Preparation of Alumina Supported Palladium-Platinum Catalyst

A NOVEL TRIBOPHYSICAL TECHNIQUE

By S. Yamaguchi

National Institute for Researches in Inorganic Materials, Sakura-mura Niihari-gun Ibaraki-ken, Japan

Economic considerations require that platinum metals and alloys used as catalysts should have a high surface to volume ratio, thus extremely small particles are required. This article describes a tribophysical process for producing such particles uniformly dispersed on alumina. The catalytic activity and life of the materials produced have been tested for the oxidation of hydrocarbon gas and the results are discussed.

A method of producing alumina supported platinum group metal alloy catalysts has resulted from a preliminary study which employed a tribophysical method for platinum catalyst preparation. Initially the surface of a platinum plate was mechanically polished with an abrasive suspension consisting of gamma-alumina (1) and water, in the ratio 1:1 by weight. During this polishing operation the suspension changed into a grey coloured paste, samples of which were structurally analysed.

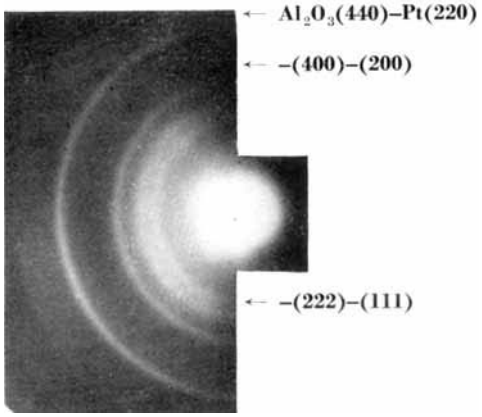

Fig. 1 Electron diffraction pattern obtained from the paste produced when a platinum plate was mechanically polished with gamma-alumina abrasive. This pattern verifies the presence of particles of uniform size, estimated to be about 50Å.

Wavelength of the electron beam used: 0.0312 Å. Distance between the object and the photographic plate: 50 cm. Positive enlarged ×2.3

The electron diffraction pattern which was obtained from the paste is shown in Figure 1 and demonstrates the formation of an emulsion in which the platinum and the alumina particles are uniformly dispersed (2, 3, 4). The result of the analysis of Figure 1 is given in the table. The reflections of the gamma-alumina coincide with those of the platinum, since the lattice of the former (space group: Fd3m, cell edge: 7.90 Å) approximates to

Results of the Analysis of Figure 1

Interplanar Spacings d(Å)	Reflections	
	Al_2O_3	Pt
4·56	111	—
2·80	220	—
2·38	311	—
2·28	222	111
1·97	400	200
1·52	333	—
1·40	440	220

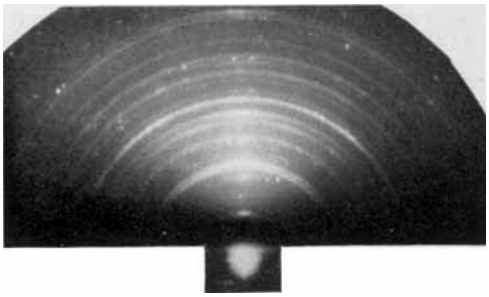

Fig. 2 Electron diffraction pattern from the platinum-10 weight per cent palladium alloy. The reflections correspond to an intermetallic compound with a superlattice structure whose long period is 86.5 Å, and is presumed to be Pt_3Pd

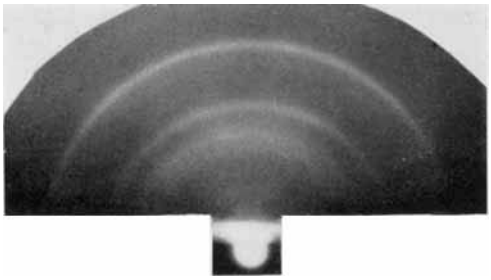

Fig. 3 Diffraction pattern of the platinum-palladium on alumina paste prepared from the alloy illustrated in Figure 2. This pattern is similar to that shown in Figure 1

that of the latter (space group: Fm3m, double the cell edge: 7.84 Å). From the half-width value of the reflections found in Figure 1, the mean size of the particles is estimated to be about 50 Å, a particle size suitable for heterogeneous catalysis (5).

Further work has established that the platinum content of a catalyst produced by this technique can be controlled by varying the duration of the polishing operation.

Platinum-Palladium Alloy Catalyst

It is, of course, well known that palladium metal is an able catalyst for the slow oxidation of hydrocarbons, however its catalytic life is short in comparison with that of platinum. This is because palladium is susceptible to oxidation, and the oxide formed is rather volatile. In an attempt to surmount these difficulties the tribophysical procedure employed to produce the platinum on alumina catalyst was used to try to produce a palladium–platinum catalyst.

The starting materials were an ingot of the binary alloy 10 weight per cent palladium–platinum and the aqueous suspension of gamma-alumina. Figure 2 reproduces the electron diffraction pattern of the alloy used, the reflections as a whole corresponding to the intermetallic compound characterised by a superlattice structure. When the surface of the alloy ingot was polished mechanically with the abrasive alumina suspension, the latter became dark. The electron diffraction pattern obtained from a sample of the dark paste so prepared is shown in Figure 3 which is similar to Figure 1, the alloy particles being uniformly scattered on the alumina support. This colloidal emulsion, whose palladium–platinum content was about 20 per cent by weight, was utilised as a catalyst.

Testing of Catalytic Activity

The alumina supported platinum metal and palladium-platinum alloy catalysts produced by this tribophysical method have been tested for catalytic activity and life. In the initial test, to which both catalysts were subjected, thin fibres of asbestos smeared with catalyst paste containing approximately 20 per cent by weight of platinum group metal were

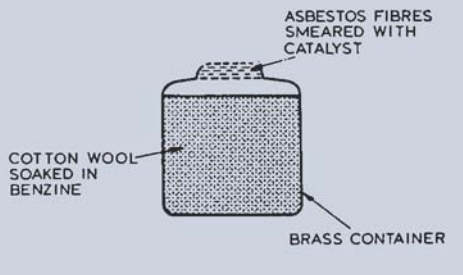

Fig. 4 A device for testing the catalyst consists of a container, 5 cm × 5 cm × 1 cm, holding cotton wool soaked in benzine. Asbestos fibres smeared with the catalyst paste are positioned at the top of the vessel

utilised for the slow combustion of hydrocarbon gas. The asbestos supported catalyst was arranged (Figure 4) at the top of a vessel containing cotton wool soaked with benzine having a boiling point between 50 and 120°C. Thus the catalyst surfaces were always immersed in a vapour of benzine mixed with air. After the catalyst had once been ignited a slow continuous combustion of the hydrocarbon gas took place on the surface of the catalyst particles at a temperature of about 400°C. The catalysts were found to have a long active life with activity still intact after continuous use for three months.

In addition catalysts prepared and tested as described could be distinguished from those obtained by the thermochemical decomposition of platinum compounds in two important ways. In the former catalyst, which was prepared at room temperature, there was no loss of surface area due to sintering of the particles, while the latter conventionally prepared catalyst could be contaminated by the reaction products.

The platinum on alumina catalyst prepared by the tribophysical method was also subjected to an additional test which involved the combustion of isobutane on the surface of the catalyst. Two coiled resistance elements, each having ten turns, made from 0.03 mm diameter platinum wire were covered with platinum/alumina paste, the platinum content again being about 20 per cent by weight. These two elements were then arranged as the two resistances in a Wheatstone's Bridge and maintained at a temperature of about 400°C by applying an electric current. After the meter showed that the Wheatstone's Bridge had been satisfactorily balanced one of the resistance elements was surrounded by an atmosphere of air and 0.6 weight per cent isobutane. Since combustion of the isobutane then took place on the catalyst surface, and consequently the resistance of the element in question changed, a potential difference was recorded on the meter.

The experimental results are shown in Figure 5 where potential differences against time are plotted both for this tribophysical catalyst and also for a reference platinum on alumina catalyst produced in the more usual way by the thermal decomposition of the platinates. It is apparent that while in the initial stage the conventionally produced material is the more active, the tribophysical catalyst has a superior catalytic life.

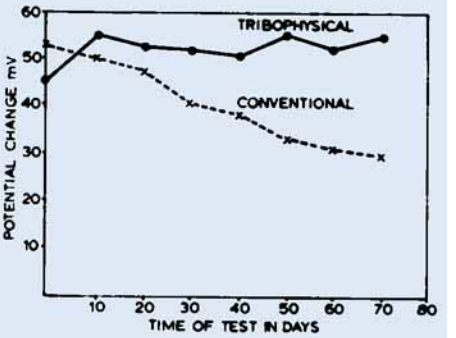

Fig. 5 The catalytic life of material produced by the tribophysical method, shown by the solid line, compared with that of conventionally produced material, broken line, by means of the potential change shown by the recorder when the catalytic activity is taking place. Apart from the initial period, the tribophysical material is superior

Conclusions

Using established techniques it is difficult to prepare a metal alloy catalyst, but the tribophysical procedure which has been developed enables this to be done and the results obtained with such catalysts show them to have long active lives.

It is interesting to note that in the process presented an emulsion of alumina serves both as an abrasive and as the catalyst carrier.

References

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