Continued Importance of Platinum Metals Catalyst Systems

Catalytic Naphtha Reforming, Science and Technology

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Catalytic reforming is used in oil refineries to improve the octane number of naphthas or light distillates to convert them into the motor fuel required for high compression ratio internal combustion engines. It is also a major source of aromatics for the petrochemicals industry. In this book the editors have collected together fifteen useful contributions on this important area of catalytic processing technology, based on the use of supported platinum on alumina catalysts. The net effect of catalytic reforming the naphtha feedstock is to convert the paraffins and naphthenes into aromatic hydrocarbons.

The first section of the book deals with the chemistry and processing of petroleum and the chemical reactions which take place in the presence of reforming catalysts. The relationships between chemical composition of the fuel, its octane number, and its performance are indicated, and the various petroleum conversion processes outlined.

The second part of the book gives methods for the preparation and characterisation of the various bi- and multimetallic platinum catalysts used in reforming processes. Preparative techniques for multimetallic catalyst systems include successive impregnation, co-impregnation, successive ion exchanges, and use of metals in alumina sols. Although platinum catalyst technology was first used commercially in the late 1940s, much research and development has been performed since that time. This has resulted, for example, in the introduction of bimetallic catalyst systems, such as those involving platinum/rhenium, platinum/tin, platinum/iridium and platinum/germanium combinations. It is thought, however, that improvements in catalyst formulation and preparation procedures are still possible and that more fundamental studies are required in order to achieve better control of the individual preparative steps. The acidity of the high surface area alumina support is normally promoted with halogen, usually chlorine. There is still a perceived need for new preparation routes which would lead to highly tuned multimetallic catalysts and also for entirely new formulations. Some less well established patented bi- and multimetallic catalysts are listed in a useful Table.

For characterisation, both the acidic and metallic functions of these bifunctional catalyst systems must be considered. Methods to determine the characteristics of the alumina supports are given, including surface area, porosity and acidity. The chemical state of the metal in platinum on alumina catalysts may be assessed using numerous techniques, such as dispersion, XRD, TEM and chemisorption. The application of various aspects of these techniques to the characterisation of supported platinum/rhenium, platinum/tin and other bimetallic catalysts and platinum on alkaline L zeolites is also considered. The relationships between the method used for preparation and the structure of the resulting catalyst are discussed.

For a commercial plant, the pre-treatment and operation procedures appear to produce a catalyst having a high platinum dispersion. The combination of high dispersion and low metal loading does, however, mean that most of the experimental characterisation techniques have only limited value for commercial catalysts. One useful indicator is that the hydrogen:platinum ratio for chemisorption of hydrogen should closely approach or exceed unity. The relationships between catalyst composition and structure and its performance receive detailed consideration in two chapters. In view of the large volume of naphtha throughput in reforming plants, the characteristics of the catalyst performance can have very big implications on the economic returns.

In a third section of the book, catalyst deactivation and regeneration during use in commercial processes is discussed. The mode of operation during manufacturing procedures is considered in detail and processes such as coking, poisoning, and sintering are described. Methods used to regenerate and re-activate the catalysts are given. For optimum performance of the catalyst it is crucial that a proper balance between metal and acid function is maintained. If the metal function is too strong, excessive hydrogenolysis to produce C_1 to C_4 gases and dehydrogenation to give polyolefinic coke precursors can occur; but if it is too weak then excessive coking also takes place and the catalyst deactivates rapidly. An acid function which is too strong leads to excessive hydrocracking and coke laydown on the catalyst; but if it is too weak the rate-determining carbonium ion reactions involved in dehydroisomerisation and dehydrocyclisation do not proceed fast enough, and this in turn leads to an increase in C_1 to C_4 gas production and a decrease in the yield of liquid product. Recovery of platinum and rhenium from spent reforming catalysts is also an important part of the total economic picture and a chapter on the methods used is included.

In a final section of the book the plant aspects of catalytic reforming processes are discussed. The main elements of reforming process technology include operating strategy and steady-state optimisation, process control, catalyst selectivity and stability, environmental control, integration with other refinery units and refinery energy balance. The reforming process continues to satisfy changing gasoline pool requirements, but refiners and catalyst manufacturers must seek means to improve catalyst performance to enhance the selectivity to aromatics and high octane reformate.

Several commercial reforming processes are available for licensing worldwide, these include UOP-Platforming, IFP Reforming, Engelhard Magnaforming, Exxon Powerforming, Chevron Rheniforming, Amoco Ultraforming, and Houdriforming; and the similarities and differences between these various processes are considered. Catalytic reforming enjoys a virtual monopoly of supplying aromatics to the petrochemical industry.

Changes in process design are frequently accompanied by modification of the catalyst for improved performance to achieve one of the following objectives:

- Higher reformate octane yields
- More efficient catalyst regeneration
- Longer catalyst life and enhanced surface stability
- Lower-pressure operation and less hydrogen recycle

A chapter in this section discusses modelling commercial reformers, and a final chapter describes recent developments in reforming. The increasing world demand for unleaded and higher octane gasoline as well as for aromatics will continue to spur the development of more efficient catalysts and processes. The implementation of clean air regulations, which restrict the benzene and aromatics content of gasoline will also have an effect on reforming. Catalysts which isomerise the lighter C_6 and C_7 hydrocarbons to the branched isomers with higher octane numbers will be much in demand. Vapour pressure constraints will result in the elimination of butane from gasoline. The use of cleaner alternative fuels, such as oxygenates, may reduce the demand for aromatics in gasoline, but the increased demand for aromatics from the petrochemicals industry means that processes which result in high aromatics will continue to be important.

This book contains some interesting articles on various aspects of catalytic naphtha reforming, and has a useful subject index. The authors are from industry, universities and research institutes in a number of countries, but the picture presented is reasonably unified; however, there is repetition as most writers introduce the topic in a general way. Many chapters in books and review articles in journals are available on aspects of this subject, but it is still useful to have a one-volume up-to-date collection of contributions on this very significant aspect of catalytic processing which affects important facets of our daily lives, and to have pointers to likely future developments. D.T.T.