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Title:

Hydrogen Production via Dimethyl Ether Steam Reforming

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Hydrogen Production via Dimethyl Ether Steam Reforming

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Inroduction

This study investigates dimethyl ether (DME) steam reforming for the generation of hydrogen rich fuel cell feeds for fuel cell applications. Methanol has long been considered as a fuel for the generation of hydrogen rich fuel cell feeds due to its high energy density, low reforming temperature, and zero impurity content. However, it has not been accepted as the fuel of choice due its current limited availability, toxicity and corrosiveness. While methanol steam reforming for the generation of hydrogen rich fuel cell feeds has been extensively studied, the steam reforming of DME, $CH_3OCH_3 + 3H_2O = 2CO_2 + 6H_2$, has had limited research effort.

DME is the simplest ether (CH_3OCH_3) and is a gas at ambient conditions. DME has physical properties similar to those of LPG fuels (i.e. propane and butane), resulting in similar storage and handling considerations. DME is currently used as an aerosol propellant and has been considered as a diesel substitute due to the reduced NOx, SOx and particulate emissions. DME is also being considered as a substitute for LPG fuels, which is used extensively in Asia as a fuel for heating and cooking, and naptha, which is used for power generation. The potential advantages of both methanol and DME include low reforming temperature, decreased fuel processor startup energy, environmentally benign, visible flame, high heating value, and ease of storage and transportation. In addition, DME has the added advantages of low toxicity and being non-corrosive. Consequently, DME may be an ideal candidate for the generation of hydrogen rich fuel cell feeds for both automotive and portable power applications.

The steam reforming of DME has been demonstrated to occur through a pair of reactions in series, where the first reaction is DME hydration followed by MeOH steam reforming to produce a hydrogen rich stream. The reaction scheme is

$$CH_3OCH_3 + H_2O \rightleftharpoons 2CH_3OH \quad \text{DME-Hydration}$$
$$\underline{CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2 \quad \text{MeOH-SR}}$$
$$CH_3OCH_3 + 3H_2O \rightleftharpoons 2CO_2 + 6H_2 \quad \text{DME-SR}$$

DME-hydration occurs over an acid catalyst (e.g. γ-alumina), while the MeOH-SR reaction occurs over the traditional Cu/Zn/Al2O3 catalysts. Therefore, DME-SR requires a composite catalyst or a physically mixed catalyst charge that contains both of these agents.

Scope of Research

- Investigate catalyst acidity on DME hydration characteristics, $CH_3OCH_3 + H_2O \rightleftharpoons 2CH_3OH$
- Investigate physical mixtures of commercial $Cu/Zn/Al_2O_3$ and acid catalysts on the DME-SR process, $CH_3OCH_3 + 3H_2O \rightleftharpoons 2CO_2 + 6H_2$
- Investigate novel composite Cu/Zn catalyst preparations prepared via incipient wetness with varying degrees of catalyst support acidity
- Investigate DME decomposition characteristics over various supports and catalysts

Results

Physical mixtures of commercial $Cu/Zn/Al_2O_3$ (BASF K3-110) and acid catalysts (e.g. γ-alumina, ZrO2, ZSM-5, etc..) resulted in complete conversion of DME via steam reforming producing a hydrogen rich stream at temperatures less 400°C. The acid component is needed for the DME hydration reaction while the $Cu/Zn/Al_2O_3$ is needed for the methanol steam reforming reaction. DME-SR did not proceed over commercial $Cu/Zn/Al_2O_3$ catalysts.

In the absence of water, DME decomposition occurred over all catalysts and supports tested for temperatures less than 500°C. The main products were methane, carbon dioxide, hydrogen, carbon monoxide and carbon. However, in the presence of water DME decomposition is suppressed.

Conclusions

Conversion of DME to a hydrogen rich fuel cell feed was observed over physical mixtures of acid catalysts and commercial $Cu/Zn/Al_2O_3$ catalysts within the temperature range of 250°C to 400°C. DME decomposition was also observed to occur within the same temperature range of DME-SR. DME is a viable alternative fuel to methanol, ethanol, gasoline and methane for producing a hydrogen rich fuel cell feed stream for both portable power and transportation applications.

Hydrogen Production from the Steam Reforming of Dimethyl Ether and Methanol

205th ECS Meeting

San Antonio, TX; May 09 - 13

Troy A. Semelsberger and Rodney L. Borup

DOE Program Manager: Nancy Garland

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Objectives and Scope

Fuels for Fuel Cells

- Fuel cells show promise for high efficiency
- Fuel cells have highest power density with operation on hydrogen
- Reforming of traditional hydrocarbons (gasoline, diesel, NG) require high temperatures, complicated systems, start-up difficulties
- Low temperature reforming have inherent advantages

Objectives

- Determine the feasibility reforming DiMethyl Ether (DME) for automotive and portable power-fuel cell applications

Scope

- Does DME meet the criteria of alternative fuels?
- Are there any thermodynamic limitations on DME-SR?
- At what temperatures, experimentally, does DME-SR proceed?
    - By what reforming mechanism does DME proceed?
- What products are observed during DME-SR?

DME: A Multipurpose Fuel
Dimethyl ether ($CH_3 - O - CH_3$)

- **Transportation**
  - **Diesel Substitute (cetane#: 55-60)**
    - **Diesel Additive**
    - **Demonstrated lower diesel emissions**
      - **Particulates, SOx, NOx**
  - **Hydrogen carrier for Fuel Cells?**

Source: Hansen, J, *DME as a Transportation Fuel*

- **Domestic Fuel**
  - **Liquefied Petroleum Gas (LPG) Alternative**
    - **Household Heating Fuel**
    - **Cooking Fuel**
- **Power Generation**
  - **Gas Turbine Fuel**
  - **Stationary Power via Fuel Cells**

Courtesy of NKK Corp.

Criteria for Alternative Fuels Applied to DME

- Methanol reforming has been examined for on-board hydrogen production
- MeOH concerns include infrastructure, toxicity, water contamination, etc.
  - DME addresses the concerns with methanol

DME Characteristics

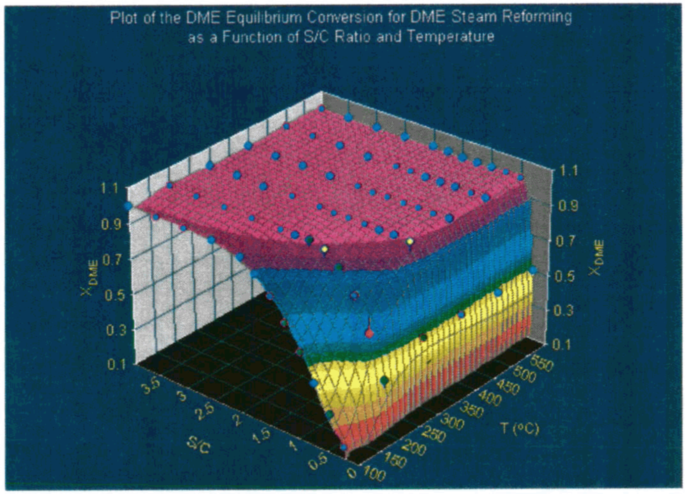
- **Health**
  - Used as an aerosol propellant
    - Non-toxic
    - Non-Carcinogenic
    - Non-Mutagenic
    - Non-Teratogenic
- **Infrastructure**
  - DME can be distributed using the pre-existing infrastructure existing for natural gas and LPG fuels
  - Japan potentially implementing DME (by end of decade?)
- **Safety**
  - Analogous to LPG
    - Storage and handling
    - Non-corrosive
    - Visible blue flame
    - Non-peroxide forming
    - No odorant needed

Criteria for Alternative Fuels Applied to DME

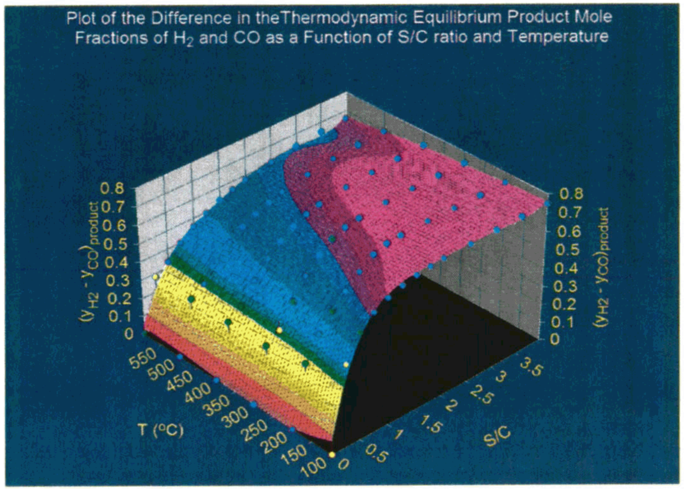
- **Environment and Emissions**
  - Ozone depletion potential of zero, ODP = 0
  - Never reaches stratosphere (ozone layer)
  - Global warming potential (GWP) – negligible
  - Zero potential for ground water contamination or spills
  - Significant reductions in emissions (as diesel fuel:)
    - Particulate matter
    - Carbon monoxide
    - Reduced NOx and Sox

- **National Security**
  - Fuel source or raw materials can be non-petroleum
    - Renewables or Fossil Fuels

DME-SR Thermodynamics



Plot of the DME Equilibrium Conversion for DME Steam Reforming as a Function of S/C Ratio and Temperature



Plot of the Difference in theThermodynamic Equilibrium Product Mole Fractions of H_2 and CO as a Function of S/C ratio and Temperature

$$CH_3OCH_3 + 3H_2O \rightleftharpoons 2CO_2 + 6H_2$$

$$\Delta H_r^o = +135\ {}^{kJ}\!/_{mol}$$

$$\sim 100\%\ X_{DME} = \begin{cases} T \geq 200\ {}^oC \\ {}^S\!/_C \geq 1 \end{cases}$$

The DME-SR process exhibits a wide range of operating conditions resulting in 100% DME conversion. (P = 1 atm)

No Thermodynamic Limitations:
→ Exception is CH_4

What We Know

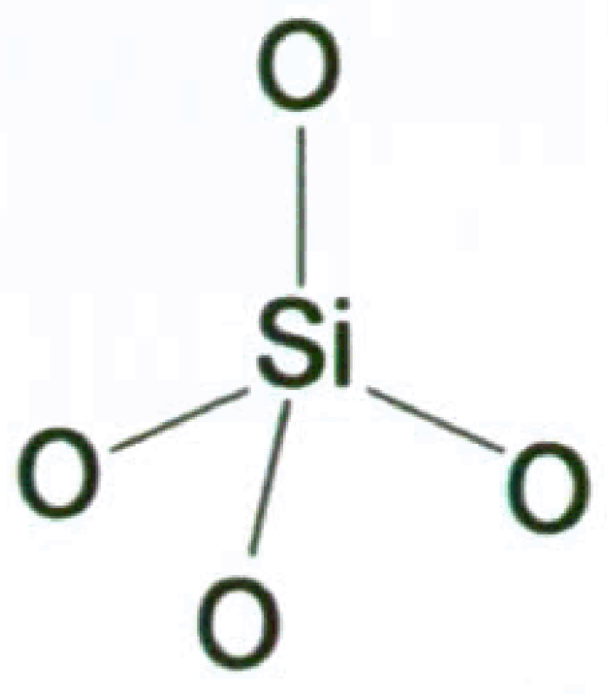
- DME hydration occurs over acid catalysts, ZrO_2 and γ-Al_2O_3

$$CH_3OCH_3 + H_2O \underset{Catalyst}{\overset{Acid}{\rightleftharpoons}} 2CH_3OH$$

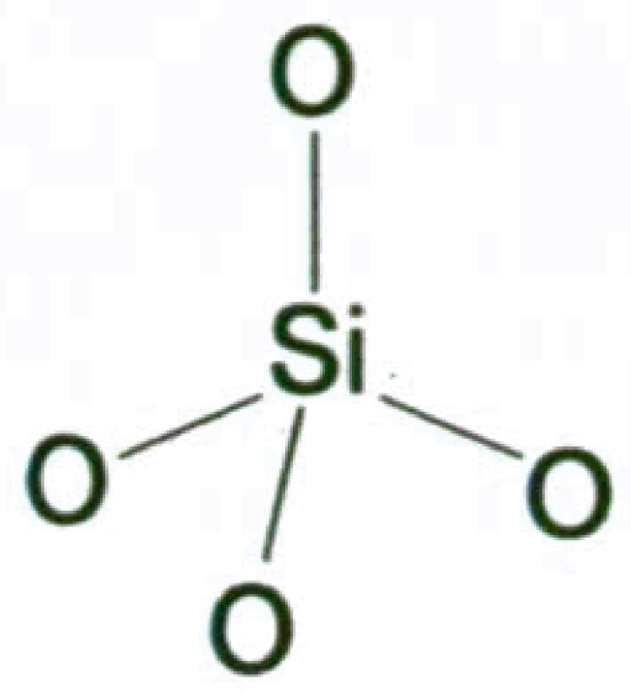
- DME decomposition occurs over BASF K3-110, ZrO_2 and γ-Al_2O_3

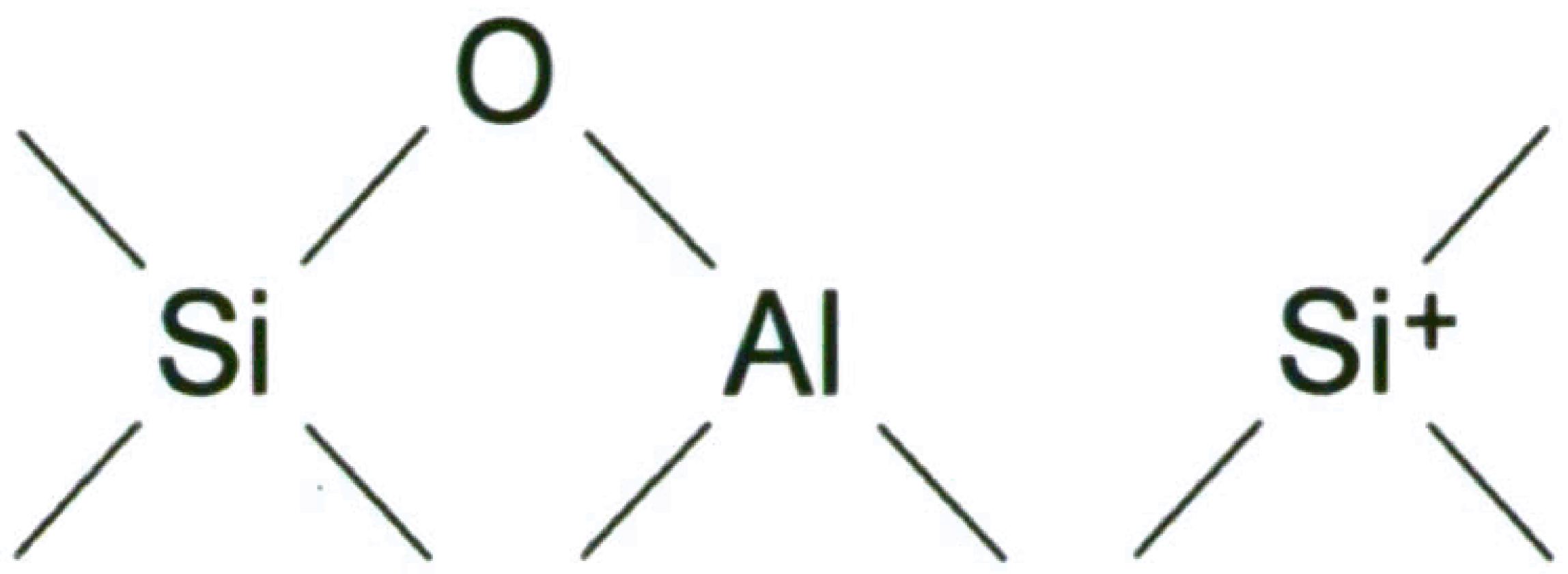
- DME hydration and reforming occurs over Cu/ZnO diluted with γ-Al_2O_3

$$CH_3OCH_3 + 3H_2O \underset{Catalyst}{\overset{Acid}{\rightleftharpoons}} 2CH_3OH + 2H_2O \overset{Cu/Zn}{\rightleftharpoons} 6H_2 + 2CO_2$$



Zeolite Background

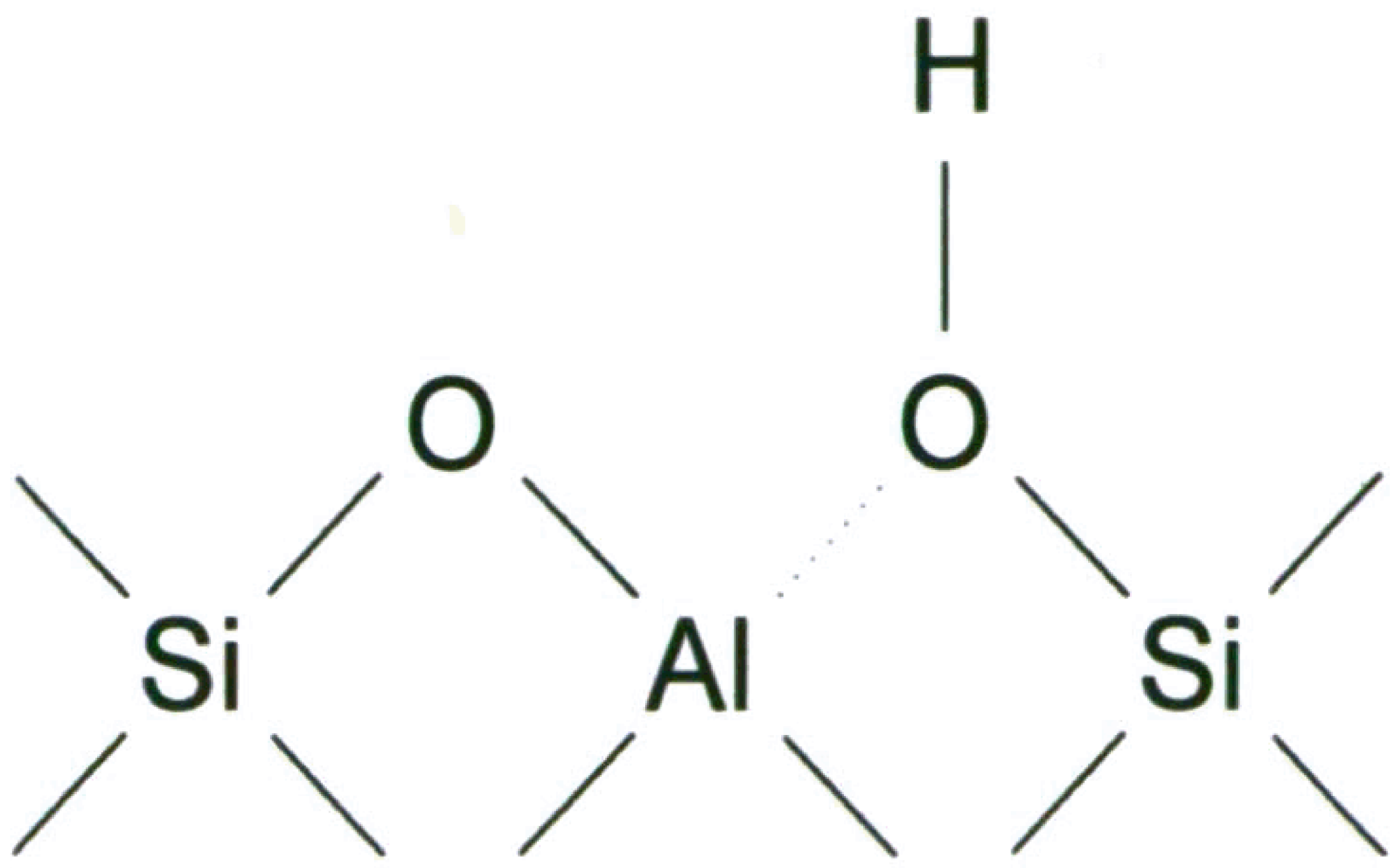




Lewis Acid Site

Strength of acid sites is a function of Si/Al ratio;

Zeolite Variables
Type
Si/Al Ratio



Bronsted Acid Site

$$\uparrow(\downarrow)\,{}^{Si}\!\!/_{Al} \Rightarrow \begin{cases} \downarrow(\uparrow)\ \#Acid\ Sites \\ \uparrow(\downarrow)\ Acid\ Site\ Strength \end{cases}$$

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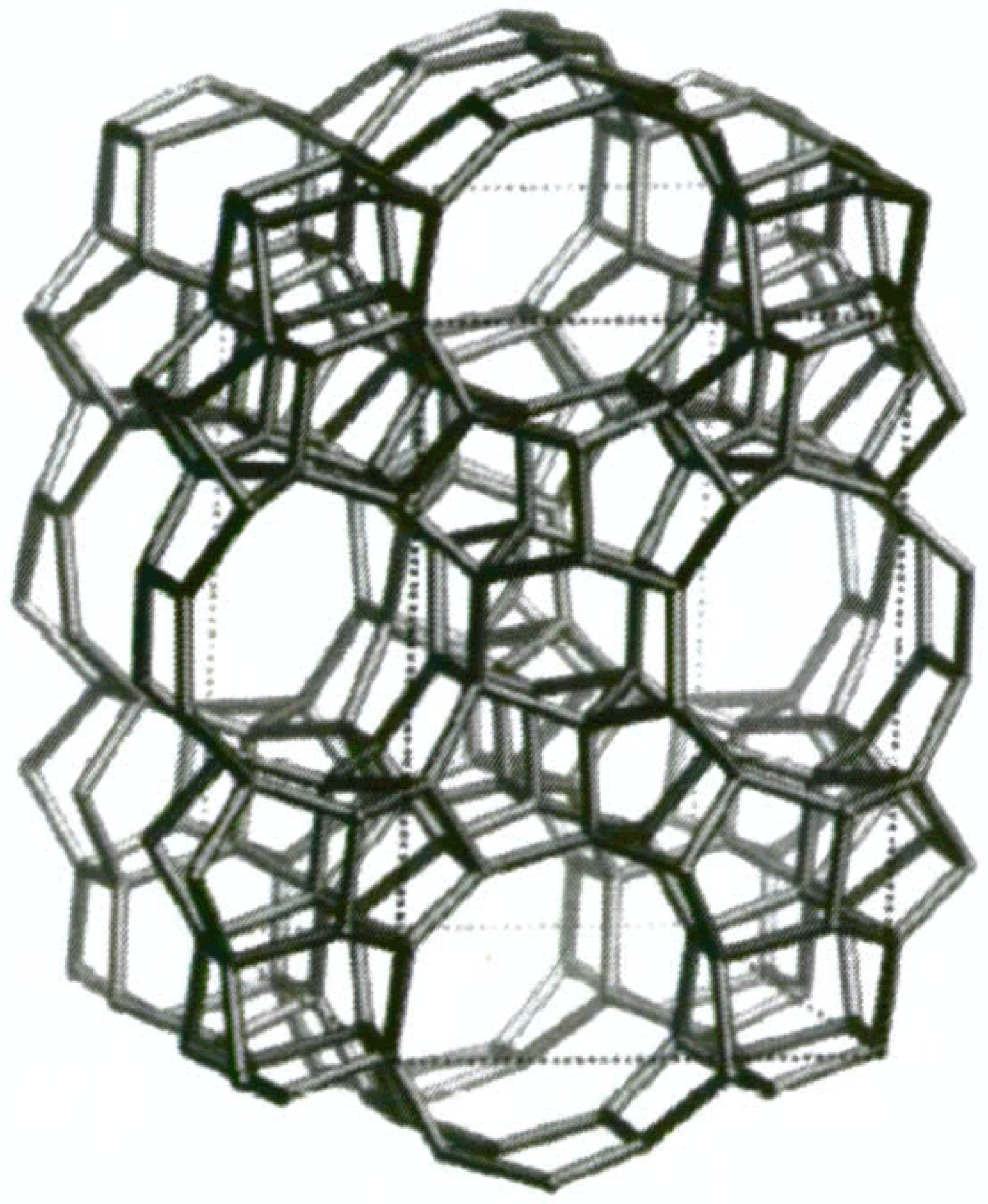
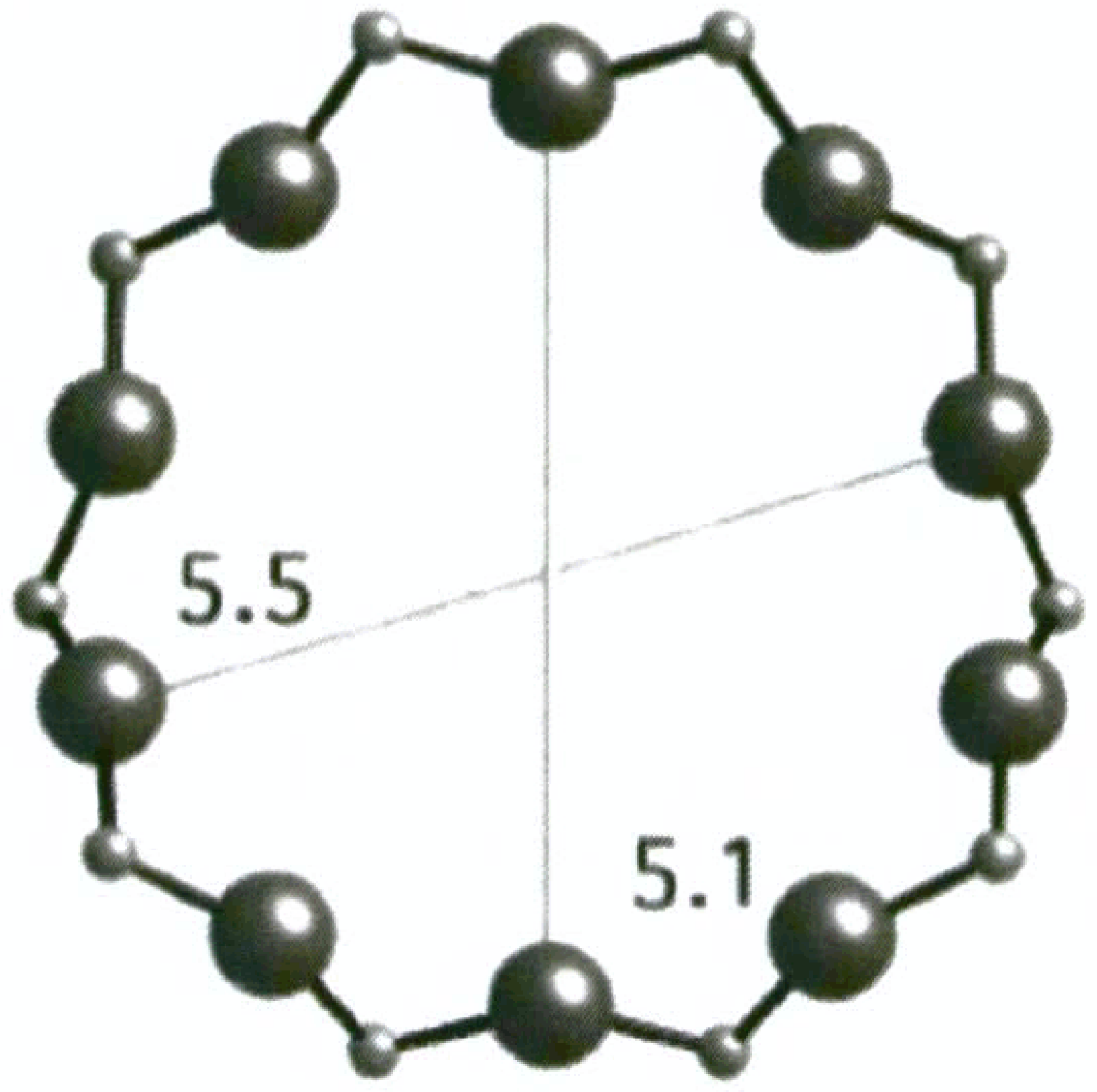
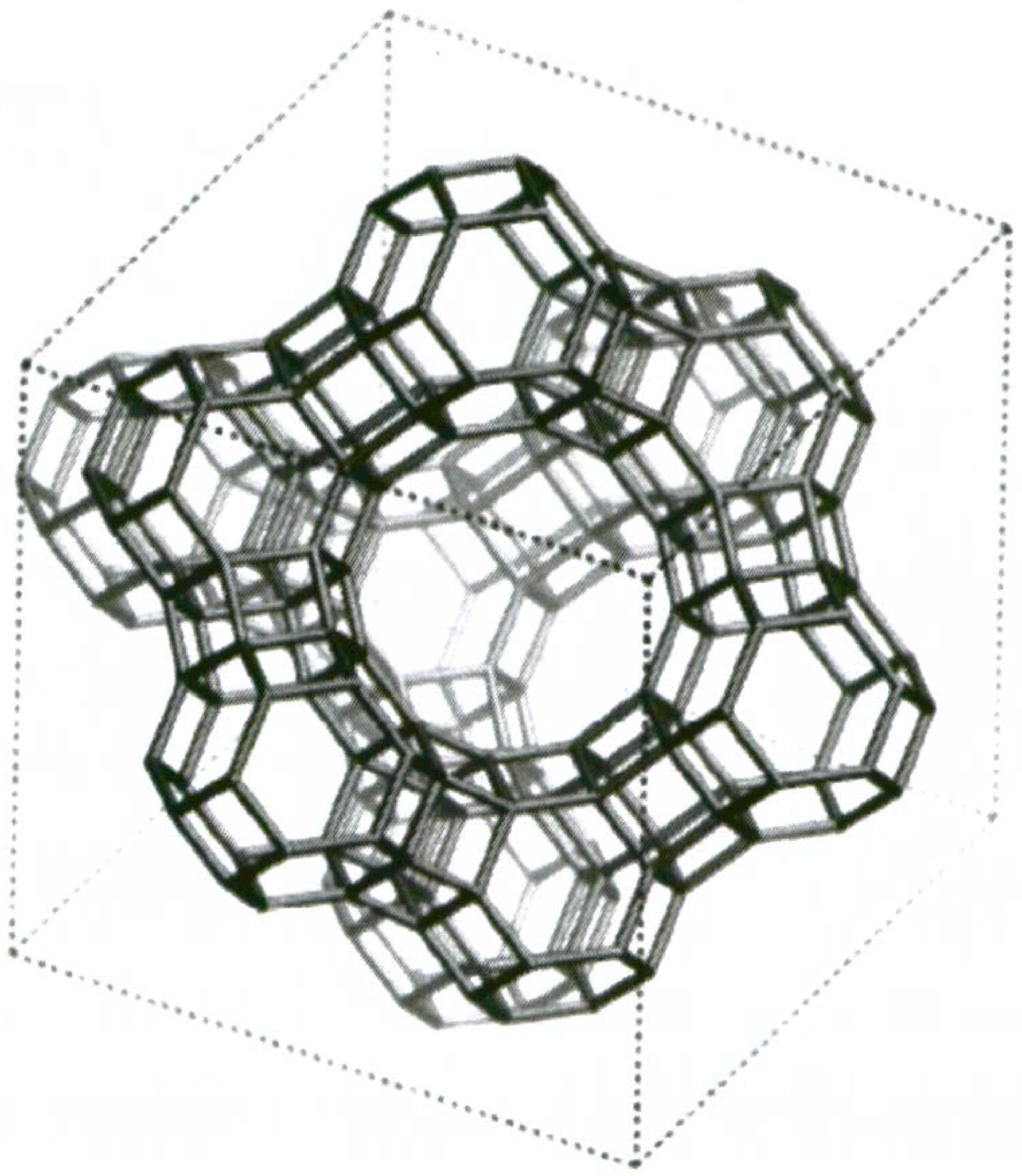
Zeolite Background

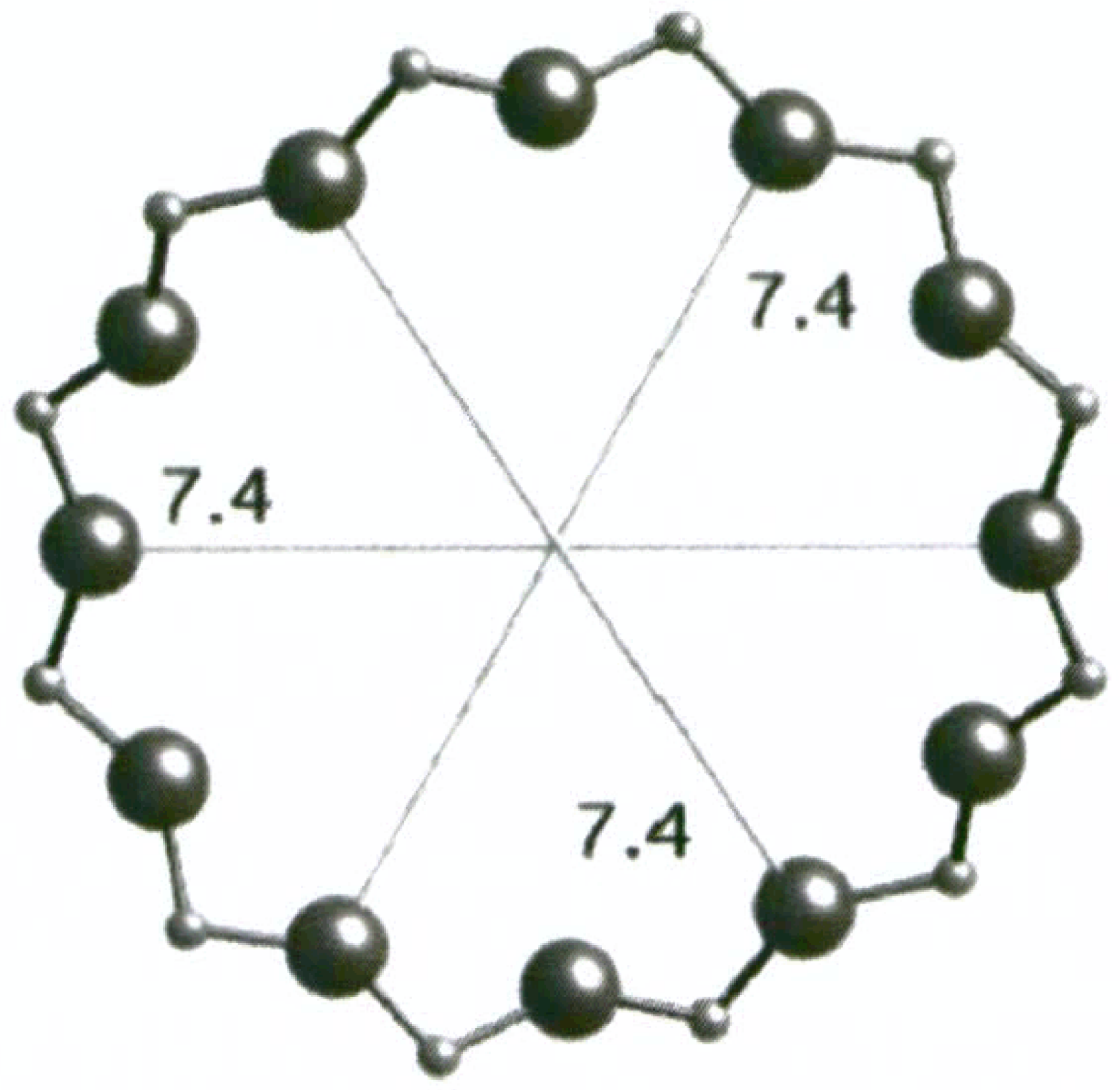




10-ring viewed along [100]

Nomenclature: *MFI*, ZSM-5 (*five*), Zeolite Socony *Mobil-5*

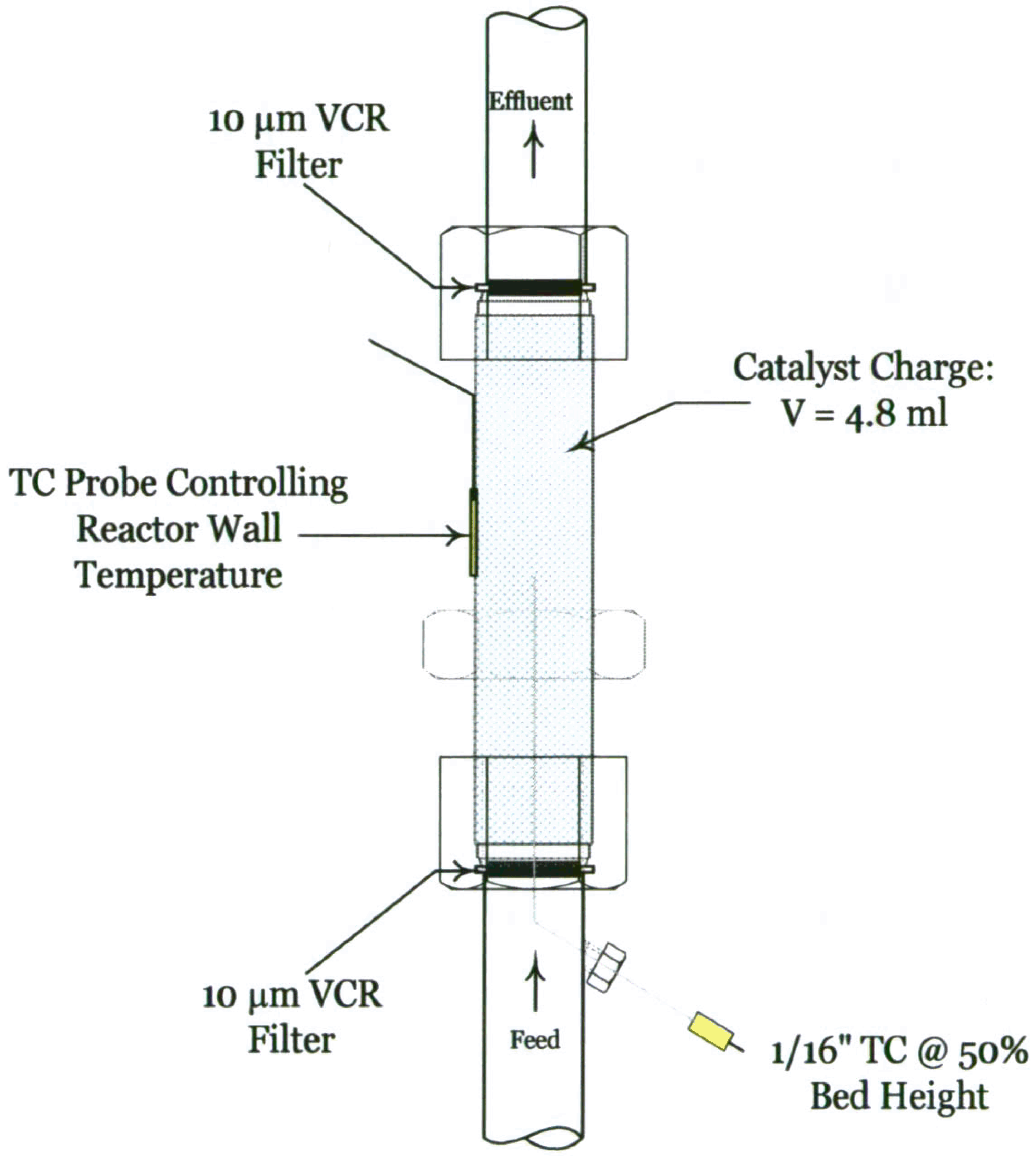




12-ring viewed along <111>

Nomenclature: Faujasite (FAU), Zeolite Y

Experimental



Catalyst	Si/Al	Typical Masses
ZSM-5: Z(Si/Al)	15, 25, 40, 140	1.7- 3.4 g
Y: Y(Si/Al)	2.5, 15	1.2 - 2.5 g
ZrO_2	-	2.8 - 5.8 g
SiO_2	-	2.2 - 2.4 g
γ-AL_2O_3	-	1.8 - 3.7 g
BASF K3-110 ($Cu/Zn/Al_2O_3$)	-	2.5 - 5.0 g

Additional catalysts include Cu and Zn co-impregnated and co-ion-exchanged analogs

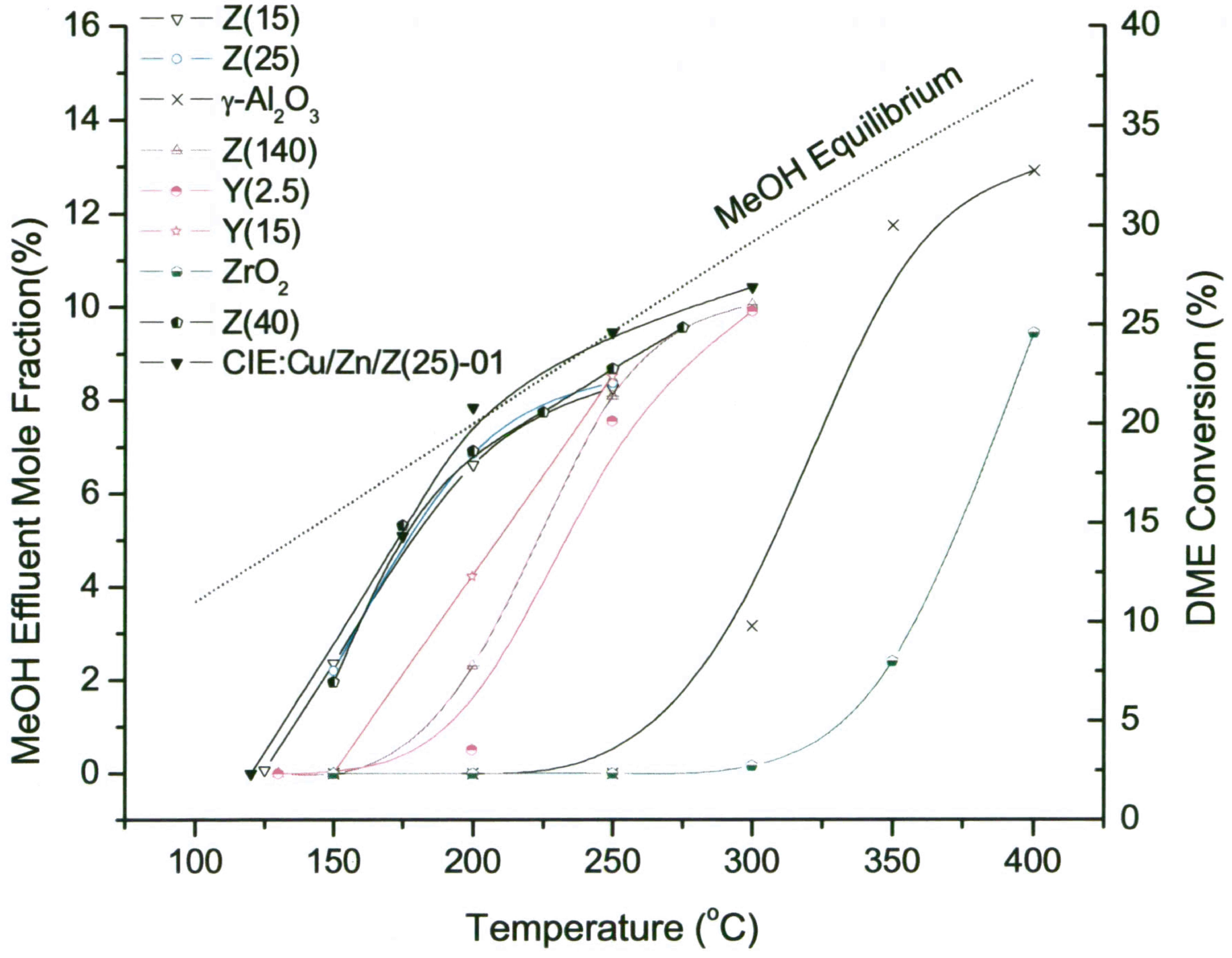
DME-SR Feed Conditions (S/C = 1.5): 20% N_2, 20% DME, 60% H_2O

MeOH-SR Feed Conditions (S/C = 1.0): 20% N_2, 80% @ 1:1 MFR MeOH/H_2O

All Reactions performed at a space time, τ = 1.0 s

Results: Acidity Effects on DME-Hydration

Comparison Chart for DME Hydration Reaction: tau = 1.0 s, S/C = 1.5



- ➢DME-hydration occurs over all acid catalysts
- ➢MeOH production approaches equilibrium
- ➢MeOH Activity over ZSM-5 trends with Si/Al ratio but not for Zeolite Y
- ➢MeOH activity over Z(15) does not correlate with Y(15)
- ➢SiO_2 is un-reactive toward DME-hydration

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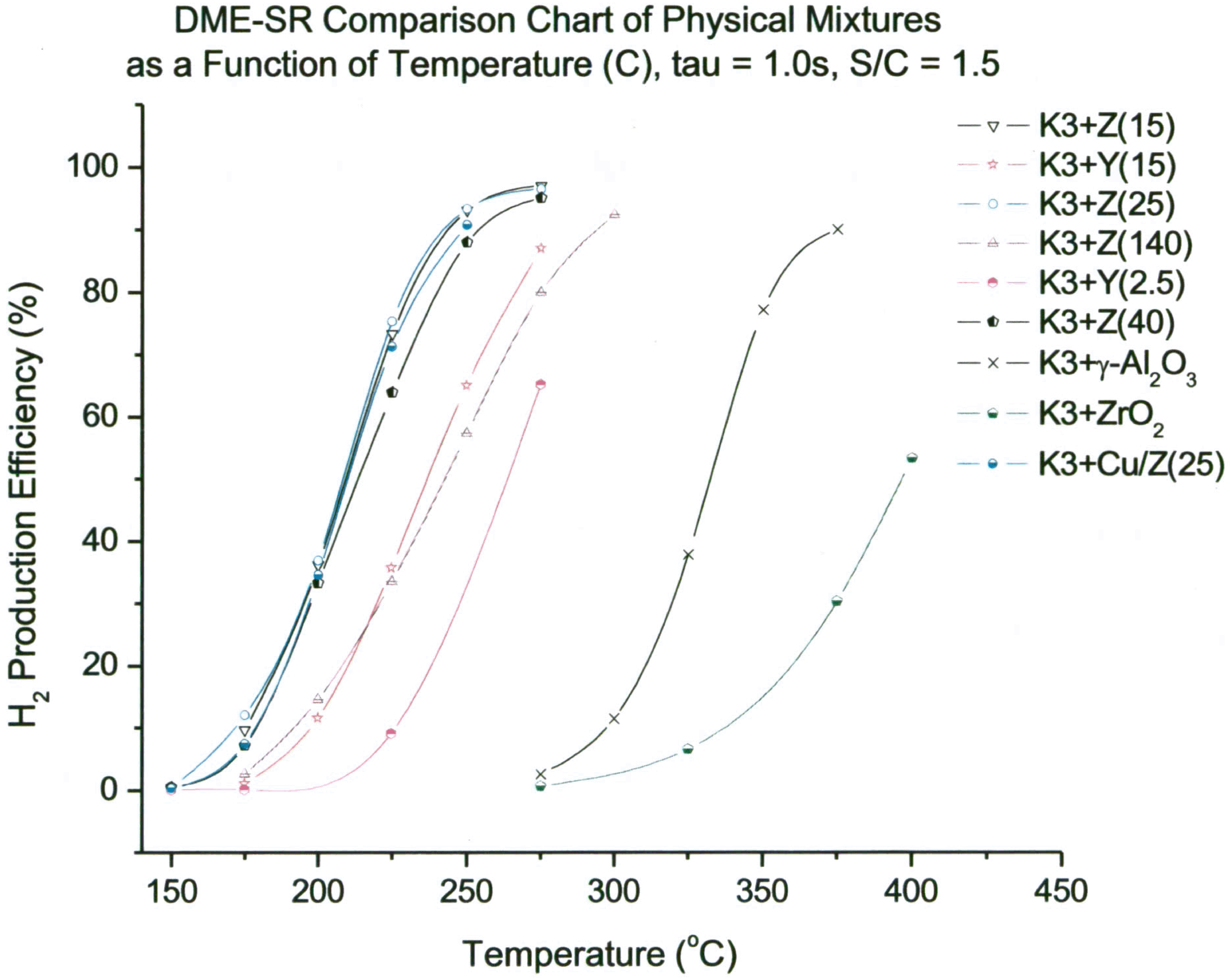
DME-SR over Physical Mixtures of BASF K3-110 and Various Acid Catalysts



DME-SR Comparison Chart of Physical Mixtures as a Function of Temperature (C), tau = 1.0s, S/C = 1.5

- ➢DME-SR occurs over all physical mixtures
- ➢DME-SR activity trends the same as DME-hydration
- ➢WGS reaction inhibits 100% H_2 production

K3+Z(25) @ 275 °C &
99% DME Conversion
CO = 3.9%
MeOH = 0.0%

K3+γ-Al_2O_3 @ 375 oC &
99% DME Conversion
CO = 7.5%
MeOH = 0.0%

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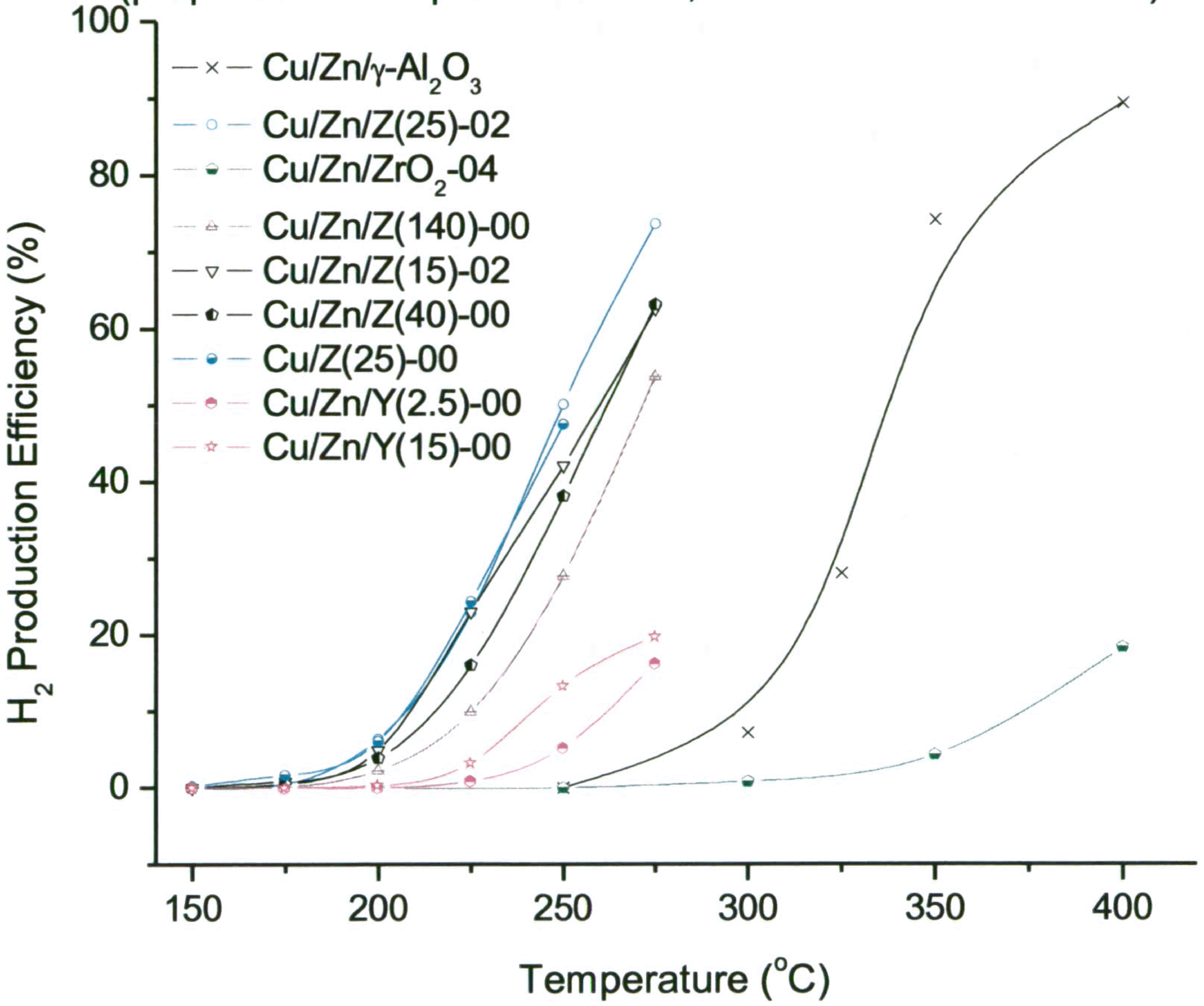
DME-SR over Incipient Wetness Prepared Catalysts

DME-SR Comparison Chart of Cu/Zn catalysts and the H_2 Production Efficiency (prepared via Incipient Wetness, tau = 1.0s and S/C = 1.5)



- DME-SR occurs over all incipient wetness(IW) prepared catalysts
- Cu/Zn/Z(25)-02 is the most active IW prepared catalyst
- Inefficiencies include WGS and/or unconverted MeOH

Cu/Zn/Z(25)-02 @ 275 °C &
61% DME Conversion
CO = 0.0%
MeOH = 1.9%

Cu/Zn/γ-Al_2O_3-00 @ 400 °C &
99.9% DME Conversion
CO = 9.2%
MeOH = 0.0%

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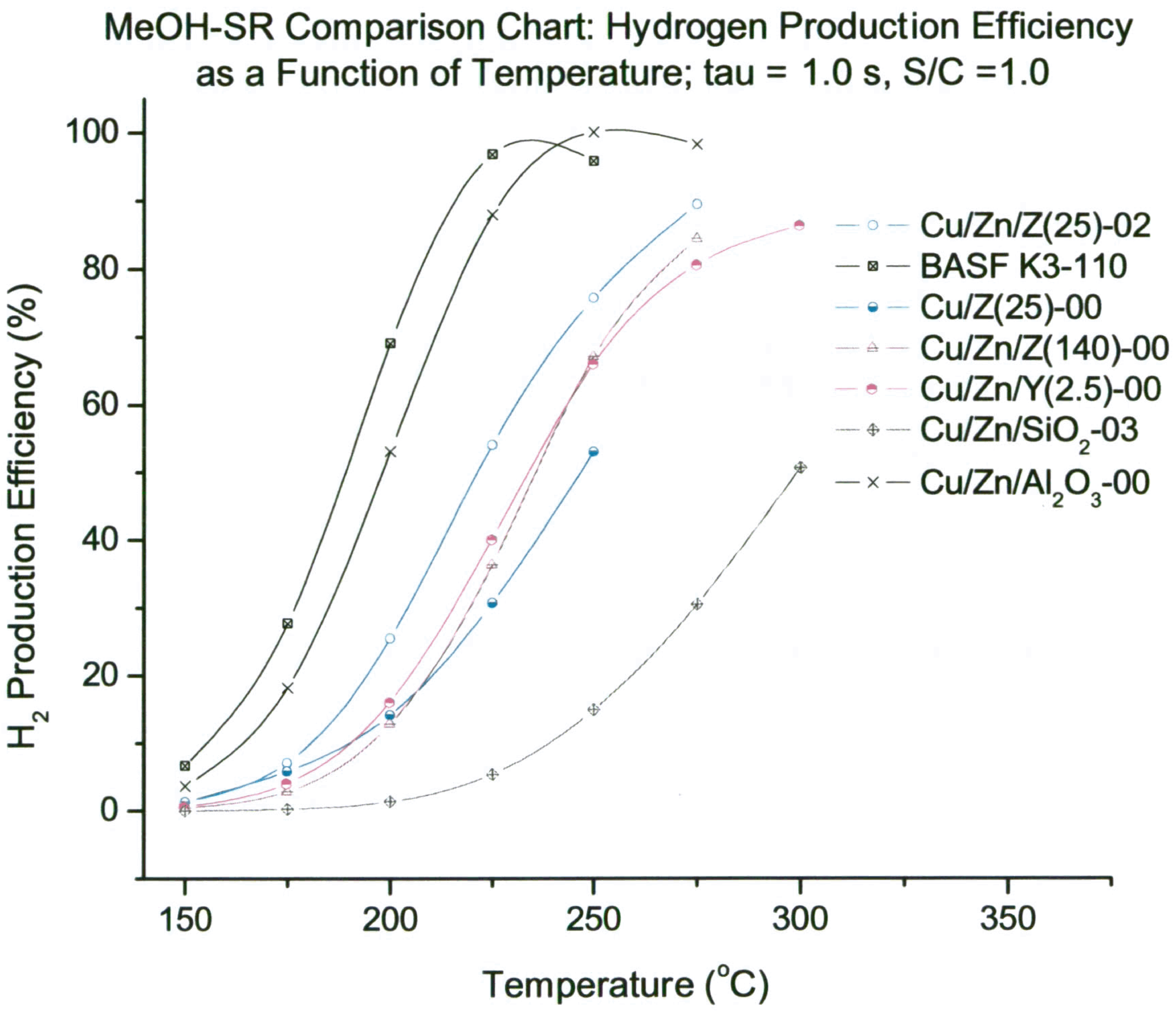
MeOH-SR over Incipient Wetness Prepared Catalysts



- MeOH-SR occurs over all incipient wetness(IW) prepared catalysts
- Inefficiencies include WGS and/or unconverted DME

Cu/Zn/Z(25)-02 @ 275 °C &
61% MeOH Conversion
CO = 0.54%
DME = 2.05%

Cu/Zn/γ-Al_2O_3-00 @ 275 °C &
99.9% MeOH Conversion
CO = 3.3%
DME = 0.07%

BASF K3-110 @ 250 °C &
99.9% MeOH Conversion
CO = 3.0%
DME = 0.0%

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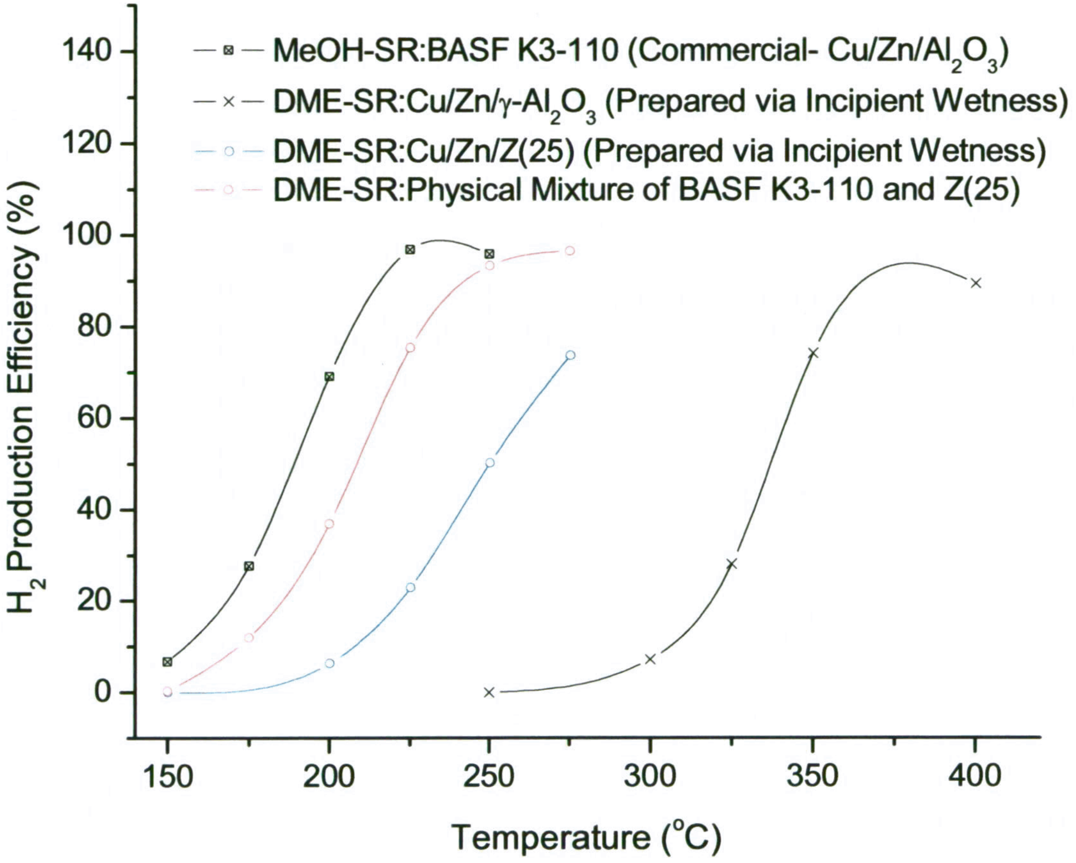
Comparison of MeOH-SR to DME-SR

Comparison of MeOH-SR to DME-SR over Various Catalysts;
MeOH-SR--tau = 1.0s, S/C = 1.0, DME-SR--tau = 1.0s, S/C = 1.5



- ➢MeOH-SR occurs over all incipient wetness(IW) prepared catalysts
- ➢Inefficiencies include WGS and/or unconverted DME/MeOH

K3 + Z(25) @ 275 ^{o}C &
  99% DME Conversion
    CO = 3.9%
    MeOH = 0.0%

Cu/Zn/γ-Al_2O_3-00 @ 400 ^{o}C &
  99.9% MeOH Conversion
    CO = 9.2%
    DME = 0.0%

BASF K3-110 @ 250 ^{o}C &
  99.9% MeOH Conversion
    CO = 3.0%
    DME = 0.0%

Conclusions

- DME is potentially a viable alternative fuel for fuel cells
  - Infrastructure, toxicity and other issues not a severe as with MeOH

- Thermodynamics of DME-SR
  - Produces a hydrogen-rich fuel-cell feed without conversion limitations.
  - Occurs over a wide range of T and S/C ratios
    - $T > 200$ °C and S/C ratios > 2.0.

- DME decomposition
  - Carbon formation was observed over all supports and catalysts tested.
  - Decomposition occurs in same temperature range as DME-SR
    - Care must be taken to prevent unwanted side reactions

- DME was observed to form methoxy and formate species over both γ-Al_2O_3 and ZrO_2.

Conclusions

- **DME-SR over Cu/ZnO diluted with an acid catalyst produces a H_2 rich stream.**
  - **The mechanism for DME-SR produces methanol via DME hydration.**
    - **Reforming of methanol producing H_2 follows.**

$$\begin{array}{ll} CH_3OCH_3 + H_2O \rightleftharpoons 2CH_3OH & \textit{DME Hydration} \\ CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2 & \textit{MeOH -SR} \\ \hline CH_3OCH_3 + 3H_2O \rightleftharpoons 2CO_2 + 6H_2 & \textit{DME}-\textit{SR} \end{array}$$

- **DME-SR did not occur over undiluted $Cu/ZnO/Al_2O_3$ catalysts.**

Acknowledgments

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Program Manager: Nancy Garland