

# Relating Pentane Isomerization Activity to the Acidic Properties and Surface Density of WO<sub>x</sub>/ZrO<sub>2</sub>

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## Introduction

Acidic metal oxide catalysts received enormous attention by a great percentage of the industrial and academic community in the last decade. As an alternative to sulfated zirconia, tungstated zirconia (WO<sub>x</sub>/ZrO<sub>2</sub>) exhibits significantly higher thermal stability with only slightly lower acidity. Among the different probe reactions that have been used to study the acidic properties of these materials are alcohol dehydration [1,2], o-xylene isomerization [3] and paraffin isomerization reactions [4,5]. New insights into the nature of the acidic catalytic active sites that were reported recently provided new understanding for WO<sub>x</sub>/ZrO<sub>2</sub>. Distorted Zr-WO<sub>3</sub> nanoparticles were identified [2], with higher concentrations occurring at average surface densities, suggesting a new structural origin of surface acidity.

In this study, the catalytic activity of WO<sub>x</sub>/ZrO<sub>2</sub> for pentane isomerization was investigated as a function of WO<sub>3</sub> surface density. The optimum strength and concentration of Brønsted sites were studied using the Pyridine FTIR technique, and correlated to catalytic activity. The reaction mechanism was probed using olefins as a co-feed.

## Materials and Methods

Two series of WO<sub>x</sub>/ZrO<sub>2</sub> catalysts were synthesized by incipient wetness impregnation into two commercially available amorphous metastable ZrO<sub>x</sub>(OH)<sub>4-2x</sub> supports using an ammonium metatungstate precursor. Samples were characterized by N<sub>2</sub>-Physisorption, X-ray diffraction, Raman and Pyridine FTIR. N-pentane isomerization reactivity studies were performed on an isothermal packed bed reactor under differential conditions.

## Results and Discussion

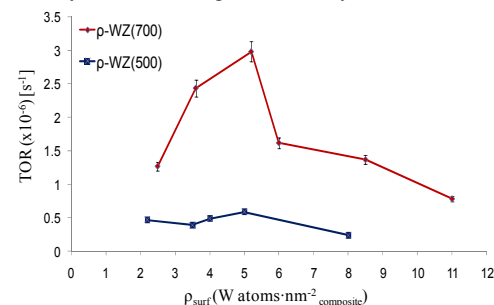
Preliminary data for one of the two series show a maximum in nC<sub>5</sub> turnover rate at ~5 W/nm<sup>2</sup> (Figure 1), where increased distorted Zr-WO<sub>3</sub> concentrations were observed [2]. By comparing the activity between two samples calcined at different temperatures (500°C and 700°C), but with similar surface densities, it is observed that activity increases 7 times from 500°C to 700°C.

In order to test the effect of surface density and temperature on the acidic properties of WO<sub>x</sub>/ZrO<sub>2</sub> a series of Pyridine FTIR experiments was performed. It was observed that the acidic site concentration increases with surface density (not shown here), even above 5 W/nm<sup>2</sup>. This proves that there is no direct correlation between the number of sites and the maximum activity observed. As seen from the Pyridine FTIR experiments (Figure 2), maximum reactivity

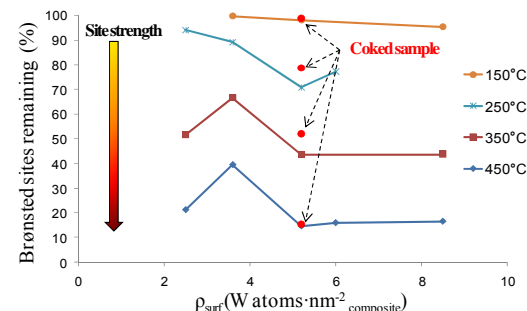
is correlated to average Brønsted site strength. Coke deposition occurs mainly on the sites of lower to average strength, which appear to be the most active sites for this reaction.

## Significance

By understanding the nature of active sites and the parameters that promote the formation of distorted Zr-WO<sub>3</sub> we can synthesize a very active material that could eventually replace the unstable chlorinated catalysts that are being used currently.



**Figure 1.** Steady state turnover rates for samples calcined at 700°C and 500°C with different surface densities  $\rho_{\text{surf}}$ .



**Figure 2.** Pyridine FTIR Desorption Results. Remaining Brønsted sites (%) after pretreatment at T= 150–450°C with an increment of 100°C

## References

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