GREEN CATALYTIC PROCESSES: SUBSTITUTION OF VOLATILE LIQUID ACIDS WITH SOLID ACIDS

Israel E. Wachs

Operando Molecular Spectroscopy & Catalysis Laboratory

Dept. of Chemical Engineering

Lehigh University

Bethlehem, PA 18015 USA

www.lehigh.edu/operando

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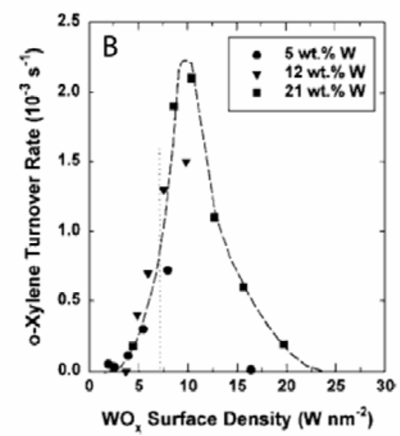
Operando Molecular Spectroscopy & Catalysis Research Lab

GREEN CATALYTIC PROCESS: SUBSTITUTION OF VOLATILE LIQUID ACIDS WITH SOLID ACIDS

- Alkylation of n-Alkanes with Liquid Acids (H_2SO_4, HF, $AlCl_3$, HCl, etc.) is Employed to Synthesize Antiknock Components for Motor Fuel
- Strong Acids Required for Alkane Isomerization Step
  - Isomerization Step: Conversion of n-Alkanes to Branched Alkanes
  - Alkylation Step: Reaction of Branched Alkanes with Olefins
- Technical Problems Associated with Liquid Phase Alkylation
  - Corrosion
  - Volatility
  - Spills
- Strong Solid Acid Can Potentially Replace Liquid Acids
  - No Corrosion
  - No Volatility
  - No Spills

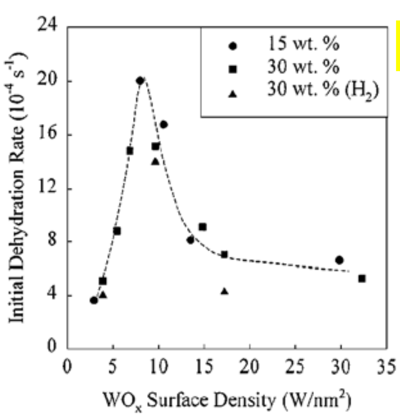
SOLID WO_3-ZrO_2 CATALYTSTS IDENTIFIED AS STRONG SOLID ACIDS

Iglesia & coworkers (UC-Berkeley)



Barton *et al*., *J. Catal*., **1999**, *181*, 57

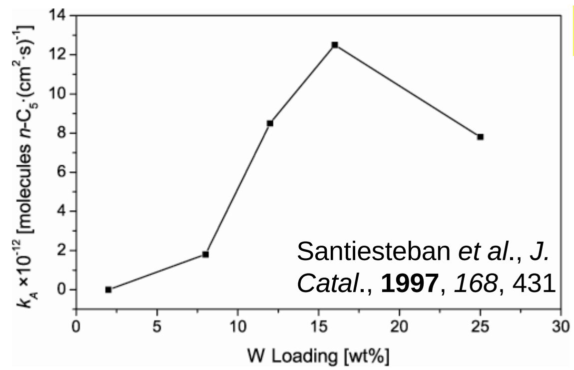
- *o*-xylene isomerization
- IW impregnation WO_3-ZrO_2
- 250 °C
- ~1 bar
- Excess H_2 feed



Baertsch *et al*., *J. Catal*., **2002**, *205*, 44

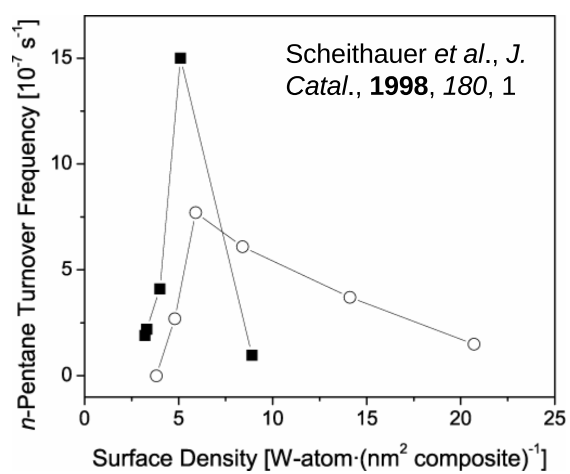
- 2-butanol dehydration
- IW impregnation WO_3-ZrO_2
- 100 °C
- ~1 bar
- Excess H_2 feed

Santiesteban & coworkers (ExxonMobil)



- *n*-pentane isomerization
- coprecipitated WO_3-ZrO_2
- 210 °C
- 24 bar
- 2 H_2:1 n-C_5 molar feed ratio

Knözinger & coworkers (U. of München)

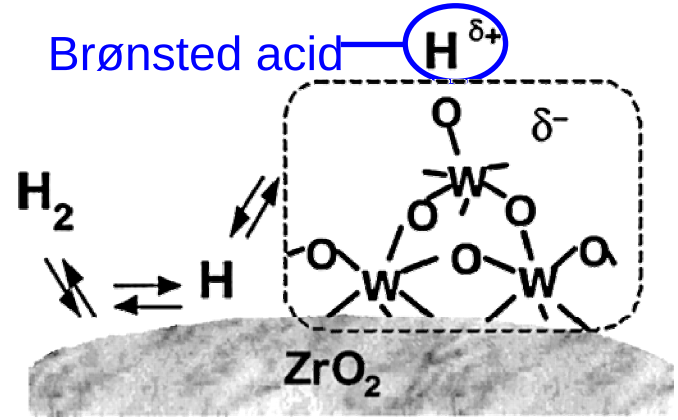


- *n*-pentane isomerization
- equilibrium adsorption WO_3-ZrO_2
- 250 °C
- ~1 bar
- Pure n-C_5 feed

- **High Surface Acid Activity Occurs at Intermediate WO_x Content**

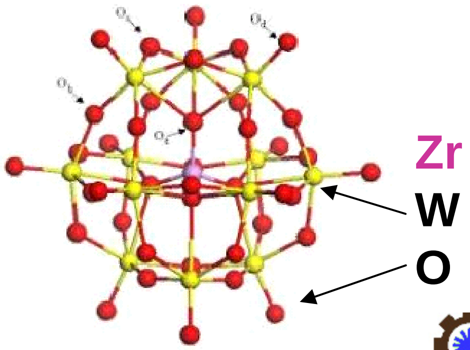
PROPOSED MODELS FOR ENHANCED ACIDITIY OF SUPPORTED $WO_3/ZrO_x(OH)_{4-2x}$ CATALYTS

- **Surface Polytungstate $W^{+(6-n)}$ Domains (Surface WO_x Monolayer)**

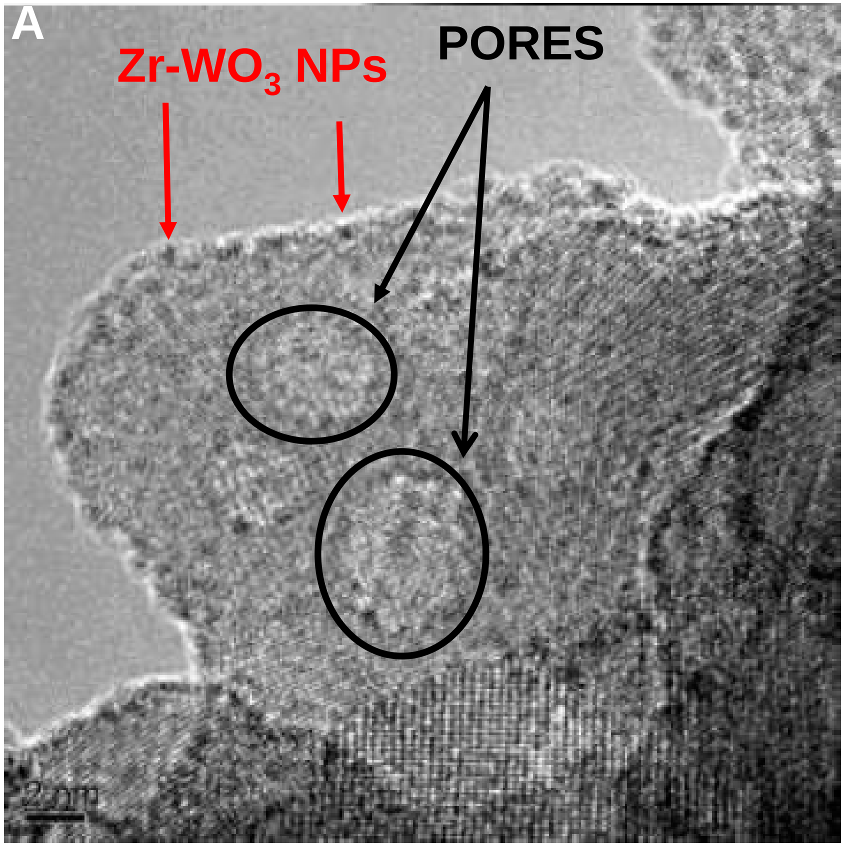


Baertsch *et al*., *J. Phys. Chem. B*, **2001**, *105*, 1320

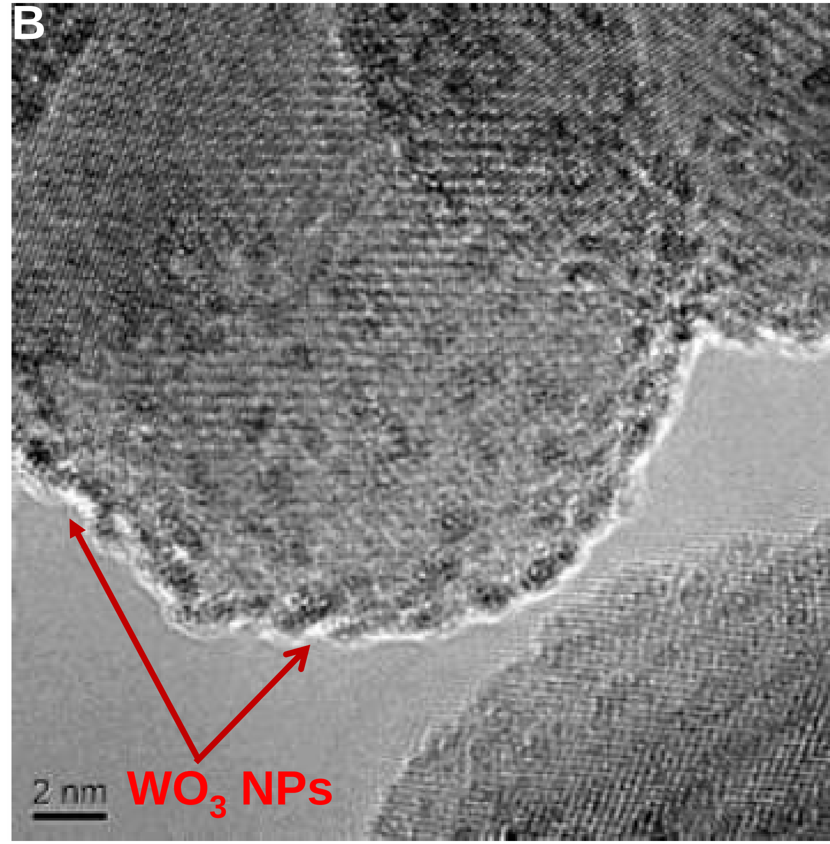
- **Polytungstate Domains Containing Zr Cations (Keggin-like structure)**



Zr-STABILIZED POORLY ORDERED WO_3 NPs RESPONSIBLE FOR STRONG ACID SITES

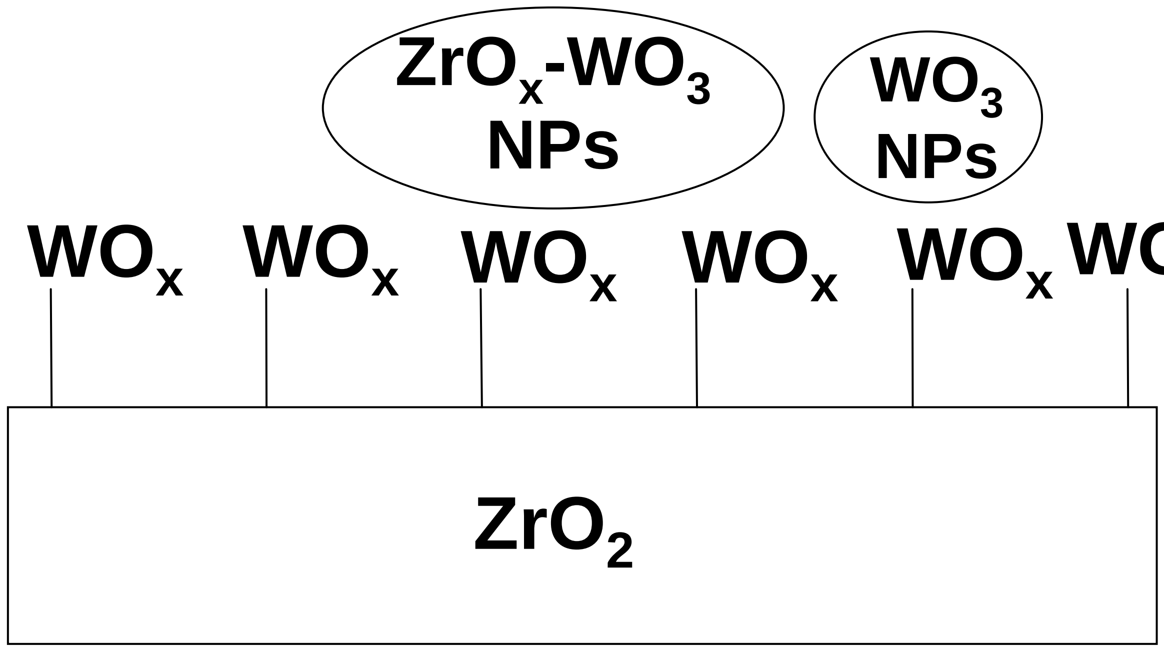


[A] 10.1WZrOH-1073(6.2)
- Surface WOx Monolayer
- Poorly Ordered $Zr-WO_3$ NPs (~0.6 nm)
- Strong Acid Sites



[B] 19.5WZrOH-1173(20.2)
- Surface WOx Monolayer
- Crystalline WO_3 NPs (~1.2 nm)
- Modest Acid Sites

CATALYTIC ACTIVE SITES PRESENT IN SUPPORTED WO_3/ZrO_2 CATALYSTS



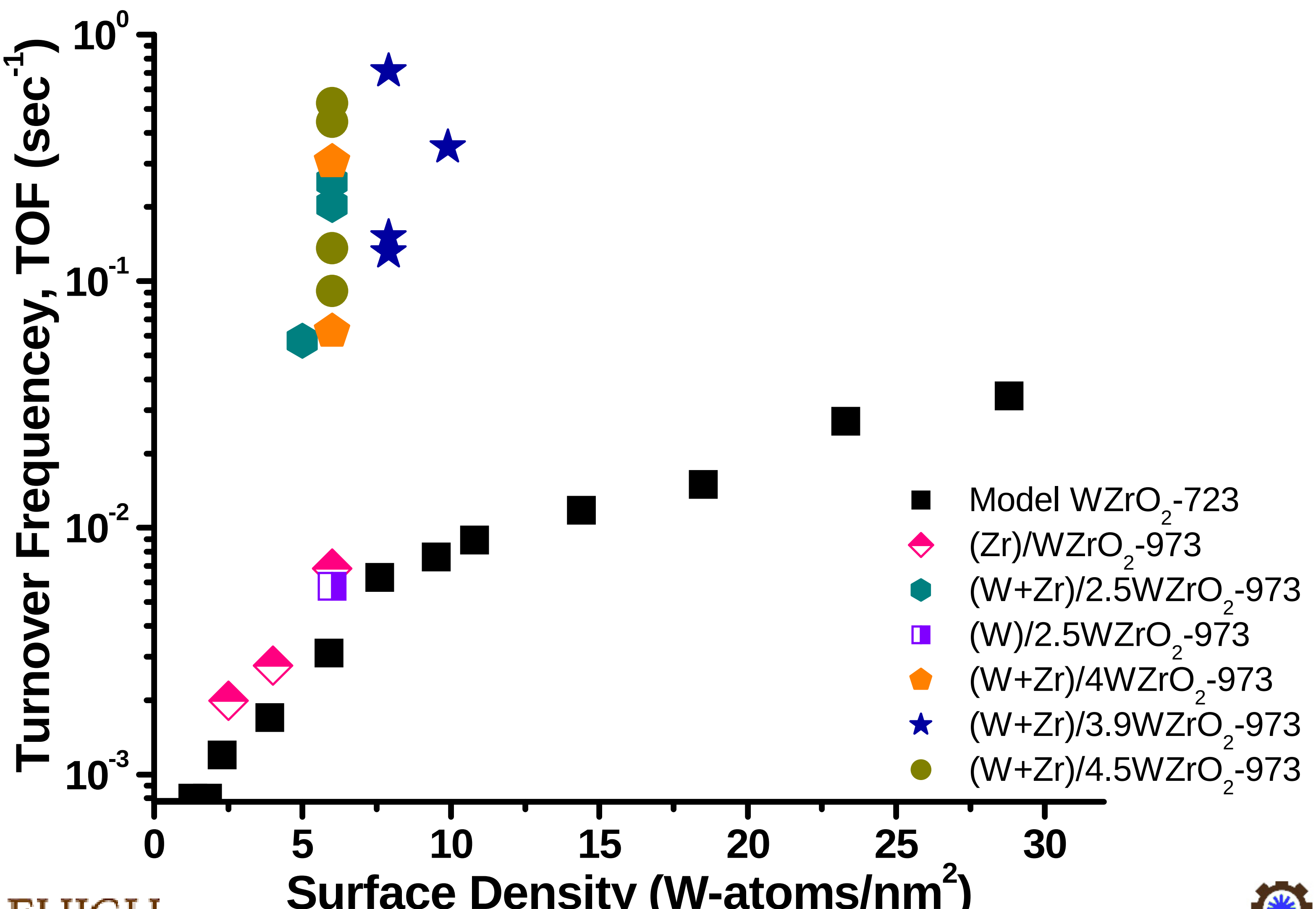
Surface WO_x Species &
***Zr-Stabilized WO_3 NPs* & WO_3 NPs**

- **Zr-KEGGIN NOT THERMALLY STABLE**

CATALYST BY DESIGN: ENHANCE SOLID ACIDITY WITH MORE Zr-WO_3 NPs

- Catalyst Synthesis
  - Aqueous Solutions of $(NH_4)_{10}W_{12}O_{41}*5H_2O$
  - Toluene Solutions of $Zr[OC(CH_3)_3]_4$
- Support Material: Model WO_3/ZrO_2 Catalysts
- Calcined at 973 K for 4 hr in Air

POORLY ORDERED Zr-STABILIZED WO3 NPs RESPONSIBLE FOR ENHANCED PERFORMANCE CATALYTIC ACTIVE SITES



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CONCLUSIONS

– ***Poorly Ordered Zr-Stabilized WO_3 NPs*** **Responsible for** **Strong Acidic *Catalytic Active Sites***

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M. Neurock – University of Virginia (Theory)