

Bimetallic nanocatalysts for the conversion of muconic acid to adipic acid†

John Meurig Thomas,^{*ac} Robert Raja,^{*b} Brian F. G. Johnson,^{*b} Timothy J. O'Connell,^{ab} Gopinathan Sankar^a and Tetyana Khimyak^b

^a Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, U.K W1X 4BS

^b Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, U.K CB2 1EW

^c Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, U.K CB2 3QZ

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Adipic acid (2) production currently entails use and generation of environmentally harmful materials: an efficient catalyst, consisting of nanoparticles of Ru₁₀Pt₂ anchored within the pores of mesoporous silica, facilitates the production of (2) by hydrogenating muconic acid, that may be derived biocatalytically from D-glucose.¹

Because of the need to expedite the greater utilisation of chemical feedstocks derivable from plant or other replenishable sources, research efforts are focused on developing high-performance catalysts that yield desirable industrial products in an environmentally benign fashion.^{1–3} The currently favoured method of producing adipic acid, (2), starts with cyclohexane, that is first prepared by the hydrogenation of benzene, a volatile, carcinogenic substance which is invariably derived from non-renewable fossil fuels.^{4,5} Aerial oxidation of the cyclohexane in the presence of dissolved salts of cobalt as homogeneous catalysts yields a mixture of cyclohexanol and cyclohexanone (so-called K–A oil), and this, in turn, is treated with concentrated nitric acid to produce (2). But for every molecule of (2) that is formed, two molecules of N₂O are liberated, which adds greatly to global warming and also to the destruction of the ozone layer.^{6,7}

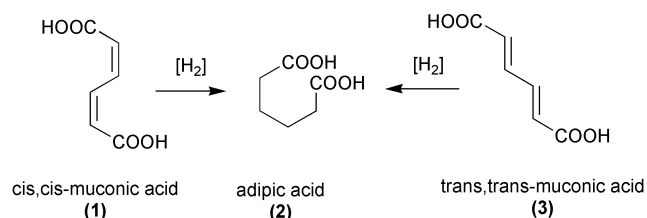
Recently, several less environmentally destructive methods of synthesizing (2) have been evolved, most of them starting from cyclohexene.⁸ When this alkene is oxidized by a strong aqueous solution of H₂O₂, in the presence of an appropriate homogeneous,^{8b,c} or phase-transfer^{8a} or heterogeneous catalyst,^{8d} (2) is formed (in the absence of N₂O). But large quantities of H₂O₂ are consumed (4 moles per mole of (2) produced). Benign microporous catalysts, such as FeAlPO-31 and CoAlPO-18, have also been designed for the syntheses of (2) from either cyclohexane or *n*-hexane, respectively, by aerial oxidation.^{9–11}

It has, however, been shown by Frost,^{1,12} that microbe-catalysed conversions of simple, plentiful and renewable carbohydrates, such as D-glucose, offer potentially attractive new routes to desirable materials such as (2) — which is used mainly in the manufacture of nylon 6,6 and also in the production of gelatins, jams, polyamides, polyurethanes and lubricants. In particular, new biosynthetic pathways, involving appropriate genetic manipulation so as to convert D-glucose into *cis,cis*-muconic acid, (1) have already been worked out.¹ (This feedstock is currently synthesized from D-glucose under controlled fermentation conditions using a microbial catalyst under aerobic conditions. A manufacturing process of this feedstock would be somewhat similar to the microbial synthesis of L-lysine from D-glucose under fermentation conditions¹³ and the cost of adipic acid, starting from this feedstock, is estimated to be \$2.46 kg⁻¹. The current purchase price of resin-grade adipic acid is \$1.52 kg⁻¹¹⁴ and it is quite obvious that the estimated cost of synthesizing adipic acid from carbohydrates

requires significant cost reduction. This acid, along with its *trans,trans*- analogue, (3), may, with an effective catalyst, be hydrogenated to (2) (Scheme 1).

We have developed¹⁵ a number of highly active bimetallic nanocatalysts, such as Ru₆Sn, Ru₆Pd₆, Ru₁₂Cu₄, Ru₅Pt₁, Ru₁₀Pt₂, Ru₁₂Ag₄, Ru₁₀Ag₃ and Pt₃Cu, that have been shown to retain their activity and selectivity for a number of single-step and solvent-free hydrogenations of key organic compounds,¹⁶ under mild, environmentally benign conditions. Such catalysts are prepared¹⁵ by decarbonylating the precursor mixed-metal cluster carbonylate anions, which, in association with a suitable counter cation (such as Et₄N⁺ or PPN⁺, where PPN stands for {bis(triphenylphosphine)iminium}) are first encapsulated within, and firmly anchored to the walls of the pores of mesoporous silica, as described previously.^{15–18} The catalytic precursor material, which was characterized by FTIR revealed that the carbonyl cluster was still intact within the pores prior to gentle thermolysis that denudes the carbonylates and drives off all organic molecular remnants, the two central carbide carbons, however, are still retained as an integral part of the double octahedra. (In reality, the stoichiometry of the nanocatalysts is, for *e.g.* Ru₁₀Pt₂C₂). EXAFS (extended X-ray absorption fine structure) analysis showed that the structure of the pure, unsupported mixed-metal carbonyl clusters are exactly identical to those of the species adsorbed into the mesoporous silica. EXAFS data of the denuded clusters shows that, in general, the coordination environment of the two component metals in the clusters are different from the corresponding environments in the parent material.^{15,19} Fig. 1 shows the relevant structures in the parent and (anchored) denuded states of the best catalyst (see Fig. 2) for the hydrogenation of (3) to (2).

The structure²⁰ of the activated Ru₁₀Pt₂ cluster supported on MCM-41 has been investigated using both Ru K and Pt L_{III}-edge EXAFS.¹⁹ As in our previous EXAFS work on, for example Ru–Cu and Ru–Sn bimetallic catalysts anchored on mesoporous silica, we used^{15,16} the simultaneous refinement procedure to achieve a unique model for the activated cluster. To do so, we generated a model based on the crystal structure data available for the free Ru₁₀Pt₂ cluster compound; only part of the symmetrical structure is essential to produce the final structural model. First, we tested this model against the EXAFS data of the free cluster compound and the structural parameters were found to be in good agreement with the crystallographic data (details of the best fit for the starting material are given in



Scheme 1 The hydrogenation of *cis,cis*-muconic acid and *trans,trans*-muconic acid to adipic acid.

† Electronic supplementary information (ESI) available: experimental details, EXAFS fit and refined EXAFS parameters. See <http://www.rsc.org/suppdata/cc/b3/b300203a/>

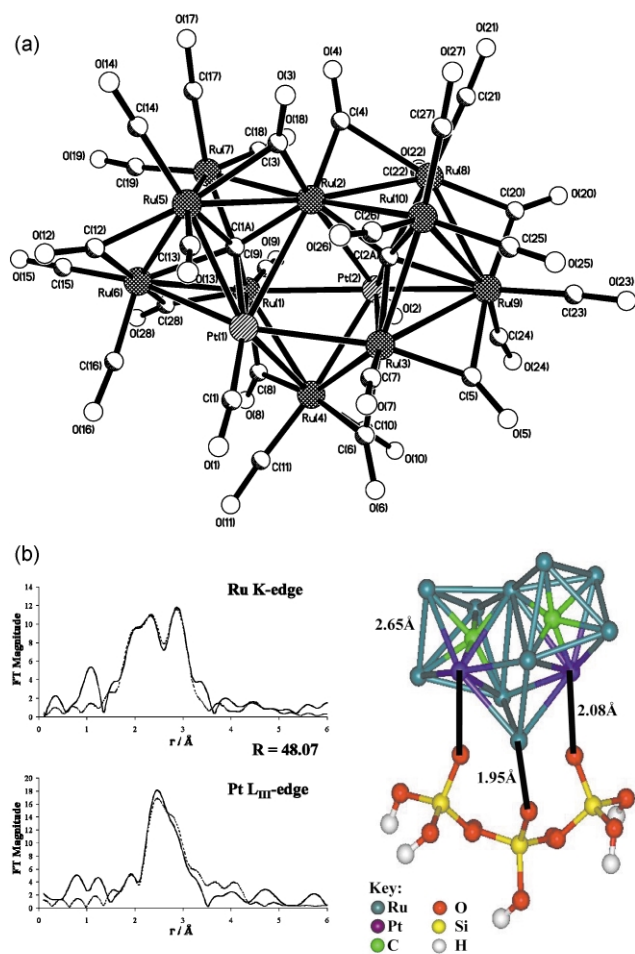


Fig. 1 (A) Typical parent anionic carbonylate of $[\text{Ru}_{10}\text{Pt}_2\text{C}_2(\text{CO})_{28}]^{2-}$, from which naked nanoparticle (10 to 15 Å diameter, depending upon the constituents of the bimetallic core) catalysts are generated. (B) Fourier transform fits from the multiple edge EXAFS refinement of the $\text{Ru}_{10}\text{Pt}_2$ cluster adsorbed on mesoporous silica after activation (see ESI† for experimental details), and a proposed model for the binding of $\text{Ru}_{10}\text{Pt}_2$ to the silica surface based on the EXAFS refinement.^{12,15} The experimental data is the full line, the model data is the dotted line.†

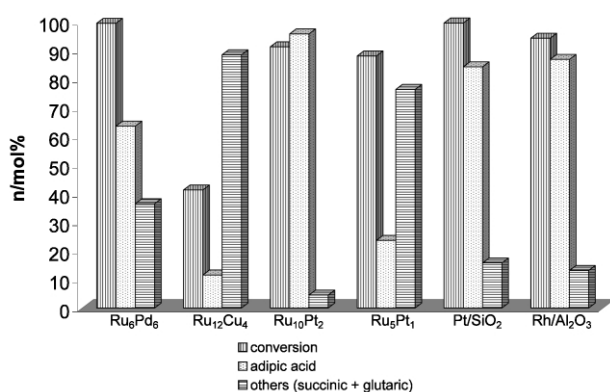


Fig. 2 The activities and selectivities of the four anchored bimetallic nanocatalysts (Ru_6Pd_6 , $\text{Ru}_{12}\text{Cu}_4$, $\text{Ru}_{10}\text{Pt}_2$, Ru_5Pt_1) are compared with commercially available Pt/SiO_2 and $\text{Rh}/\text{Al}_2\text{O}_3$ for the hydrogenation of *trans,trans*-muconic acid to (2). **Reaction conditions:** substrate \approx 5.0 g (dissolved in 100 ml of ethanol); catalyst = 50 mg, H_2 pressure = 30 bar, temp. = 353 K; t = 5 h.

the ESI†). Employing the same model as the starting geometry, but without the presence of carbonyl ligands (in agreement with the *in situ* FT-IR studies which showed that all the bands related to the carbonyl group disappear upon heating in vacuum at ca. 175 °C), yielded a good fit to the experimental EXAFS data. This suggests that there is no significant rearrangement of the

metals from the original structure indicating that the essential integrity of the original double octahedra structure is retained in the activated form. (There is however, a significant reduction in the metal–metal distances, compared to the parent cluster compound, a fact which is consistent with our previous observations on other bimetallic cluster catalysts). The final model derived from the simultaneous refinement of both Ru and Pt edges shows that, apart from the metal–metal contacts, there are oxygen neighbours; in particular the platinum centres have one oxygen neighbour for each platinum in the nanoparticle catalyst and at least one of the ruthenium centres has one oxygen neighbour in the activated form. This oxygen is undoubtedly part of the silica support to which the bimetallic nanocluster is anchored. The final structure is depicted in Fig. 1.

It is seen from Fig. 2 that one of the bimetallic catalysts prepared by us, $\text{Ru}_{10}\text{Pt}_2$, is superior in its selectivity to all the other bimetallic nanocatalysts that we have so far studied. It is also superior to the monometallic, supported catalysts such as Pt and Rh. This augurs well for the future use of high-area, thermally stable, bimetallic nanocatalysts in the wide range of hydrogenations that may be effected to yield desirable chemical products from plant crop sources.^{17,18} It is also of relevance to point out that D-glucose may also serve as a source of hydrogen as recently demonstrated.²¹

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