higher alcohols from syngas over K-promoted Cu/Zn/Al catalysts**



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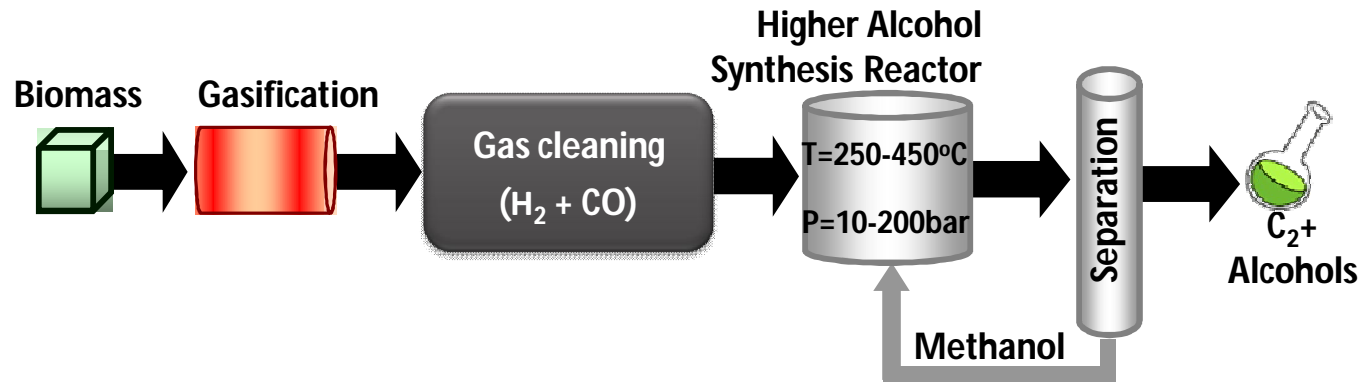
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## Introduction



### Uses

- ❖ Fuel additives for octane or cetane enhancement
- ❖ Intermediates for MTBE production

### Catalytic materials used so far

- (1) Modified high and low temperature methanol synthesis catalysts based on ZnO/Cr<sub>2</sub>O<sub>3</sub> and Cu-ZnO/Al<sub>2</sub>O<sub>3</sub> respectively
- (2) Modified Co and Fe Fischer-Tropsch catalysts
- (3) Mo-based materials in oxidic and sulfided form

*Alkali promotion (Li, Na, K and Cs) was found to improve selectivity to oxygenates*

### Challenge

**Low yields and poor catalyst selectivity!**

## Scope of Study

Production of higher alcohols over K-promoted and unpromoted Cu/Zn/Al catalysts

Investigation of the effect of

**(1) Cu, Zn and Al molar composition**

**(2) K-promotion**

on the physicochemical characteristics and the catalytic behavior in higher alcohols formation

### Catalysts

Cu<sub>60</sub>/Zn<sub>30</sub>/Al<sub>10</sub>

Cu<sub>60</sub>/Zn<sub>30</sub>/Al<sub>10</sub>/K<sub>0.3</sub>

Cu<sub>45</sub>/Zn<sub>45</sub>/Al<sub>10</sub>

Cu<sub>45</sub>/Zn<sub>45</sub>/Al<sub>10</sub>/K<sub>0.5</sub>

Cu<sub>33</sub>/Zn<sub>33</sub>/Al<sub>33</sub>

Cu<sub>33</sub>/Zn<sub>33</sub>/Al<sub>33</sub>/K<sub>0.5</sub>

### Preparation method

- ❖ Co-precipitation of Cu, Zn and Al from aqueous solutions of nitrate precursors with Na<sub>2</sub>CO<sub>3</sub> solution (1mol/l) @ 70°C and pH of 6-7
- ❖ Drying @ 120°C/24h
- ❖ Calcination @ 350°C/air/4h
- ❖ K promotion: dry impregnation with K<sub>2</sub>CO<sub>3</sub> aqueous solution - Calcination @ 350°C/air/4h

### Characterization

XRD

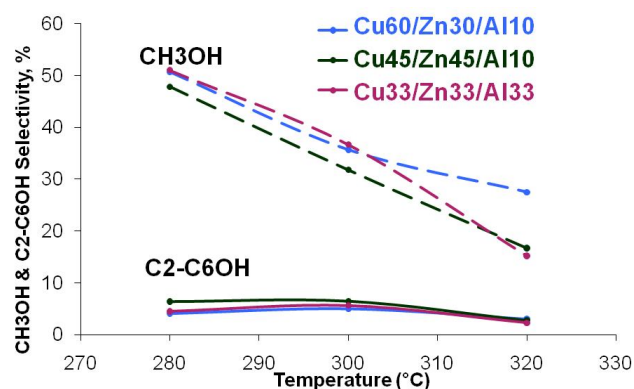
BET

ICP

H<sub>2</sub>-TPR

# Catalyst Evaluation

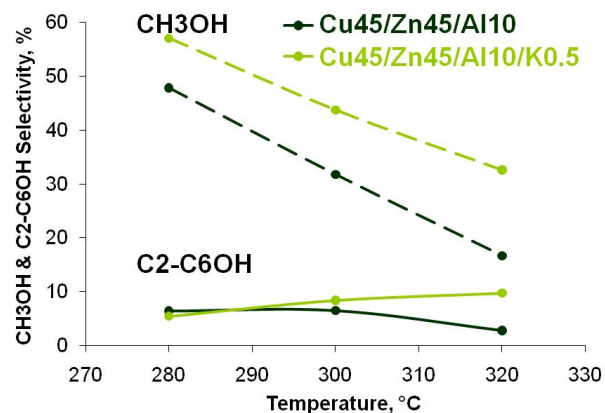
## 1. Effect of Cu/Zn/Al molar Composition



- ❖ Pretreatment: reduction with H<sub>2</sub> at 350°C/3h
- ❖ Pressure: 40bar
- ❖ Inlet feed composition: CO/H<sub>2</sub>/N<sub>2</sub>=21%-43%-36%
- ❖ W/F ratio: 0.64g-s/cm<sup>3</sup>

- ❖ Main reaction products: **methanol** and **CO<sub>2</sub>**
- ❖ Variation of the molar composition induces only **small changes** to the catalytic performance
- ❖ Optimum Catalyst: Cu45/Zn45/Al10

## 2. Effect of K-promotion



- ❖ The effect of **K-promotion is beneficial** to the formation of higher alcohols
- ❖ K addition decreased CO conversion and increased **C<sub>2</sub>-C<sub>5</sub> alcohols selectivity** in expense to hydrocarbons formation