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
- There is a renewed interest in dimerization of shale gas derived ethylene to produce n-butenes.
- In industry, ethylene dimerization is carried out with homogeneous catalysts, 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 Zr-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% C2H4/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)

- Peaks ~435 and ~539 nm → Ni2+O2 coordination
- Intensity of Ni2+ peaks decrease with reaction time → coking or Ni2+ reduction
- Peak at 303 nm appears for NiSO4/ZrOH → coking or allylic species
- 5NiO-8SO4/ZrOH has lower activity → reduces/cokes faster than 8SO4-5NiO/ZrOH

Order of Impregnation May Influence Oxidation State of Ni & Coking

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

- Peak at 303 nm appears for 5NiO/ZrOH → coking or allylic species
- 8SO4-5NiO-ZrOH has lower activity → reduces/cokes faster than 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