Upgrading of Polynuclear Aromatics by Selective Catalytic Ring Opening

Jens Weitkamp
Institute of Chemical Technology, University of Stuttgart

Polynuclear aromatics in diesel and jet fuels possess a number of undesirable properties, such as very poor ignition characteristics and cetane numbers, unfavorable cold-flow properties, a propensity for soot formation and a very low hydrogen content which inevitably results in high specific carbon dioxide emissions from the engine. For these reasons, the content of polynuclear aromatics in, *e. g.*, diesel fuel, is currently limited to 8 wt.-% in the European Union, and an even more far-reaching reduction is under discussion. Certain refinery streams which are notoriously rich in polynuclear aromatics, such as light cycle oils from fluid catalytic cracking or middle distillate fractions from delayed or fluid cokers, can sometimes be blended into diesel fuel in a limited amount only. The issue of polynuclear aromatics will be aggravated, when significantly larger portions of non-conventional, hydrogen-poor heavy oils will be processed in the future, such as bitumen from oil sands or ultra-heavy oils of the Orinoco type. Selective hydrodecyclization of polynuclear aromatics occurring in middle distillates into hydrogen-rich, high-value fuel components, like one-ring naphthenes or, even better, alkanes without degradation of the carbon number continues to be a major challenge of heterogeneous catalysis.

Around 2000, various groups started publishing their results obtained in catalytic ring opening of model hydrocarbons, mostly decalin or tetralin. In this lecture, an attempt will be made to critically review this recent literature. For the most part, bifunctional catalysts consisting of platinum on zeolites Y or Beta were used, but monofunctional acidic catalysts were tested as well. Surprisingly few studies were devoted to hydrogenolytic ring opening on noble metals. Prior to ring opening, polynuclear aromatics are fully hydrogenated to the corresponding naphthenes. On a bifunctional catalyst, these react further at temperatures of ca. 250 to 350 °C, the fastest reaction being skeletal isomerization followed by opening of one naphthenic ring. Typical yields of one-ring naphthenes with the carbon number of the feed are in the range of ca. 20 to 45 %. Interestingly, virtually nothing has been reported concerning the formation of the particularly desired alkanes with the carbon number of the feed. Just one group is mentioning the occurrence of decane isomers in the hydroconversion of decalin on a Pt,Ir/H-Y zeolite catalyst, but their best yield of the desired alkanes was as low as 4 %.

Finally, very recent results obtained by our group in a cooperation with Eni S.p.A., San Donato Milanese, Italy, will be presented in which advanced methods were applied for the analysis of the very complex product mixtures generated by ring opening of decalin. It will be shown that noticeable amounts of open-chain decanes can be produced if appropriate catalysts are used. Moreover, it will be demonstrated that hydrodecyclization of multi-ring naphthenes can proceed either via bifunctional catalysis or via hydrogenolysis. The salient features of both pathways will be discussed, and novel catalysts will be disclosed that enable yields of open-chain decanes beyond 30 %.