Upgrading Fischer-Trospch Waxes on Anion-Modified Zirconia Catalysts

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Introduction

The Fischer-Tropsch (F-T) synthesis is a very attractive route for the production of transportation fuels from natural gas, coal or biomass. The F-T synthesis is usually operated in high alpha values; over 60 wt% of the F-T products are waxes under these conditions. The conversion of these waxes is an important step to obtaining liquid fuels. Currently, the usual process of converting F-T waxes into jet/diesel fuels is by hydroprocessing using bifunctional noble metal promoted solid acid catalysts, such as Pt-promoted silica-alumina or Pt-promoted zeolites. These processes are operated at about 350°C and high H_2 pressure.

Work has been carried out on upgrading F-T waxes using anion-modified zirconia catalysts. The waxes can be converted into jet/diesel fuel over Pt-promoted tungstated zirconia (Pt/WO_3-ZrO_2) at low temperatures (200-220°C) and pressures.

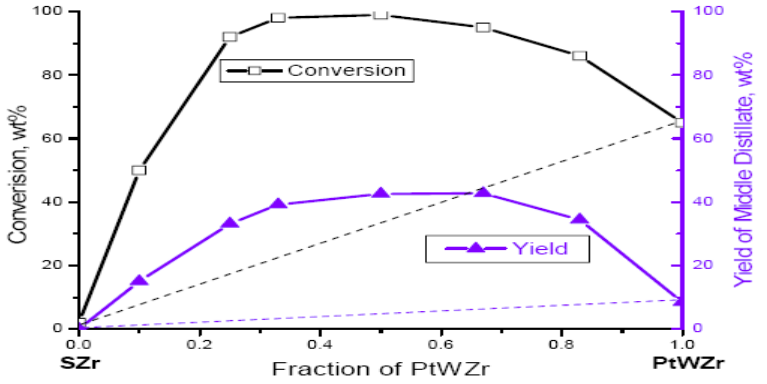
Activities and selectivities to these fuels can be markedly improved by the use of hybrid catalysts such as combining Pt/WO_3-ZrO_2 with SO_4-ZrO_2, with beta zeolite, or with mordenite. In this paper, several long chain hydrocarbons were used as model reactants. Experiments with waxes obtained from Sasol and from Energy International were also carried out.

Materials and Methods

Tungustated zirconia (12.5 wt% tungstate, designated as WZr) and sulfated zirconia (6.0 wt% SO_3, designated as SZr) were obtained from MEL Chemicals (Magnesium Elektron Ltd.). The received samples were calcined at 700°C (WZr) for 3 hours and at 600°C (SZr) for 3 hours. Pt was added to calcined WZr and SZr by incipient wetness impregnation with $H_2PtCl_6.6H_2O$, 38-41 wt% of Pt solution; the final loading of Pt is 0.5 wt%. designated as PtWZr and PtSZr respectively. The hybrid catalysts were made by mixing PtWZr with a strong acid catalyst, such as SZr, beta zeolite or mordenite. Detailed catalyst preparation could be found elsewhere[1]. Catalysts were calcined at 550°C for 3 hours before loading into the reactor. Reactions were carried out in a batchwise microautoclave reactor with 27 ml capacity, shaking at 200 rpm. The reactor was submersed in a preheated sand bath for fast and evenly heating. The reaction was terminated with a predefined time periods. For convenience, we define the products as gasoline (C5-C9), jet/diesel (C10-C20) and lub-base oil (C21-C32, branched hydrocarbons).

Results and Discussion

At the same conditions, conversions of long chain hydrocarbons increase with the length of the model reactants. For example, at 220°C and 500psi H2, 15 minutes reaction time, conversions of C20, C24 and C28 in a model mixture are 20%, 62% and 90% respectively. At lower conversions, products are mostly isomerized. With conversion as high as 95%, hydrocracking starts to increase. Essentially, hydroismerization and hydrocracking are consecutive reactions. To increase transportation fuel production from F-T waxes, the hydrocracking ability of the employed catalyst should be enhanced; We combine the PtWZr with a strong acid catalyst. The long chain hydrocarbon, n-C36 was used for comparison of different hybrid catalysts. Those hybrid catalysts have higher activities and better selectivities for converting long chain hydrocarbons to middle distillates than PtWZr or SZr alone is shown in Figure 1. Synergistic interactions are observed with the hybrid catalysts. The hybrid catalysts were characterized by XRD and SEM; results show that the hybrid catalysts are physical mixtures.



Catalyst: 0.2 g; Reactant: 0.8 g n-C_{36}; Reaction conditions: 200 °C, 25 min.

Figure 1. Conversion of n-C36 with SZr-PtWZr hybrid catalyst at 300 psig of H_2

Hydrogen pressure has a negative effect on catalysis with PtWZr and a positive effect with PtSZr. Hydrogen pressure can fine tune the contribution of these two catalytic components and therefore affect activity and production distribution.

F-T waxes from Energy International show little activity when the raw wax was used directly. After hydrogenation with Pt/Al_2O_3 catalyst at 200°C for 2 hours, the wax became pure white and could be easily converted to liquid fuels. The F-T wax obtained from Sasol is pure white; it could be converted into high yields of jet/diesel fuels using the hybrid catalyst. The fraction in the gasoline range consisted mainly of branched hydrocarbons which enhanced the octane number of the gasoline.

Significance

Pt-promoted tungstated zirconia catalysts can isomerizes long chain hydrocarbons to isomers. It can be combined with a strong acid catalyst to provide an excellent low temperature and low H_2 pressure process for producing jet/diesel, and gasoline fuels.

References

(1) Zhou, Z.; Zhang, Y. L.; Tierney, J. W.; Wender, I. *Fuel Process Technol* **2003**, *83*, 67-80.