

Duofunctional Platinum Catalysts in the Petroleum Industry

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The transition of petroleum refining from relatively simple thermal operations to more selective and efficient catalytic processes has been one of the major advances of industrial chemistry in modern times. This transition has been made possible by the development of highly selective catalysts designed to meet the exacting requirements of modern petroleum conversion processes. Of such catalysts, those containing platinum as an active component have dominated the petroleum refining art during the past decade.

The ability to "tailor-make" catalysts for specific purposes is well illustrated by the case of four duofunctional catalysts developed for the petroleum refining industry by Universal Oil Products Company and widely used in processes licensed by it throughout the Western hemisphere. These catalysts—Platforming, Penex, Butamer and Hydrar*—all contain platinum as one of the functional agents. The other function is provided by several types and degrees of acidity built into the specially prepared catalyst support in such a way as to provide the necessary balance and co-action between the platinum, the acid function and the support for the specific feedstocks and operating conditions characteristic of the process involved.

Platforming Process

Platforming is a method of catalytically reforming petroleum naphthas to improve their anti-knock properties. Chemically speaking, the naphtha feed contains three types of hydrocarbons (paraffins, naphthenes and aromatics), each of which is capable of

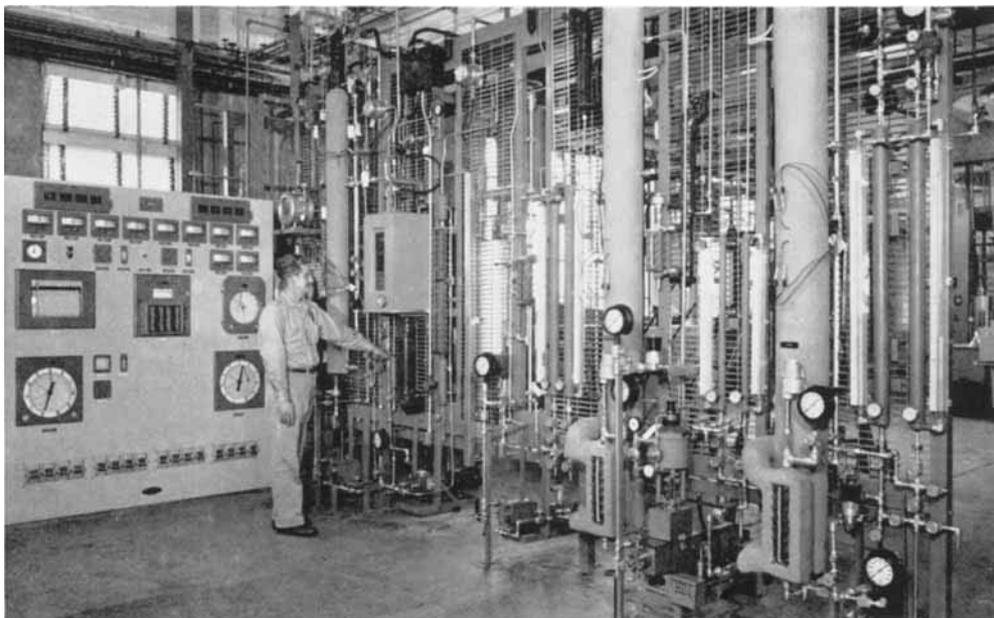
undergoing a number of reactions under the conditions of high temperature and pressure prevalent in the reactor. The platinum and acid functions in co-action with each other and with the support are balanced with the operating conditions to achieve a proper control of the several possible reactions of each of these hydrocarbon types, so that the course of the reaction is directed toward the production of a maximum yield of desired product with a minimum amount of undesirable by-products.

Catalytic reforming involves four primary reactions. These are dehydrogenation of naphthenes containing either five- or six-membered rings to aromatics, the dehydrocyclisation of paraffins to aromatics, the hydrocracking of higher to lower boiling paraffins, and the isomerisation of paraffins to more highly branched structures.

The acid function incorporated in the Platforming catalyst accelerates the isomerisation, cracking and cyclisation of hydrocarbons. The platinum function accelerates hydrogenation and dehydrogenation, such as the conversion of naphthenes into aromatic hydrocarbons, and the dehydrogenation of paraffins to olefins as one of the initiating steps in paraffin cracking and isomerisation.

These two functions are combined in the Platforming catalyst on a rugged, specially prepared alumina support through which the active components are uniformly dispersed so as to provide ready access to the catalyst sites for the enormous hydrocarbon traffic required for an economical process. In addition to its primary function in the main Platforming reactions, platinum also plays

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Intensive research over a long period of years by Universal Oil Products Company has provided the petroleum industry with a number of highly selective platinum catalysts of widely different properties. Here catalyst performance is being investigated on a pilot plant scale

of the reactions involved (for example hydrocracking to yield gaseous isobutane as shown in equation (4)) must be minimised and the other reactions maximised, if theoretical yields are to be approached. Yet, the apparent paradox must be faced that the same catalyst function required for the desirable reactions likewise induces those which must be minimised. It is clear, therefore, that in the design and manufacture of a catalyst, as well as in the engineering of the process in which the catalyst is employed, there must be a very fine balance among the number of catalyst sites, their location with respect to each other, and the operating conditions employed. As refining needs have changed, it has been possible to vary this balance to maintain a high level of performance.

Penex Process

It is characteristic in the Platforming process just discussed that the isoparaffins formed (for example isobutane and isopentane) are present in higher than equilibrium

concentration in their respective fractions. It is apparent that the Platforming catalyst, under Platforming conditions, does not isomerise the isoparaffins first formed as a result of hydrocracking sufficiently to achieve equilibrium; nor is it desirable to isomerise the light isoparaffins. An increase in effectiveness of the acid function would not only cause such unwanted isomerisation, but the catalyst would be unbalanced for the other reactions necessary for successful Platforming.

For this reason, it was necessary to develop a catalyst for paraffin isomerisation that incorporated a different balance of acid *v.* platinum functions than is present in Platforming catalyst. The resulting Penex catalyst was developed specifically for the hydroisomerisation of pentanes and hexanes to highly branched isomers desirable as components in high octane fuels. Its increased acidity, as compared with that of the Platforming catalyst, permits operation at temperatures of approximately 250 to 375°C—sufficiently lower than the operating range in Platforming to take advantage of the

higher equilibrium concentrations of iso-compounds which are possible at the lower temperatures.

Like Platforming, the Penex process operates in a hydrogen atmosphere to ensure long catalyst life through continuous cleansing via the platinum component, thereby eliminating the need for frequent catalyst regeneration and providing process economy. The Penex process can be employed for isomerisation of pentane alone, or of hexane alone, or for isomerisation of a light naphtha comprising a mixture of the two. So selective is the catalyst and the process which employs it that volumetric yields of isopentane of over 99 per cent have been obtained commercially in the isomerisation of pentane.

The isomerisation of hexane may be conducted either to obtain a higher octane-number hexane product, or selectively to produce individual isomeric products. Thus, 2,2-dimethylbutane may be isolated as the

lowest-boiling product and all other isomers recycled to obtain nearly quantitative ultimate yields of this isomer.

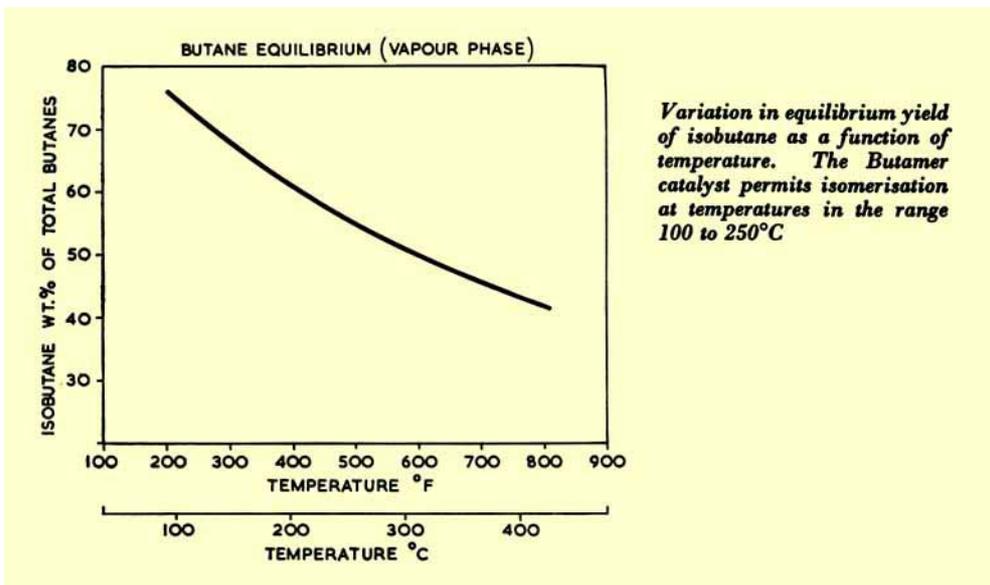
Butamer Process

The need for a catalyst even more effective than the Penex catalyst for butane isomerisation—one that would operate at several hundred degrees below the effective temperature for Penex operation—led to the development of the Butamer catalyst. Such a catalyst could take advantage of the marked increase in the isobutane equilibrium yield as a function of temperature as shown in the graph on page 6.

The Butamer catalyst is a platinum-containing, duofunctional, solid hydroisomerisation catalyst of such enhanced activity and selectivity that it permits isomerisation of butane (or pentanes and hexanes) substantially to equilibrium at temperatures in the range of 100 to 250°C. This catalyst



The Penex process employs a platinum catalyst specifically designed for the hydroisomerisation of pentanes and hexanes to highly branched isomers for use in high octane fuels. This Penex unit forms part of a refinery in Louisiana

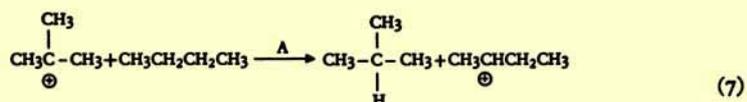
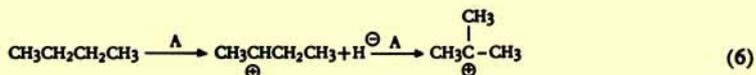
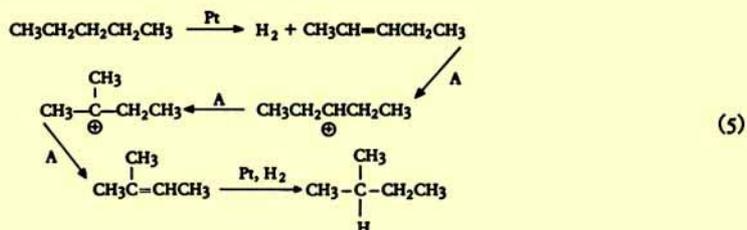


represents a significant extension of platinum catalysis to a lower temperature region of hydrocarbon conversions than hitherto was considered feasible. Like the Platforming and Penex catalysts, the Butamer catalyst brings about hydroisomerisation in a continuously self-cleansing manner, so that it is

capable of uninterrupted use for many months or even years.

It will be noted that the mechanism of isomerisation illustrated in equation (5) involves dehydrogenation of the paraffin by the platinum function to an olefin as an initiating step, followed by conversion of the

Hydroisomerisation of Paraffins



Pt=Platinum Site
A=Acid Site



A Hydrar process unit at an Oklahoma refinery. A platinum catalyst is used for the conversion of benzene to high purity cyclohexane, mainly for subsequent oxidation to adipic acid in the preparation of Nylon-type polyamides

olefin to a carbonium ion by the acid function, isomerisation of the carbonium ion, generation of an iso-olefin from the isomerised ion and, finally, rehydrogenation of the iso-olefin to an isoparaffin. At the lower temperatures of operation, desired because of favourable equilibrium conditions for butane isomerisation, the dehydrogenation step is so slow as to offer a serious obstacle to feasible reaction rates if catalysts of the Penex or Platforming type are used.

As a result of the enhanced acidity of the Butamer catalyst, it is believed that the initial paraffin activating step differs from that of the higher temperature operation employed with Penex or Platforming catalysts. The Butamer initiating reaction is thought to be one of hydride abstraction via the acid function, as shown in equation (6). Once the reaction has been initiated, it is propagated by a chain mechanism under the influence of the exceedingly acidic sites of the Butamer

catalyst as shown in equation (7). The platinum serves to maintain catalyst cleanliness and high activity through continuous hydrogenation of polymeric carbonaceous by-products, thus permitting their continuous removal.

Hydrar Process

Thus far we have considered three processes employing acidic platinum-containing catalysts in which the acidity has been modified to conform with the requirements of each process. In the Hydrar process, a platinum-containing catalyst is used for the conversion of benzene to high purity cyclohexane.

Such cyclohexane is mainly used for oxidation to adipic acid in the preparation of Nylon-type polyamides. So exacting are the purity requirements of cyclohexane for this use that no more than trace amounts of other hydrocarbons may be tolerated.

Since the Hydrar reaction is conducted at a temperature at which from about 2 to 6 per cent of methylcyclopentane might be formed if an isomerisation equilibrium with the cyclohexane product could be established, it was necessary to employ a catalyst that did not induce isomerisation. In addition, to assure virtually quantitative yields of cyclohexane, it was necessary to suppress all cracking to open-chain compounds.

It will be noted from equations (2) and (4) that the acid function of duofunctional catalysts plays a key role in both the isomerisation and cracking of naphthenes. The Hydrar catalyst which was developed for benzene hydrogenation is, therefore, one in which the platinum is disposed on a specially prepared support in which the acidity has been virtually completely suppressed. As a result, benzene is hydrogenated cleanly to cyclohexane of over 99.7 per cent purity in the Hydrar process. If a pure benzene is used as

the feedstock, essentially quantitative yields of cyclohexane are produced during several years of continuous operation without contamination or deactivation of the catalyst.

Summary

The Platforming catalyst for reforming naphthas, the Penex catalyst for hydroisomerisation of pentanes and hexanes, the Butamer catalyst for hydroisomerisation of butane, and the Hydrar catalyst for conversion of benzene to cyclohexane, provide examples of four supported platinum catalysts of widely differing properties obtained by regulating the acidity of the catalyst composite. Through proper balance of the platinum hydrogenation-dehydrogenation function with the acid function, in co-action with the support, such duofunctional catalysts can provide a high degree of selectivity for hydrocarbon conversion processes operating under widely different conditions.

Oxygen Injection Engine for Space Research

PLATINUM ALLOY VALVE SEATS AND FACES

Formidable design problems are encountered in the development of a reciprocating power unit for use in space research programmes. One of the most severe of such problems met with by the Vickers Inc. Division of Sperry Rand Corporation in developing a light-weight hydrogen-oxygen internal combustion engine (shown on the right) concerned the selection of materials for the oxygen injector valve. As this valve, operating at very high speed, handles gaseous oxygen at high temperatures, it must be made of a material that will resist oxidation and also maintain adequate strength and impact characteristics.

Tests were carried out on austenitic stainless steel, a nickel-chromium-molybdenum alloy and 10 per cent rhodium-platinum alloy for the poppet valve face, and on stainless steel, 10 per cent rhodium-platinum and the latter alloy flame-plated with alumina for the valve seat. The best combination was found to be a rhodium-platinum poppet face against a flame-plated rhodium-platinum seat. This combination has endured several hours of operation without leakage or deterioration of

the plating surfaces and with good ability to compensate for minor misalignment.

