

Mixed Metal Catalysts for the Synthesis of Azelaic Acid

ACTIVITY OF A PALLADIUM-IRON COMPLEX

By D. T. Thompson

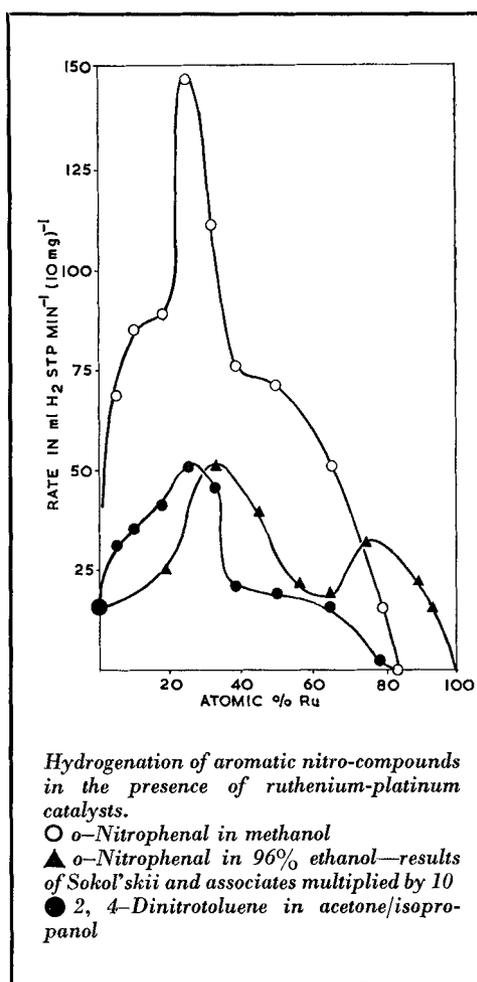
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Azelaic acid is an important intermediate in the production of a speciality Nylon, and it is shown that a palladium-iron system may be used very selectively in its preparation. This work was described at the recent Chemical Congress at York by the author, who is now Manager of the Catalyst Department in the Johnson Matthey Research Laboratories.

There are numerous examples reported in the literature showing clear evidence that mixtures of metal oxides, or indeed of the metals themselves, produce increased catalytic activity by comparison with the individual metal oxides or metals respectively.

Bond and Webster (1), using mixed metal catalysts derived from mixed oxides using a modification of the Adams method, demonstrated that a mixed ruthenium-platinum catalyst is more effective in the reduction of organic nitrocompounds than either of the pure metals. (See Figure.) The mixed oxides are reduced by hydrogen under ambient conditions to yield what are thought to be finely divided alloys of the two metals. It was shown by Rylander (2) that catalysts made by fusing platinum and palladium, rhodium, iridium, or ruthenium salts with sodium nitrate varied widely in hydrogenation activity and showed marked synergistic effects. Platinum-rhodium catalysts were especially active for reduction of nitrobenzene, nitropropane, cyclohexanone oxime and xylenes, whereas platinum-palladium catalysts were most active for hydrogenation of butyenediol.

On the industrial manufacturing scene there are examples of both heterogeneous and homogeneous mixed metal systems. A mixture of bismuth and molybdenum oxides is used as a catalyst for the partial oxidation



of propylene to acrolein. The best results are obtained when the Bi:Mo ratio is 1:1. In the Haber ammonia synthesis the most widely used catalyst is α -iron containing an oxide such as molybdenum for widening the lattice and enlarging the active interface of the catalyst with the substrates. In biological systems both molybdenum and iron are necessary in the nitrogen fixation process.

Perhaps the most spectacular use of two metals in a heterogeneous catalyst is in the Ziegler-Natta titanium-aluminium systems for polymerising α -olefins. The important species involved is thought to be either a chlorobridged dinuclear molecule or a species having direct Ti-Al bonds. Some soluble Ziegler's have been reported to be stereospecific under certain conditions. Stereospecific polymerisation is helped by the catalyst surface in the heterogeneous variety but the orientation of the monomer can also be controlled during the critical propagation step in the homogeneous systems provided that the monomer has at least two sites capable of co-ordinating to the catalyst (e.g. $\text{CH}_2=\text{CHCN}$ or $\text{CH}_3\text{CH}=\text{CH}_2$ at low temperatures). Butadiene has also been polymerised stereospecifically in homogeneous media. Wilke has shown that certain π -allylic nickel compounds such as π -allyl nickel chloride are active homogeneous

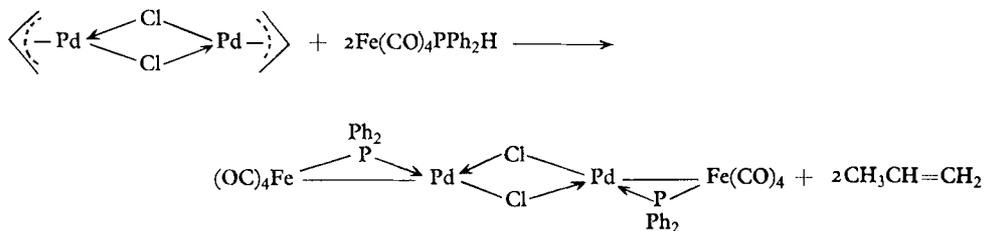
species is probably a halogen bridged nickel-aluminium compound.

Another homogeneous reaction carried out successfully in industry using two metals simultaneously is the Hoeschst-Wacker oxidation of ethylene to acetaldehyde in the presence of Pd(II). The Pd(O) thus produced can be reoxidised to Pd(II) using CuCl_2 , and the Cu(I) thus produced reoxidised in turn with oxygen. The presence of both palladium and copper simultaneously makes the reaction catalytic with respect to metal and it is quite possible that a discrete copper-palladium species is present in solution. A similar situation may be present in the catalyst system necessary to convert ethylene to vinyl acetate.

There is therefore considerable evidence that both in heterogeneous and in homogeneous systems and both in the laboratory and on the industrial scale mixed metal effects can be useful. We therefore investigated ways of synthesising mixed metal complexes.

Synthesis and Activity of a Palladium-Iron Catalyst

One of the most interesting compounds synthesised was a palladium-iron tetranuclear complex formed by reaction between π -allyl-palladium chloride and diphenylphosphine-iron tetracarbonyl in toluene (3):



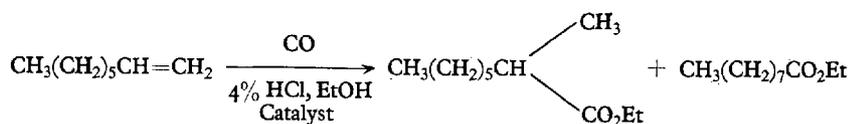
catalysts for dimerising olefins, and it has now been shown that the rate of dimerisation can be greatly accelerated if aluminium alkyl is added to the nickel catalyst. The active

This palladium-iron compound is a good selective hydrogenation catalyst ($175^\circ\text{C}/100$ atm/1 h) for the hydrogenation of hex-1-yne in the presence of hex-1-ene. Under test conditions (10 p.p.m. moles metal/mole

substrate), 93 per cent of a sample of hex-1-yne in benzene was reduced to hexene and only 3 per cent to hexane. This is unexpected since palladium is normally an excellent catalyst for the hydrogenation of olefins. The effect probably results from easier formation of a palladium-acetylene coordinate bond than a palladium-olefin bond. The rate of hydrogenation of the olefin on its own is in fact faster than the acetylene on its own. The effect is analogous to those found with

hydrocarbons to carboxylic acids and esters under "mild" conditions (e.g. 60°C, 300-700 atm for 1,5-cyclooctadiene) using PdCl₂(PPh₃)₂ as catalyst. The use of the PPh₃ ligands had considerably increased the yield of ester per mole of palladium compared with the use of non-ligated PdCl₂ (7).

The carbonylation of oct-1-ene was studied under mild conditions using both the palladium-iron complex and PdCl₂(PPh₃)₂ and the results of the two series of experiments compared:



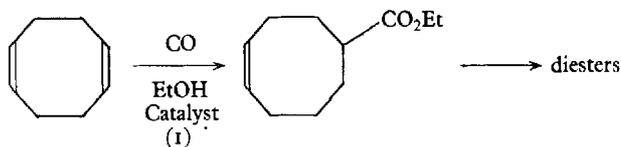
supported palladium catalysts (5 per cent Pd-BaSO₄) and described as molecular queueing (4).

This Pd-Fe complex is also a selective isomerisation catalyst and in its presence oct-1-ene is isomerised to oct-2-ene but not to the 3- and 4-isomers. Most palladium complexes promote the isomerisation of Δ¹-octene to a mixture of Δ¹, Δ², Δ³, and Δ⁴ octenes (5) and the reason for the selectivity in this case may be steric in that Δ¹-octene may be more accessible to the palladium than the Δ²-octene.

At 75°C, 50 atm, the total yield of esters was ten times greater for the mixed metal catalyst than for PdCl₂(PPh₃)₂. The threshold temperature for the reaction was ca. 30°C lower in the palladium-iron case than in the palladium. The isomer distribution of products is, however, ca. 1:1 in both cases, with a tendency for the *iso* to predominate.

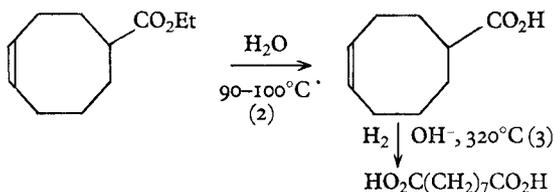
Carbonylation of 1, 5-Cyclo-octadiene

Since the 50:50 *n:iso* ratio obtained with linear olefins had comparatively little industrial interest we next turned our attention to 1,5-cyclooctadiene (1,5-COD):



Extension of this work into the field of carbonylation was prompted by the appearance of a review article by Bittler et al. (6), who described carbonylation of unsaturated

If the reaction could be stopped selectively at the first stage (I), it was known that this ester could be converted into azelaic acid in < 80 per cent overall yield by means of two straightforward hydrolysis steps:



Hydrolysis of Ethylcyclooct-4-ene-1-carboxylate

The atmospheric pressure, aqueous hydrolysis of the cyclic ester carbonylation product obtained from 1,5-COD and ethanol to give cyclic acid (step 2), was found to be complete

Azelaic acid is of interest since it is an intermediate needed in the manufacture of the commercially important nylon-6,9. For the carbonylation step, a series of experiments using PdCl₂(PPh₃)₂ and *p*-toluene sulphonic acid showed that the optimum temperature for producing the monoester (I) was ca. 110°C (8). At this temperature no diester is formed (not detectable by g.l.c. at high sensitivity). Lower temperatures gave lower rates according to the normal rate laws. Higher temperatures also gave lower rates, presumably due to catalyst decomposition. The optimum pressure seems to be ca. 100 atm. Higher pressures give little change in rate. Lower pressures reduce the rate and increase the amount of isomerisation of unchanged 1,5-COD to 1,3-COD. The pressure and temperatures are, however, interrelated as far as ideal conditions are concerned.

Optimisation of the reaction at 110°C/100 atm showed that yields of up to 7000 moles ester/g.atom Pd could be obtained using anhydrous ethanol (rather than MeOH), PPh₃ ligand (rather than PBu₃) and a Lewis acid such as FeCl₃, TiCl₄ or NbCl₅. Highest yields were obtained when the catalyst was preformed rather than prepared in situ from PdCl₂ and PPh₃ and when a common chloride ion was used. Under these conditions, no 1,5-COD isomerised to 1,3-COD—unchanged starting material could therefore be recycled. The Pd-Fe complex was also an effective catalyst but not as good as PdCl₂(PPh₃)₂/FeCl₃, which could be giving [PdCl(PPh₃)₂]⁺[FeCl₄]⁻.

after 0.5–1.0 h in refluxing solution. The mixture had become homogeneous after this time and isolation of the product gave yields of ca. 96 per cent. With the ethyl ester, as the temperature is raised to 90 to 95°C a strongly exothermic reaction sets in and the mixture becomes homogeneous during a few minutes.

It is acceptable to use “crude” ester product from step (1) in this stage of the reaction and then remove the ethanol and 1,5-COD at the end of this stage. The removal of the ethanol before stage (3) is essential. Most of the palladium is then precipitated during this stage (a very small quantity of palladium is also found on the walls of the glass liner in the carbonylation stage) and is removed by filtration. The black solid obtained dissolves readily in nitric acid, and would presumably dissolve in aqua regia to give H₂PdCl₆. Evaporation of the aqua regia would give PdCl₂ which could be readily converted to the catalyst with PPh₃ (via Na₂PdCl₄).

Conversion of Cyclooct-4-ene-1-carboxylic acid to Azelaic Acid

The caustic cleavage step was performed in closed Inconel autoclaves under a self-generated pressure of up to 1000 p.s.i.g. water, and approximately 250 p.s.i.g. hydrogen. The use of ca. 320°C (internal temperature) for 1 hour was found to give higher yields of purer product than 300°C for 10 hours. Since the reaction is complete after 1 hour it is preferable to discontinue

heating at this point to prevent discolorisation and condensation of the product. The shorter heating period may therefore account for the greater purity of this "crude" azelaic acid compared with samples obtained after longer heating periods. Two comparative g.l.c. traces for the esterified products from our work and the currently available acid derived from the ozonolysis of castor oil showed a single product in our case, whereas the commercial product contained 8 per cent of impurities. We therefore have an excellent, potentially commercial route to azelaic acid from 1,5-cyclooctadiene, the three stages of which proceed in almost theoretical organic yield to give a pure "crude" product.

Most of the practical work was performed by Mr. R. Jackson and I would like to express my thanks to him, and to Dr. D. E. H. Jones for discussions on aluminium chemistry.

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Selective Rhodium Plating for Electrical Contacts

The use of rhodium for light duty contact purposes is well established, as are the techniques for restricting this expensive metal to those areas required for contact only. The problems of cracking, microcracking and exfoliation have been well documented and these factors are covered extensively in a paper presented by Afsar A. Khan of G.T.E. Automatic Electric Laboratories Inc., North Lake, Illinois to the meeting of the American Electroplaters' Society in New York during March 1975.

The paper discusses controlled depth selective electrodeposition of rhodium on iron-base alloys for dry reed contact applications. Selective plating of reed blades is a necessary design requirement rather than a cost reduction approach since rhodium deposits, while needed on the contact area, are detrimental to glass-to-metal sealing. Nominal plating thickness should be held to within ± 13 per cent. The plating area is mainly controlled by maintaining a smooth laminar flow of the recirculating plating solution in the tank through a series of baffles and also by maintaining a uniform depth of immersion of the contact reeds to ± 0.010 in. Temperature is 40 to 50°C to minimise solution evaporation and to provide even plating thickness on the rack.

In this case the substrate is unusual in that the iron-base alloy for reed switches is easily attacked by the rhodium sulphate electrolyte.

All rhodium plating solutions yield highly stressed deposits but as phosphate solutions are prone to higher levels of stress and cracking than sulphate solutions, the latter are the natural choice for plating crack-free rhodium in thicknesses up to 200 μ m. To minimise the problem of attack by these solutions the author states that a gold undercoat is used to protect the iron-base alloy but he does not specify the thickness of this undercoat.

Experience elsewhere has shown that a low stress gold deposit beneath rhodium can give rise to marked changes in the stress cracking of the rhodium deposit. Unless the quality of the undercoat is very carefully controlled this can have a significance greater than the methods outlined in this paper. The recommended careful attention to cleanliness, frequent carbon treatment together with the attendant filtration, and careful exclusion of organic contamination are all, of course, useful contributions to good rhodium plating practice.

The sections devoted to the correction of faults in deposits are interesting, particularly those parts concerned with defects associated with the evolution of hydrogen at the work face. No explanation is attempted for why a momentary "dwell" in the electrolyte before plating commences leads to elimination of this problem.

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