

Overcoming the Deleterious Effects of Hafnium in Tungsten-Zirconia Catalysts

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Introduction

Hafnium is a common impurity in some zirconia precursors that is difficult and expensive to separate because of its chemical similarity to zirconium. This work focuses on the effect of hafnium on the catalyst morphology and ultimately the isomerization activity of Ni/WO₃/ZrO₂. Thermal treatments and aluminum doping are presented as an efficient means of mitigating the adverse effects of hafnium. Special care has been taken to track catalyst morphology as function of calcination temperature. While the materials presented in this work do not possess all of the properties necessary for a commercialized catalyst, the results show that relatively inexpensive and impure catalyst precursors, in combination with base metals, can be engineered to produce considerable hydroisomerization activity.

Materials and Methods

Ni/WO₃/ZrO₂ catalysts were prepared from zirconia precursors with and without the addition of hafnium and aluminum. Following precipitation of zirconyl chloride by aqueous ammonia, ammonium metatungstate and nickel (II) nitrate were deposited by sequential impregnation. Nickel and tungsten content were kept essentially constant on a per weight basis. Variations in calcination temperature produced series of catalysts with a range of surface areas and tungsten surface loadings.

Catalytic measurements were taken using a typical 3/4-inch outer diameter down flow packed bed reactor. Liquid feed was metered using a syringe pump while gases were supplied by mass flow controllers. Pressure was maintained using a Moore regulator. Analysis of the reactor effluent was completed using a slipstream line to an online gas chromatograph.

Catalysts were characterized using N₂ physisorption, x-ray fluorescence and x-ray diffraction. Refinements of x-ray patterns were used to link catalytic activity to structural features.

Results and Discussion

The presence of hafnium templates the formation of a stable cubic zirconia phase as well as a thermally unstable monoclinic phase (Figure 1). While higher calcination temperatures convert this monoclinic phase to the catalytically active tetragonal phase, there is no effect on the cubic phase. The presence of hafnium retarded the formation of tetragonal zirconia, ultimately requiring a calcination temperature of 800°C to reproduce the activity and crystalline composition of a hafnium-free material calcined at 600°C. The addition of aluminum to these materials prevents the formation of the low temperature monoclinic phase,

though does not affect the cubic phase. In effect the addition of small amounts of aluminum (1 wt %) provides the same benefit as a 200°C increase in calcination temperature.

All tungsten-zirconia materials contained an orthorhombic zirconia phase that has not (along with the cubic zirconia phase) been addressed in the literature concerning the catalytic activity of these materials. Though crystallographically very similar to the tetragonal phase, the addition of the inactive orthorhombic phase allows for a better prediction of catalytic activity.

In some materials, the poor hydrogen spillover activity of nickel was the rate determining process for hexane isomerization. Though the same control could not be exerted over the nickel hydrogenation activity as was applied to the zirconia phases, the generation of appreciable activity could ultimately lead to the replacement of precious metals for some fundamental energy related applications.

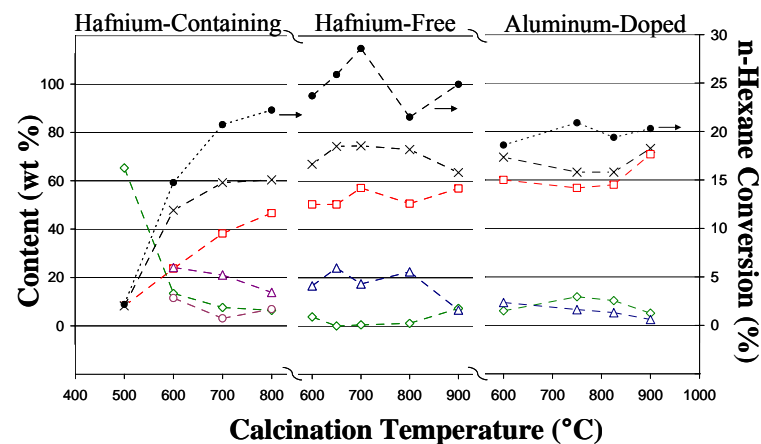


Figure 1: Zirconia phase distribution and initial n-hexane isomerization activity as a function of calcination temperature and metal dopant. □ = tetragonal, ◇ = monoclinic, Δ = orthorhombic, ○ = cubic, × = tetragonal + orthorhombic and ● = conversion (288°C, 200 psi, H₂/nC₆ = 0.7, LHSV = 17 hr⁻¹)

Significance

Tungsten-zirconia catalysts, particularly in the presence of hafnium, are far more structurally complicated than previously thought. The management of hafnium-imposed structural changes allows for significant isomerization activity using materials substantially cheaper than hafnium-free zirconyl chloride. The use of nickel, while not a perfect replacement more traditional precious metals, shows that management of hydrogenation activity as well as zirconia crystal phase allows for the preparation of less expensive isomerization catalysts.