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# Platinum Catalysts in Oil Refining

## STUDIES OF REACTION MECHANISMS

One of the most important processes in petroleum refining is the catalytic reforming of naphtha feeds, using platinum on alumina catalysts, to yield the high-octane gasoline required in automobiles. Since this process was first introduced by Universal Oil Products in 1949 there have been many attempts to elucidate the mechanisms of the catalytic reactions, and a recent article by S. R. Tennison of the BP Research Centre at Sunbury, Middlesex reviews the current position (*Chem. Br.*, 1981, **17**, (11), 536-540). This interesting paper describes the use of advanced surface examination techniques to increase our understanding of the physics and chemistry of the catalyst surfaces, but as the author admits, a number of questions remain unanswered.

Naphtha feeds are distillate fractions consisting of alkanes, cycloalkanes and aromatics, boiling at 70 to 190°C and with research octane numbers (RON) in the range 20 to 50. Catalytic reforming raises the octane number to between 85 and 95, and the addition of alkyl lead compounds further increases the RON to the 93 to 100 for sale at the pump. The principal upgrading reactions serve to increase the concentrations of *iso*-alkanes and aromatics, using temperatures of 500 to 525°C and 25 bar pressure. A typical catalyst for this reaction is 0.3 weight per cent platinum supported on alumina and promoted by about 1 weight per cent chlorine, although more recently 0.3 weight per cent of a second metal may also be incorporated. Under such conditions, hydrogen to hydrocarbon ratios of 6:1 are used with a liquid hourly space velocity of 2.

The reactions are thought to proceed

sequentially over metallic and acidic sites. The skeletal rearrangements take place on the acidic alumina sites, and the hydrogenation/dehydrogenation reactions on the metallic platinum. Two side reactions that take place on both kinds of site need to be minimised; these are cracking, which reduces the liquid yield, and coke formation which reduces the catalyst life.

Reports of platinum-support interactions to give platinum-oxygen-aluminium species are reviewed. The two most important defects of reforming catalysts are sintering and coke formation, and methods for rejuvenation and decoking are described. The use of oxygen or air to reactivate the catalysts could involve conversion back to the  $[(Al-O)_xPtCl_2]$  complex that has been observed in the fresh catalysts.

## Multimetallic Platinum Catalysts

Although monometallic catalysts are not yet fully understood, they have been superseded by bimetallic catalysts such as platinum-rhenium, platinum-gallium, platinum-germanium and platinum-tin, and tri- and tetra-metallic systems are now being studied. Bimetallics tend to produce less coke and are more stable, this permits higher severity operation giving improved liquid yields and RONs. The continued use of advanced surface analysis techniques is increasing our understanding of interactions between the two metals and the support. This knowledge will aid the design of improved catalyst systems to give the increased aromatisation activity and liquid yields necessary to reduce oil utilisation and to increase the RON as the allowable levels of lead in gasoline are reduced.

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