

Platinum-Zirconium Alloy Catalysts Supported on Carbon or Zirconia

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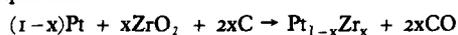
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The preparation of platinum-zirconium alloy catalyst systems is described and their characterisation reveals interesting structures. Studies on a number of catalytic reactions indicate that these alloy systems have catalytic properties significantly different from platinum on zirconia systems. In addition these catalysts do not segregate into platinum and zirconia or zirconium carbide either in air at atmospheric pressure or under conditions used in catalytic processes.

There are only a small number of elements that may be used in the metallic state under catalytic reaction conditions. It is therefore often useful to combine two metals in the form of an alloy catalyst. This is readily achieved in the case of two elements easily obtained by reduction, but very few studies have been performed on the preparation, characterisation and catalytic activity of supported alloy catalysts in which a metal such as platinum is alloyed with a Group IV element like zirconium, which by itself would be very difficult to reduce to the metallic state. This type of alloy has been investigated previously mainly in the form of electrocatalysts for phosphoric acid fuel cells (1, 2). The studies described here deal with the preparation of platinum and zirconium ($Pt_{1-x}Zr_x$) supported alloys and their catalytic properties, especially for the gas phase conversion of hydrocarbons. The effect of alloy formation on the catalytic behaviour of platinum can be rationalised in terms of dilution and/or electronic effects.

Preparation and Characterisation of the Carbon Supported Catalysts

The method used to prepare these alloy catalysts can be represented by the following equation:



The carbon acts both as the reducing agent and as the support for the metallic phase. The driv-

ing force for alloy formation could be the high free energy of formation for the well defined intermetallic compound Pt_3Zr . Ott and Raub, who studied this reaction with reference to corrosion phenomena, found that alloying started at about 900K via the formation of a face centred cubic solid solution $Pt_{1-x}Zr_x$, up to the limiting value of 25 atomic per cent zirconium at higher temperatures, where there was evidence of the intermetallic compound Pt_3Zr being formed (3). In the previous works, the starting materials used for alloy formation were mixtures of zirconia with platinum and carbon (3) or platinum on carbon (1), or the precipitation of zirconia on platinum on carbon (2).

The originality of our preparative procedure is in applying the conventional co-impregnation methods, used for the preparation of heterogeneous catalysts, to support precursor salts of the alloy components. These salts are further decomposed to obtain intimate mixtures of platinum and zirconia on the carbon support. Preparative details and other data for the catalysts are indicated in Table I (4).

Alloy formation was followed by X-ray diffraction (XRD) measurements. Figure 1 shows the variation in the percentage of zirconium alloyed as a function of temperature. The same results were obtained for the two supports. The limiting value of 25 atomic per cent zirconium alloyed is in good agreement with that reported by Ott and Raub (3). The profile of the XRD

Table I	
Platinum + Zirconia Supported on Carbon Catalysts, Heat Treated in Vacuum in the Temperature Range 673 to 1273K, for 2 hours	
Temperature, K	State of the catalyst
673 773 to 873 873 to 1273 1273	Pt + ZrO ₂ /C Onset of formation of Pt _{1-x} Zr _x /C Increase of x from 0 up to 0.25 Pt _{0.75} Zr _{0.25} /C . Per cent dispersion of the alloy phase (Pt _s + Zr _s : Pt + Zr ratio) is 13 per cent (C Merck), or 4.5 per cent (C Vulcan 6) Heterogeneity of particle size distribution . Constant Zr : Pt ratio, in all alloy particles . Zr ⁰ and Pt ⁰ are both present in the alloy particles . Surface composition is close to Pt _{0.5} Zr _{0.5}
T = 1273K, Pt _{0.75} Zr _{0.25} /C After a long time in contact with air at room temperature. Conditions to restore the initial state.	Surface segregation into Pt and ZrO ₂ . Alloy preserved inside the metallic particles Heat treatment in hydrogen at temperatures ≥ 973K

lines suggested a broad particle size distribution and this conclusion was confirmed by electron microscopy.

X-ray emission analysis performed on Pt₃Zr/C catalyst using Scanning Transmission Electron Microscopy (STEM) showed that this alloy catalyst has a very uniform composition from one particle to another (5). Electron Spectroscopy for Chemical Analysis (ESCA) experiments on the same catalyst, kept in air at room temperature after preparation, indicated the presence of both zerovalent platinum, and zerovalent zirconium. At least in the metallic particles the zirconium is present in the metallic state and not as a platinum-zirconium-oxygen solid solution.

The re-oxidation which takes place in air under atmospheric conditions is confined to the surface of the alloy particles. In fact no segregation into platinum and zirconia could be detected by XRD. Ion Scattering Spectroscopy (ISS) and Auger Electron Spectroscopy (AES) both confirmed these conclusions (6). AES proved in addition that reactivation in hydrogen at 673K did not restore the alloy surface to its initial state, but that reactivation at 973K or

above did achieve this (6), when the surface composition is then close to Pt_{0.5}Zr_{0.5}, a figure which was confirmed by hydrogen/oxygen chemisorption data (6). The oxidation state of zirconium in the outer layer of the alloy surface directly exposed to the gas phase could not be established unambiguously but "Zr₅O" is among the species likely to be present.

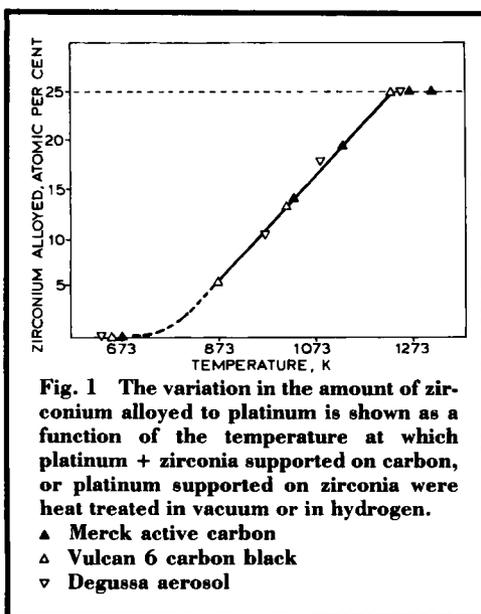
Preparation and Characterisation of the Zirconia Supported Catalysts

The reducing agent used for these preparations was hydrogen and the reaction can be represented as follows:



This reaction has been studied previously but not with the objective of preparing catalysts (7, 8). Approximately 10 weight per cent platinum catalysts supported on zirconia were prepared (6) and reduced by hydrogen for 2 hours in the temperature range 623 to 1273K.

The same temperature dependency of the extent of zirconium alloying was observed for both the (Pt/ZrO₂, H₂) and the (Pt + ZrO₂/C, vacuum) systems. The limit of solubility of zirconium in platinum (Pt₃Zr) was also found to



be the same. The particle size distribution of platinum in Pt/ZrO₂ reduced at both 673K and 1273K was very broad. The variation in dispersion of the Pt_{1-x}Zr_x as a function of the temperature of reduction has been studied using hydrogen and oxygen chemisorption (9) and

for example, the metal dispersion decreased from 11 to 12 per cent to 4 to 5 per cent as the temperature was varied from 673 to 1240K, with most of the change occurring between 873 and 973K. The surface concentration of zirconium was about twice its mean concentration over the entire range of x values in Pt_{1-x}Zr_x (which is the same as that described above for Pt_{0.75}Zr_{0.25}/C).

Catalytic Properties of Platinum-Zirconium Alloy Catalysts

The reactions studied were (a) the hydrogenation of benzene including resistance to poisoning by hydrogen sulphide, (b) the competitive hydrogenation of benzene and toluene, (c) the hydrogenolysis of ethane and (d) the hydrogenation of carbon monoxide (6, 11, 12). The results are summarised in Table II. The alloy effects may be rationalised in terms of the following factors:

Dilution of Platinum Surface Atoms (Pt_s)

The platinum atoms are surrounded by inactive zirconium surface atoms probably oxidised or carbided (Zr_sO or Zr_sC).

In fact, no significant variation of turnover

Reaction	Catalytic properties
(a) Hydrogenation of benzene	No effect of the support (C; ZrO ₂) or of alloying (Pt _{1-x} Zr _x) on the TON (per Pt _s). Once poisoned by H ₂ S, Pt _{0.75} Zr _{0.25} is more easily reactivated by heat treatment in hydrogen than platinum
(b) Competitive hydrogenation of benzene and toluene	K _{7/8} (Relative coefficient of adsorption of toluene and benzene) increases almost linearly with the at.% Zr alloyed
(c) Hydrogenolysis of ethane	Whatever the support (C; ZrO ₂) TON decreases due to Pt-Zr alloying
(d) Hydrogenation of carbon monoxide	<ul style="list-style-type: none"> . TON (Pt) (CH₄; CH₃OH) is much greater for Pt/ZrO₂ than for Pt/Al₂O₃ or SiO₂ or C . Pt_{0.75}Zr_{0.25}/ZrO₂ or C, reactivated in H₂ at only 673K, behaves like Pt/ZrO₂ . Pt_{0.75}Zr_{0.25}/ZrO₂ or C, reactivated in H₂ at 1023K, have catalytic behaviour different from Pt/ZrO₂ (in particular a greater selectivity to methanol formation)

numbers (TON) was detected in reaction (a) whereas a decrease was observed (about one order of magnitude) from platinum to $\text{Pt}_{0.75}\text{Zr}_{0.25}$ whatever the support, in reaction (c). It is generally assumed that the active sites are composed of a low number of contiguous Pt_s in reaction (a) and a larger number in reaction (c). Accordingly, a simple dilution effect of Pt_s by inactive Zr_s could account for the experimental results in these reactions.

Electronic Modifications of Platinum Due to Alloying

Reaction (b) allows the determination of the relative strengths of adsorption of toluene and benzene ($K_{T/B} = b_T/b_B$, the ratio of the adsorption coefficients), by using the kinetic analysis proposed by Tri and colleagues (10). These authors showed that $K_{T/B}$ may be related to the electron density of states of platinum in supported platinum catalysts, the larger the $K_{T/B}$ value, the more electrophilic the platinum metal (10).

On platinum-zirconium alloys, the increase of the $K_{T/B}$ value observed from platinum to $\text{Pt}_{0.75}\text{Zr}_{0.25}$ whatever the support (11) suggests a modification of the electron density of states of alloyed platinum, and this confers on it an electrophilic character. This was corroborated by poisoning experiments performed over platinum and $\text{Pt}_{0.75}\text{Zr}_{0.25}$ supported catalysts in reaction (a). In fact, alloyed platinum was found to be more resistant to hydrogen sulphide poisoning than platinum alone and was more easily reactivated by heat treatment in hydrogen; weakening of the Pt-S bond on the alloy catalyst being due to platinum electro-deficiency.

Dilution of Pt_s by Active " Zr_sO " Species

Evidence was obtained for a zirconia support effect on platinum in reaction (d): the methanation turnover numbers on Pt/ZrO_2 catalysts were found to be about 20 fold higher than those for platinum supported by alumina, silica or carbon, depending on the heat treatment of the zirconia support (12). The lower the calcination temperature of that support, the

higher was the zirconia support effect. It was further shown that the zirconia support effect needed a direct contact between platinum and zirconia since no such effect was found for mechanical mixtures of platinum on silica catalyst and zirconia support.

In the case of $\text{Pt}_{0.75}\text{Zr}_{0.25}$ alloy catalyst, reactivated in hydrogen at 1023K, an enhanced activity and a higher selectivity for methanol formation was found for both zirconia and carbon supported systems. These same catalysts behaved like platinum on zirconia when reactivated at only 673K. These results, corroborated by the ESCA, Auger, and chemisorption (H_2 , O_2) characterisation methods account for an insufficient restoration of the alloy surface in hydrogen at 673K. The surface is then presumably composed of Pt_s atoms and Zr_sO_2 "patches". Over the alloy catalysts reactivated at higher temperatures, the specific alloy effect could then be accounted for by dilution of Pt_s by $\text{Zr}_s(\text{O})$ atomic species participating in reaction (d).

The exact mechanism of action of ZrO_2 (Pt/ZrO_2) or (and) of " Zr_sO " ($\text{Pt}_{0.75}\text{Zr}_{0.25}$ reactivated at high temperature) in the (carbon monoxide, hydrogen) reaction cannot be deduced from our investigations. It seems also that it cannot be unambiguously deducible from the published scientific literature which is relevant to similar effects (11).

Conclusion

It can be said that our alloy catalysts have shown some interesting effects. For all four reactions studied the X-ray diffraction patterns were found to be the same at the end of the catalytic run as at the beginning. This strongly suggests that the $\text{Pt}_{1-x}\text{Zr}_x$ supported catalysts could be used without any segregation of the alloy components under conditions used in catalytic processes.

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The Fabrication of Ultrafine Platinum Wire

WOLLASTON'S HISTORIC TECHNIQUE FURTHER DEVELOPED

In February 1813 William Hyde Wollaston read a paper to the Royal Society describing a method that he had developed for making extremely fine wire. Initially he had been concerned to produce fine gold wires, for use as crosswires in the eyepiece of astronomical instruments. This he did by drilling a hole along the centre of a silver rod into which a length of gold wire was inserted. When the diameter of this composite had been reduced sufficiently by drawing through dies, the silver was dissolved to yield the fine gold wire. However Wollaston found it very difficult to drill the central hole in the silver so he substituted platinum for the gold and modified the technique to make use of the higher melting point of platinum. He arranged a platinum wire with a diameter of $1/100$ of an inch along the longitudinal axis of a cylindrical mould which was then filled with molten silver. Following successive reductions of the composite ingot, the silver was dissolved to give a platinum wire $1/5000$ of an inch in diameter. This was excellent for his intended use, but by exercising the utmost care both with the quality of the platinum and during the wire drawing operation he was able to produce platinum wire as small as $1/30,000$ of an inch in diameter (approximately 8500 \AA).

Wollaston's technique for producing fine wire has remained in use, and modified procedures that enable both single and multiple ultrathin platinum filaments to be produced with diameters as small as 80 \AA have recently been reported by A. C. Sacharoff and R. M. Westervelt of Harvard University and J. Bevk of AT & T Bell Laboratories, Murray Hill

(*Rev. Sci. Instrum.*, 1985, **56**, (7), 1344-1346).

A preliminary treatment of the ultrahigh purity metals to remove any surface contaminants is followed by vacuum annealing before a piece of the 0.5mm diameter platinum wire is fitted into a hole drilled along the centre of a 3.2mm diameter silver rod. Next this composite rod is slowly drawn through some seventy progressively finer dies, to an overall diameter of 0.5mm . Following a further vacuum anneal the silver:platinum composite is inserted into another annealed silver rod and the drawing continued. Although it is not possible to repeat the annealing stage again without the wire breaking up into short pieces, the other operations can be carried out as often as is necessary to reduce the platinum core to the ultrathin diameters required to test the theory of quasi-one-dimensional electronic localisation and interaction effects, at liquid helium temperatures.

Techniques have been developed that enable these ultrathin wires to be positioned for examination before the supportive silver cladding is etched off.

Multifilament Platinum Yarn

In another procedure ten platinum wires are inserted into separate holes again drilled longitudinally into a silver rod. During repeated reductions, lengths of the resulting composite wires are bundled together, reinserted in another silver rod and the sequence repeated. When finally the silver is etched away, a fine multifilament platinum yarn is obtained.
I.E.C.