

Hydroisomerization of Normal Hexadecane with Platinum-promoted Tungstate-modified Zirconia Catalysts

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The acid-catalyzed isomerization of alkanes is of growing importance in determining the nature of transportation fuels, including environmentally clean high octane gasoline, high cetane diesel fuel, low pour point jet fuel and lubricant base stocks. However, isomerization of long-chain alkanes generally precedes cracking, leading to extensive undesired cracking reactions; this tends to limit catalytic paraffin isomerization to C₄-C₆ alkanes. It is highly desirable to obtain environmentally clean catalysts that can be used to isomerize long-chain paraffins with minimum cracking. Catalysts with a certain optimal balance of metal and acid functions at suitable reaction conditions are needed to suppress cracking in order to achieve high isomerization selectivity for long-chain paraffins.

Work during the past year examined the activity, selectivity and long-term stability of platinum-promoted tungstate-modified zirconia (Pt/WO₃/ZrO₂) catalysts for the hydroisomerization of long-chain linear alkanes under relatively mild conditions, using n-hexadecane (C₁₆) as a model compound. A continuous trickle-bed reactor was used to compare the activities and selectivities of three Pt/WO₃/ZrO₂ catalysts prepared by different methods and to investigate the effects of tungsten loading and of reaction conditions for hydroisomerization of n-hexadecane. A run of 93.5 h was conducted using the most highly active Pt/WO₃/ZrO₂ catalyst which contained 0.5 wt% of well-dispersed Pt and 6.5 wt% of W. Reaction conditions were manipulated and five shutdown (feed stopped, reactor temperature lowered but H₂ flow rate maintained) and restart operations were carried out (Figure 1). This catalyst showed high activity and stability. Considerable success was also achieved in converting n-hexadecane to isohexadecanes for 100 h at temperatures of about 220°C and under H₂ pressure as low as 160 psig (Figure 2). Best results (highest iso-C₁₆ yield) were 79.1 wt% n-C₁₆ conversion, 89.9 wt % iso-C₁₆ selectivity and 71.1 wt% iso-C₁₆ yield at 218°C, 160 psig H₂, H₂/n-C₁₆ mole ratio = 2 and WHSV=1 h⁻¹. A typical spectrum of hexadecane isomers obtained is show in Figure 3.

The Pt/WO₃/ZrO₂ catalyst is rugged and has properties which allow one to propose that it has considerable likelihood of attaining commercial uses.

Research has now shifted to the hydroisomerization and hydrocracking of longer paraffinic chains; C_{24} , C_{28} and C_{32} , as well as to the conversion of Fischer-Tropsch waxes to high cetane diesel and jet fuels.

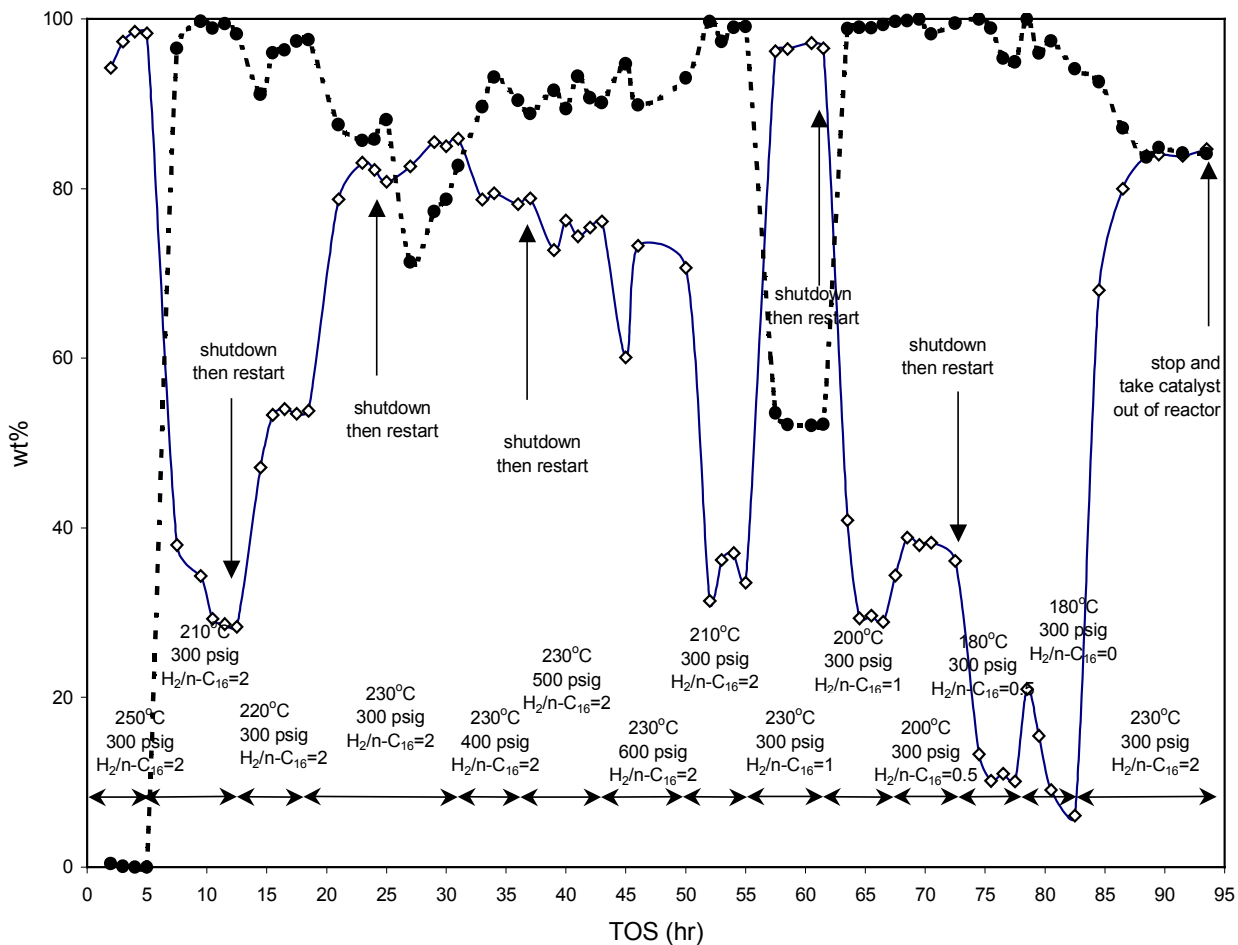


Figure 1. Effect of changes in temperature, pressure and H_2/nC_{16} on hexadecane conversion (solid line) and selectivity (dashed line).

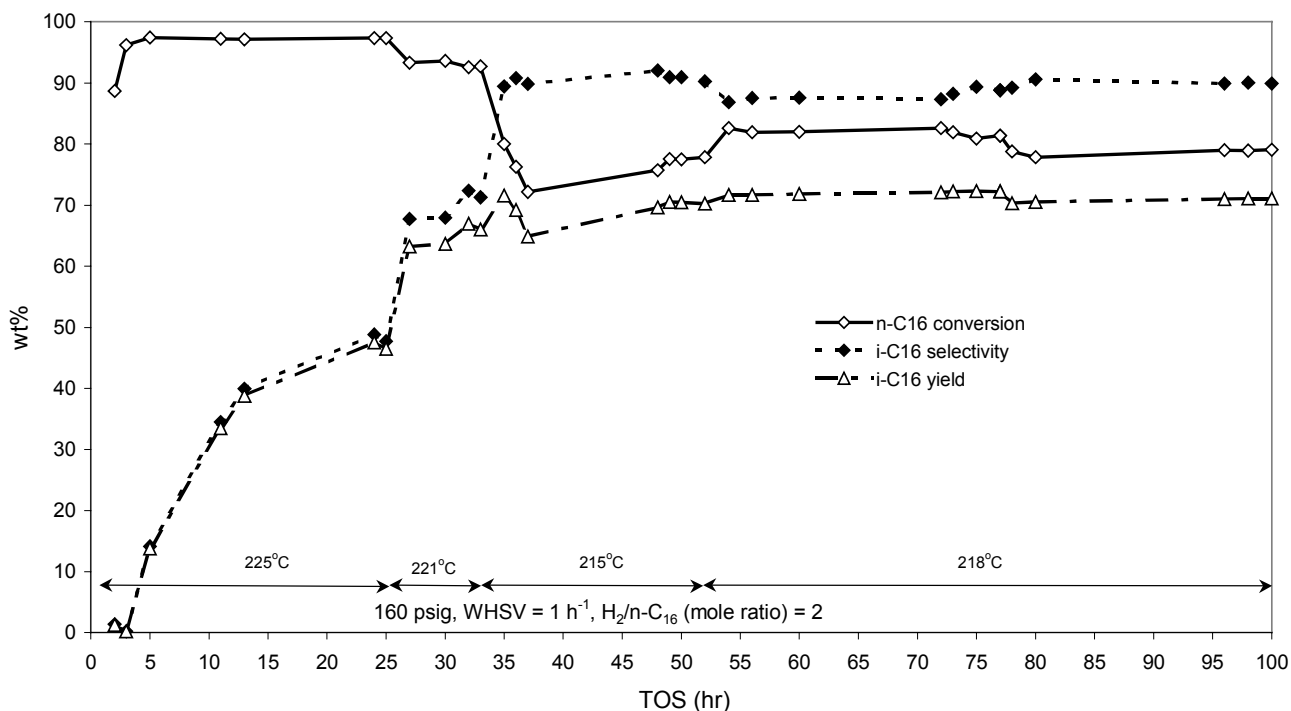


Figure 2. Effect of calcination and reactor shutdown on hydroisomerization of hexadecane.

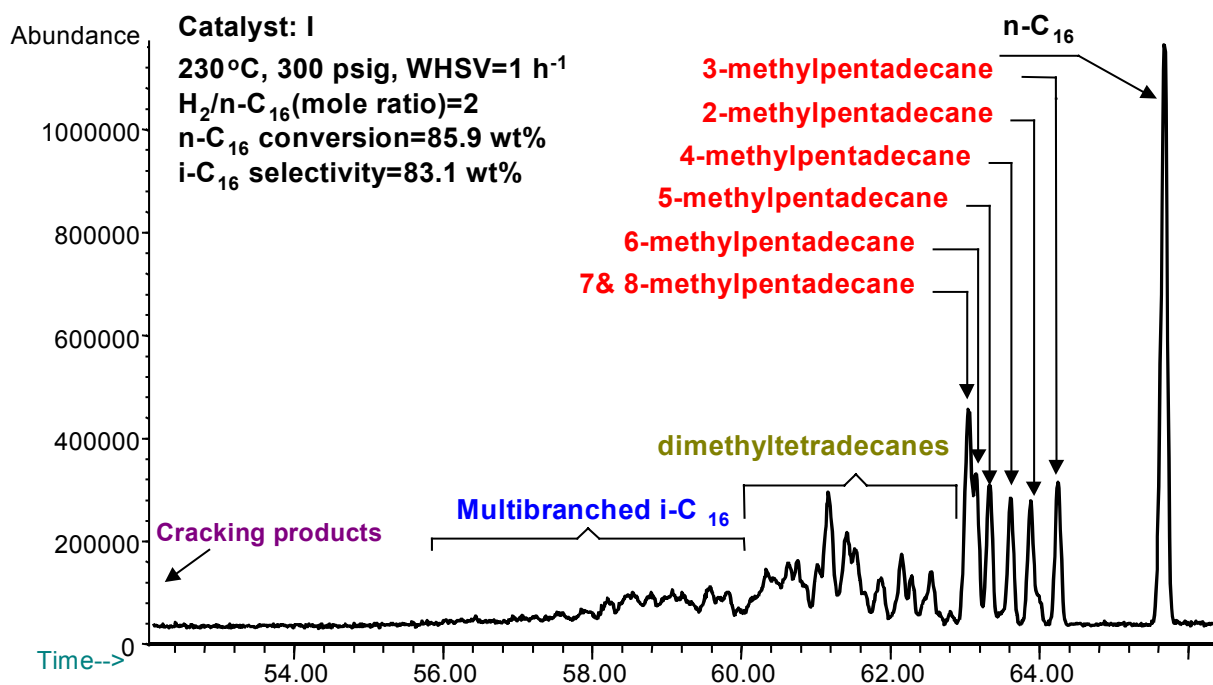


Figure 3. Typical GC-MS spectrum of hexadecane isomers in the products of n-C₁₆ hydroisomerization.