n-Butane Isomerization on Tungstated Zirconia: Site Activation

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Introduction
Solid acid catalysts for paraffin isomerization are of importance due to their ability to carry out reaction without the drawbacks of liquid acids, such as corrosion and difficulty in handling and storage. One solid acid catalyst, sulfated zirconia (SZ), has received considerable attention during the past decade [1-5]. It was found to have high selectivity for isobutane and high activity during n-butane isomerization at mild reaction conditions. However, it was also found to deactivate rapidly, even at relatively mild conditions. Coke/oligomer formation has been found to be the main reason for this deactivation [6]; however, loss of sulfur has also been reported to be a cause [7].

Tungstated zirconia (WZ) has been proposed as a better alternative for alkane isomerization than sulfated zirconia (SZ). Although less active than SZ, WZ exhibits better catalyst stability. As in the case for SZ, n-butane isomerization on WZ follows an initial reaction induction period [8]. During this induction period, potential sites become active [9]. In this study, H2 pretreatment and olefin addition during reaction of WZ were used in order to better understand the reasons for the presence of this induction period and to evaluate similarities/differences between the reaction induction on WZ compared to SZ.

Results and Discussion
The tungstate-doped zirconium hydroxide [Zr(OH)4] precursor used for this study was obtained from Magnesium Elektron, Inc. It was calcined at 800°C for 2 h in static room air to form tungstated zirconia (WZ) following the manufacturer’s recommendation with a BET surface area of 72 m²/g. Its tungsten content was determined (Galbraith Laboratories, Inc.) after calcination and found to be ca. 13 wt%.

H2 pretreatment of WZ prior to reaction decreased its activity resulting in a seemingly shortening of the induction period. This result was most likely due to a decrease in the number of the sites available, which meant that the catalyst reached its maximum activity more rapidly. The decrease in the activity was probably due to partial reduction of WO3 to form a non-active form of the oxide.

Olefin addition shortened significantly the reaction induction period at 280°C from a total time of 30 min to around 3-4 min (see Figure 1). It also increased the activity of WZ and improved its stability in the temperature range 280°C-360°C. Butene added for only 2 min at the beginning of the reaction improved the activity of WZ and was able to participate multiple times in the formation of additional isobutane, suggesting
the existence of “olefin-modified” sites as active reaction centers. Nevertheless, the number of turnovers was significantly higher on SZ (at 150°C) than on WZ (at 280°C), 700 vs. 19, respectively. Consequently, the improvement in activity was not as long lasting after discontinuing olefin addition as in the case for SZ at 150°C, and the activity of WZ eventually returned to the same level as if no olefin had been added.

![Figure 1: Impact of olefin addition on the induction reaction period of n-butane isomerization at 280°C on WZ.](image)

Based on these results, we suggest that, as in the case of SZ [9], on WZ added butene is involved in formation of “olefin-modified” sites, probably carbenium ions that can participate in the formation of isobutane multiple times. These sites on WZ are not as stable as those on SZ due in large part to the higher temperature required for reaction. A comparison of the similarities and differences in active site genesis for SZ and WZ will be presented and discussed.

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