

Erin Sobchinsky, Shiao-Chien Tsai, Israel E. Wachs

Operando Molecular Spectroscopy and Catalysis Research Laboratory, Department of Chemical and Biomolecular Engineering, Lehigh University

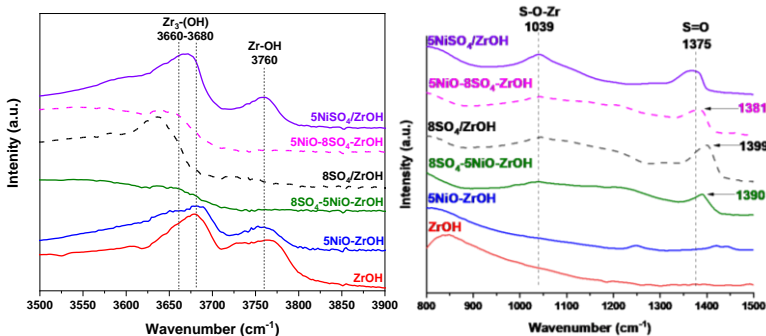
Introduction & Motivation

- Olefins are typically produced from cracking crude oil
- The growing abundance of natural gas has shifted feedstocks to lighter hydrocarbons, contributing to a shortage of *n*-butene
- This has stimulated interest in dimerization of shale gas derived ethylene to produce *n*-butene
- In industry, ethylene dimerization is carried out with homogeneous catalysts → problems with product separation, acid gas emissions, & catalyst recycling → leading to interest in developing heterogeneous catalysts
- High activity and selectivity to 2-butene reported for NiSO₄/ZrOH → solid acid catalyst, mild reaction conditions (20 °C)
- Objectives:** Determine the nature of Ni-SO₄ interactions and the molecular structure/oxidation state of surface species that enhance the catalytic activity and selectivity

Results

SO₄ Anchors at Surface Hydroxyls, NiO Anchors Adjacent to Hydroxyls

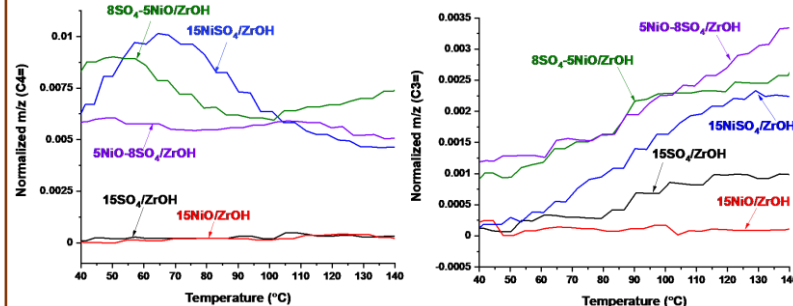
IR Spectra, Dehydrated (450 °C), 10% O₂/Ar



- Impregnating SO₄ first → terminal hydroxyls diminished
- Impregnating Ni first → tri-bridging Zr₃-OH shifts to higher cm⁻¹
- Ni anchors adjacent to hydroxyl sites or at surface defect sites
- S=O vibration shifts to lower cm⁻¹ for Ni containing catalysts → interactions between SO₄ & Ni species may weaken the S=O bond

Method of Preparation Influences Activity & Selectivity

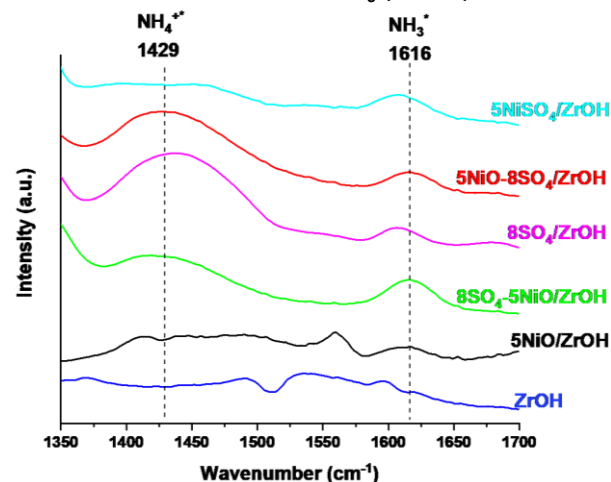
Ethylene TPSR (5% C₂=/Ar)



- Both Ni and SO₄ are needed for enhanced ethylene dimerization
- Impregnating NiO first → increased activity, lower propylene production

Method of Preparation Influences Bronsted to Lewis Acid Site Ratio

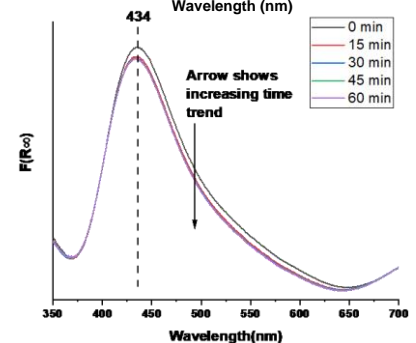
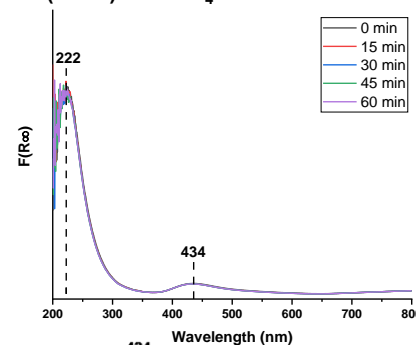
IR of Adsorbed NH₃ (120 °C)



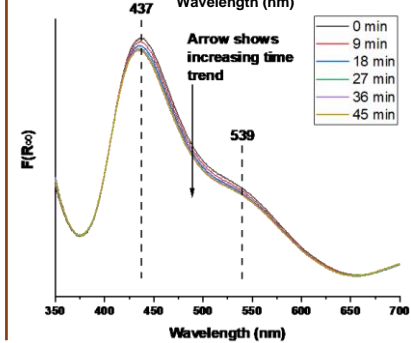
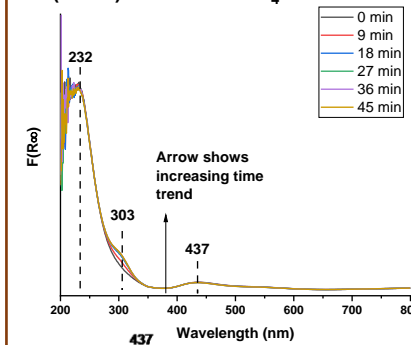
- 1429 cm⁻¹ → Bronsted acid
- 1616 cm⁻¹ → Lewis acid
- Incorporation of Ni changes Bronsted to Lewis acid ratio
- Lower Bronsted to Lewis acid ratio → higher activity
- Higher Bronsted to Lewis acid ratio → increased production of propylene
- Bronsted acid sites may be cracking butene

Order of Impregnation May Influence Oxidation State of Ni & Coking

UV-vis during reaction (50 °C) for 8SO₄-5NiO/ZrOH



UV-vis during reaction (50 °C) for 5NiO-8SO₄/ZrOH



- Peaks ~435 and ~539 nm → Ni²⁺O₆ coordination
- Intensity of Ni²⁺ peaks decrease with reaction time → coking or Ni²⁺ reduction
- Peak at 303 nm appears for 5NiO-8SO₄/ZrOH → coking or allylic species
- 5NiO-8SO₄/ZrOH has lower activity → reduces/cokes faster than 8SO₄-5NiO/ZrOH

Conclusions

- SO₄ anchors at hydroxyl sites, Ni anchors adjacent to hydroxyl sites
- Ni²⁺ present during reaction
- Both Ni and SO₄ needed for enhanced ethylene dimerization activity
- Preparation method influences the Bronsted to Lewis acid ratio and activity
- Lower Bronsted to Lewis acid ratio → enhanced activity & selectivity to *n*-butene
- Higher Bronsted to Lewis acid ratio → higher production of propylene
- Preparation methods may influence deactivation/reduction of Ni species