Development of catalysts for end point reduction of straight run diesel fractions

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Over the years, for environmental reasons, the S-content of diesel is being progressively decreased through legislation all over the world. Simultaneously, the diesel end point (say T95) is also being lowered in order to lower soot production. The present Euro-4 specification for T95 is 360°C. Lowering of the end point causes a decrease in the overall yield of diesel and the profitability of the refiner. On the contrary, the refiner's diesel pool will be larger if the cut point were higher, say 380°C. As the major components in the heavier end of diesel are the alkyl di- and poly-nuclear aromatics and long chain n-paraffins, it is possible to bring down the end point of heavier diesel fractions (T95 = 380°C) by dealkylation and ring hydrogenation of the aromatics, mild isomerization of the n-paraffins and ring opening of the naphthenes. As feed S and N are poisons for hydrogenation and isomerization reactions, in commercial end point reduction processes, the catalyst is loaded in the last reactor in a DHDS train so that it encounters a clean feed [1].

We now report our studies on the endpoint reduction of two straight run diesel feedstocks containing substantial amounts of S over different supported Ni-Mo catalysts. The catalysts were prepared using four different supports with different compositions and acidities. The supports used were alumina (gamma), alumina-USY (10%), alumina-silica (10%) and alumina-zeolite beta (50%). The two feeds possessed different S-contents and hydrocarbon compositions. Feed 1 contained 2000 ppm S and 58% aromatics, while feed 2 contained 17600 ppm S and 58% paraffins.

The different supports were characterized by XRD, surface area (S_{BET}), pore-size distribution and acidity measurements by temperature programmed desorption of NH_3. The catalysts possessed large surface areas (220 – 300m^2/g), with fairly large pore volumes in the range of 0.5 to 0.8ml/g. The pores (excluding the zeolite pores) had diameters in the range of 50 – 150Å. The TPD profiles of the supports were deconvoluted into three or more individual peaks and based on the peak-maximum-temperature of these peaks, the acidity distribution in these supports was profiled as weak, medium and strong.

The catalytic activity screening studies were carried out in a high pressure bench-scale reactor using about 200g catalyst charge. The reactions were generally carried out at temperatures in the range of 330 - 350°C, pressures between 40 – 60 atmosphere, weight hourly space velocity of 1 - 2 h^{-1} and H_2/ oil ratios of 300 v/v. The studies revealed that large end-point (T95) reduction of the feeds could be achieved over the catalysts. The end-point reduction observed was in the between 4 - 20°C over the different catalysts. The best catalyst for feed 1 was Ni-Mo-silica-alumina. An end point reduction of about 20°C was observed over this catalyst. Feed 2 was less responsive to end point reduction even over the most acidic Ni-Mo-alumina-beta catalyst, only a T90-reduction of about 8°C being observed. All the catalysts caused substantial desulfurization of the feed. The studies reveal that tuning of the catalyst properties has to be done taking into account the feed characteristics in order to develop good end point reduction catalysts.

[1] Hydrocarbon processing, Refining Processes Handbook, 2006.