The Story of Adams' Catalyst

PLATINUM OXIDE IN CATALYTIC REDUCTIONS

Among both users and manufacturers of catalysts the expression "Adams' Catalyst" has been in common usage for many years. It is, in fact, virtually a household term throughout the field of organic chemistry, whether on a research or an industrial scale. The story of its development, of the remarkable man who was first responsible for its preparation just forty years ago, and who at once realised clearly its potentialities in catalytic reductions, forms an interesting chapter in the more recent history of chemistry.

For a number of years before the First World War the liquid-phase reduction of organic compounds had been achieved with the aid of colloidal platinum or palladium, or with the so-called platinum black, a finely divided form of the metal containing an uncertain quantity of oxygen. While the colloidal catalysts were rather more active, they were limited in their use owing to the difficulty of isolating the reaction products, and platinum black was more frequently used. On the other hand, the known methods for its preparation were both numerous and uncertain, often yielding a catalyst that was not particularly active.

This state of affairs persisted until the problem was tackled by Dr. Roger Adams, Professor of Chemistry at the University of Illinois.

Born in Boston in 1889, Adams graduated at Harvard in 1909 and was awarded his Ph.D. three years later. During his college days his love of travel prompted him to work his way to England on a cattle boat, and after receiving his doctorate he again travelled to Europe, this time to study first under Otto Diels at the University of Berlin and then under Richard Willstatter at the Kaiser Wilhelm Institute in Berlin-Dahlem. Few young men can have enjoyed an introduction to research in organic chemistry under such masters—both to become Nobel Prize Winners in their subject in later years—and their influence upon Adams must have been profound.

In 1913 he returned to Harvard as a member of the teaching staff. Here he stayed for three years, moving in 1916 to the University of Illinois where, apart from intervals of war service, he has remained ever since.

Adams' great contributions to organic and pharmaceutical chemistry are well known; they covered a wide field and led to many original and valuable discoveries. But we are concerned here only with one of his relatively minor pieces of work—the introduction of the catalyst that has come to bear his name.

During his short period with Willstätter, the latter, working on alkaloids, was engaged among other activities in improving the technique, prescribed in 1890 by Loew, for preparing platinum black by treating an aqueous solution of chlorplatinic acid with formaldehyde, precipitating with alkali, filtering off the platinum black, drying in vacuo and exposing to air or oxygen before use as a catalyst. As mentioned earlier, this method did not always yield a satisfactory product. Professor Adams, in response to a request from this journal for details of his own contribution, modestly describes the broad outlines of this phase of his work:

"The story of the discovery of platinum oxide is not spectacular and involved serendipity. When I returned from war service in the spring of 1919, several of the problems I assigned my students involved catalytic reduction. For this purpose we were using as a catalyst platinum black made by the generally accepted best method known at the time, that described by Willstätter and Hatt (Berichte, 1912, 45, 1471). The students had much trouble with the catalyst they obtained in that frequently it proved to be inactive even though prepared by the same detailed procedure which resulted
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This account is of course an over-simplification of the story. The first communication, published in 1922 in the Journal of the American Chemical Society, was in the form of a summarised thesis for the M.Sc. degree in the University of Illinois by one of Adams’ students, V. Voorhees. This paper, with Adams as joint author, set out not only the method of preparation of platinum oxide catalyst, but also the details of the presumed mechanism of its operation. The presence of oxygen in platinum black had already been postulated as necessary to its activity as a catalyst in hydrogenation reactions and Adams and Voorhees concluded that the oxides of platinum, if prepared in a finely divided state, would be as effective catalysts as any that could be prepared, and would be distinctly more active than the best platinum black since the maximum amount of oxygen in the latter as platinum oxides was only around 20 per cent. It would probably make little difference, they considered, which particular oxide was obtained, since the hydrogen in the reaction would reduce higher oxides to the lower oxide which was presumably the active catalyst. Experiments reported in this first paper included the reduction of phenol and some substituted phenols to hexahydrophenols, of certain...
pyridine derivatives to piperidine derivatives, of aromatic and aliphatic aldehydes to the corresponding alcohols, and of heterocyclic compounds to the corresponding saturated derivatives.

There was to follow a considerable number of such papers, most of them with Adams as joint author, from a succession of his students. The second contribution—this time a Ph.D. thesis—came less than a year later from the late Wallace Hume Carothers, who will be so well remembered for his subsequent work as leader of the Du Pont team assembled to search for a synthetic fibre—the search concluding so brilliantly in the development of nylon. Other student co-authors over the next two to three years included R. L. Shriner, W. E. Kaufmann, J. S. Pierce, J. W. Kern, H. Heckel, W. F. Tuley and B. S. Garvey. Many variables in the details of preparing platinum oxide catalyst were explored, and many reductions investigated, much of the work being summarised in 1928 in Volume VIII of “Organic Syntheses”, the annual publication on methods for the preparation of organic chemicals founded and edited by Adams. The detailed procedure set out here provided only for a very small scale preparation yielding a few grams of catalyst. If a greater quantity was required, the reader was advised to make several runs of the size indicated rather than one large run since spattering and the evolution of gases made large amounts inconvenient to handle.

In the earlier days of its usefulness, Adams’ catalyst was prepared by the individual research worker on this modest scale, but before long its use became more extensive and in the late thirties the demand began to reach an industrial scale. The repeated preparation of very small quantities then became quite impracticable, and the problem of scaling-up was tackled by the leading platinum manufacturers in the United States and Europe. In England, Johnson Matthey collaborated with May & Baker Limited, whose needs of Adams’ catalyst for a variety of hydrogenation reactions ran at that time into several hundred grams, and a process was worked out, still based essentially on Adams’ procedure, but modified in several details to enable much larger batches to be prepared. Ammonium chlorplatinate was substituted for chlorplatinitic acid, the sodium nitrate was first fused alone, and the final melt was poured directly into water so that the excess sodium nitrate and other salts dissolved immediately, leaving the platinum oxide behind, so avoiding the tedious digestion of the melt and reducing the time required for preparation. This method has since been the subject of further modifications in terms of the temperatures employed and of the ratio of sodium nitrate to ammonium chlorplatinate, but basically it still serves as one reliable means of production, and large quantities of Adams’ catalyst have been prepared in this way over the years.

As recently as 1960 an interesting development of Adams’ original work was put forward by Dr. Shigeo Nishimura, of the University of Tokyo. Realising that rhodium behaved as a specially effective catalyst for the hydrogenation of the aromatic nucleus, but that most of the published work in this field had been concerned either with colloidal rhodium or with a supported rhodium catalyst, Nishimura set out to prepare an Adams-type catalyst consisting of rhodium oxide and platinum oxide in a ratio of three to one by weight of the metals. By fusion of a mixture of rhodium chloride and chlorplatinitic acid or ammonium chlorplatinate with sodium nitrate in exactly the same manner laid down by Adams, he obtained a mixed oxide catalyst—not identical with a simple mixture of the two oxides—which he claimed to be superior to Adams’ platinum oxide in a number of hydrogenations.

Many other types of hydrogenation catalyst have of course been developed during the past forty years, and a great—if incomplete—wealth of understanding of their behaviour has been built up. None the less Adams’ original catalyst still finds extensive use in liquid phase work.

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