and its derivatives is their remarkable resistance to progressive contamination by reduced species, which is a major cause of eventual crucible failure, due to preferential diffusion of contaminants along grain boundaries. The increased grain boundary area conferred by the highly elongate fine grain structure of these materials provides a massive sink for contaminants, which increases the time before the critical composition of a low melting point or brittle intermetallic phase is produced.

With the increasing use of oxides of elements such as bismuth and lead which readily form phases with platinum in the elemental form, particularly in high energy regions such as grain boundaries, the use of ZGS platinum has produced dramatic gains in terms of crucible durability and life. For example during the growth of bismuth germanate, lead molybdate and lithium niobate crystals the useful life of apparatus has been increased in the order of five or ten times, compared with that of conventional platinum apparatus.

P.E.S.
A.E.H.

New Bimetallic Palladium Catalysts

HIGH EFFICIENCY HYDROCARBON PROCESSING

During the catalytic reforming processes used in the oil industry to increase the octane numbers of hydrocarbon fuels, the use of bi- and multi-metallic platinum based catalyst systems is well established. Now, it is reported that a new generation of bimetallic palladium catalysts has been developed for the hydrotreatment of hydrocarbon feedstocks where selective hydrogenation is required, for example the hydrogenation of acetylene to ethylene, or butadiene to butene-1 (J. -P. Boitiaux, J. Cosyns, M. Derrien and G. Léger, *Hydrocarbon Process.*, 1985, **64**, (3), 51–59). The use of these new catalysts helps to limit the occurrence of side reactions such as saturation of the double bond and olefin isomerisation and oligomerisation, as well as catalyst poisoning by sulphur containing feeds.

Procatalyse and Institut Francais du Pétrole have produced new improved bimetallic catalyst systems which comprise palladium and a second metal deposited on an appropriate support. The catalysts have been developed following mechanistic studies involving considerations of the relevance of the hard and soft acid/base theories of Pearson and the principles of organometallic ligands, in order to ensure the appropriate degree of binding of the unsaturated substrate molecules to the catalyst.

Preparative methods have been devised which result in direct interactions between the two metals present in the catalyst. Thus, methods used for the preparation of the catalysts include decomposition of a metallic salt by another metal previously deposited on the carrier, reduction of an organometallic compound by a first metal already deposited and reduced, impregnation of the support with bimetallic clusters, coprecipitation of mixed oxides in the pores of the support and their subsequent reduction, deposition of a second metal on to another introduced previously in the oxide state as a support and using the strong metal support interaction (SMSI), and vapour condensation of the two metals on the support either in one step or two.

A palladium alloy catalyst system of this type has now been developed, for example, to hydrogenate the acetylene content (1.1 per cent) in ethylene streams using a new liquid phase process involving a recycled solvent. Similar processing techniques have also been used for the selective hydrogenation of both C_3 and C_4 streams, for the hydrogenation of propyne to propene, and for the removal of acetylenic material from butadiene, respectively.

All these processes have considerably increased life compared with conventional processes based on monometallic palladium catalysts, and palladium losses are considerably reduced in, for example, C_4 processing. Isomerisation of butene-1 to butene-2 has been limited by the addition of the second metal to palladium in the catalyst. The new palladium catalysts have been shown to give improved activity in the one-stage, selective hydrogenation of pyrolysis gasoline, where significant quantities of sulphur-containing impurities are present.

The authors conclude that their new generation of palladium catalysts meet the stringent requirements of the refining and petrochemical industries where economics dictate very high standards of performance.

D.T.T.