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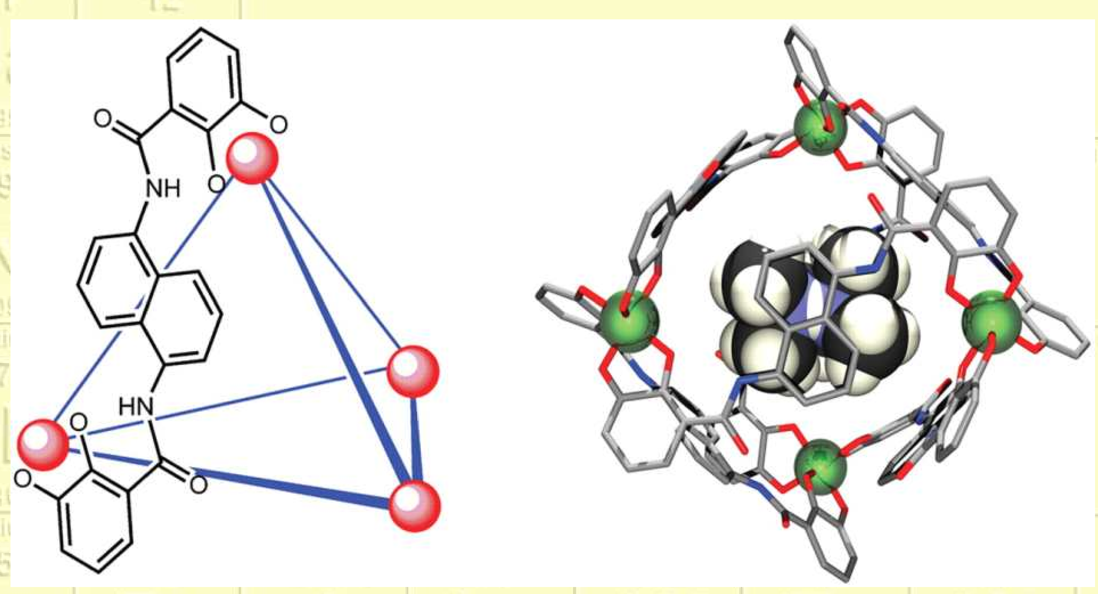
Catàlisi àcida en solució bàsica

By confining a reactant inside electrostatically tuned molecular cages, chemists have performed acid catalysis in basic solution (*Science* **2007**, *316*, 85). R. G. Bergman andcoworkers of the University of California, Berkeley, show that a water-soluble, tetrahedral metal-ligand assembly M_4L_6, with M = Ga^{III} (shown, metal ions are green), Al^{III}, In^{III}, Fe^{III}, Ti^{IV} or Ge^{IV}, thermodynamically drives the protonation of a guest molecule trapped inside its highly charged cavity. The researchers exploit this host-induced shift in the guest's ability to accept a proton to do acid catalysis in basic solution. In the presence of catalytic amounts of the host, orthoformates $[HC(OR)_3$, R = alkyl] in basic solution are trapped inside and protonated by water, resulting in rapid hydrolysis of the otherwise stable-to-base orthoformate. A similar strategy could be used to hydrolyze other acid-sensitive molecules in basic environments, the researchers note. The host's ability to select appropriately sized substrates is of particular interest, because size selectivity is often used by nature but rarely incorporated into standard homogeneous or heterogeneous catalysis.

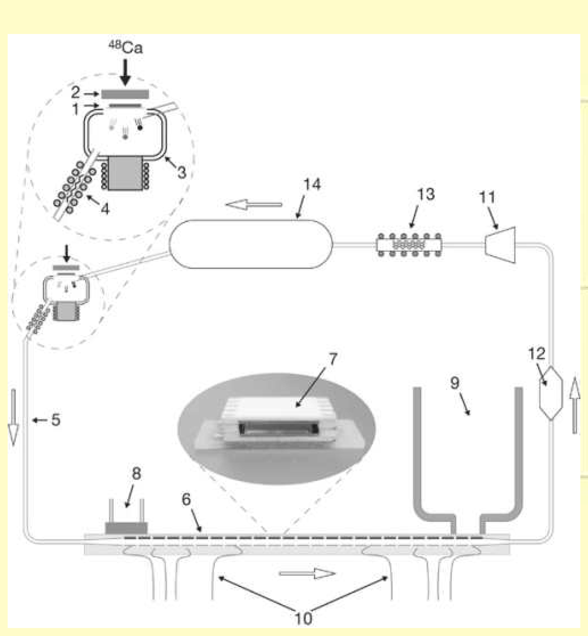


El [112]Uub completa el grup 12

Predicting electron orbital structures of transactinides is challenging because of so-called relativistic effects. That term refers to the energy-altering influence of the large concentration of positive charge in the nuclei of the heaviest elements on the electrons orbiting those nuclei. Those forces can alter the configuration of an atom's valence orbitals—and hence its chemical properties—compared with the electronic structure expected solely on the basis of an element's position in the periodic table.

In the case of element 112, the transactinide's atomic number places it in group 12 together with zinc, cadmium, and mercury. Earlier theoretical work suggests that 112 should indeed exhibit chemical behavior typical of group 12 elements. Other calculations, however, predict that 112 will behave like radon, a noble gas in group 18.

Now, a team of 25 researchers from Switzerland, Russia, and Poland reports that an experimental study that directly compared element 112's volatility and adsorption characteristics with those of mercury and radon indicates that the transactinide behaves like its lighter group-12 homolog, mercury (R. Eichler *et al.*, *Nature* **2007**, *447*, 72).

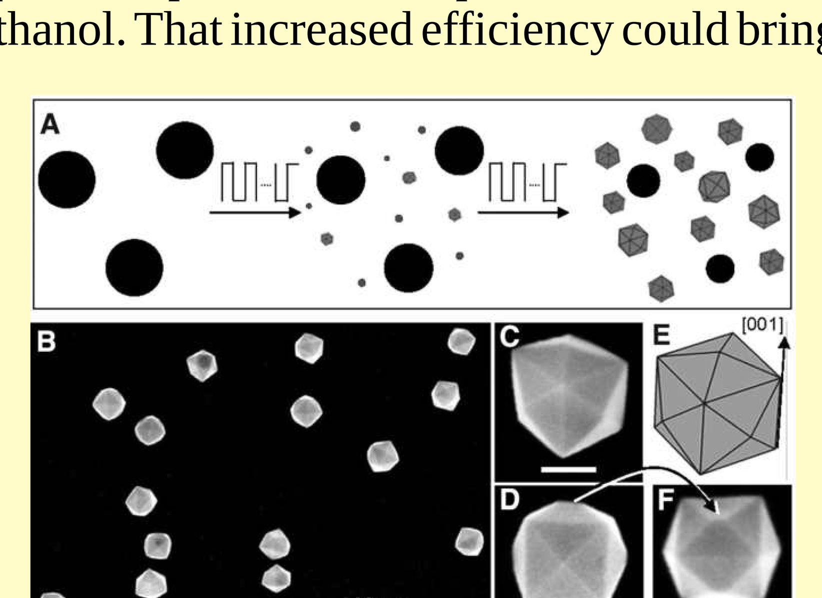


Schematic experimental set-up used to investigate the adsorption properties of element 112 on a gold surface.

Catalitzadors: quantes més cares, millor

To find the action in catalysis reactions, you've got to go to the edge—the edge of the catalyst, that is. That's because the catalyst's most reactive regions can be found at the edges' open sites, where an atom is missing one or more neighbors to which it could bind. Now, researchers at Xiamen University, in China, and Georgia Institute of Technology have created new efficient platinum nanocrystal catalysts with 24 facets (Z. L. Wang *et al.*, *Science* **2007**, *316*, 732).

The rough facets on these edgy "tetrahexahedral" structures provide unsaturated steps, ledges, and kinks, which help make the catalysts 200 to 400% more efficient than spherical platinum nanoparticles at oxidizing organic fuels such as formic acid and ethanol. That increased efficiency could bring a boost to hydrogen fuel cells.



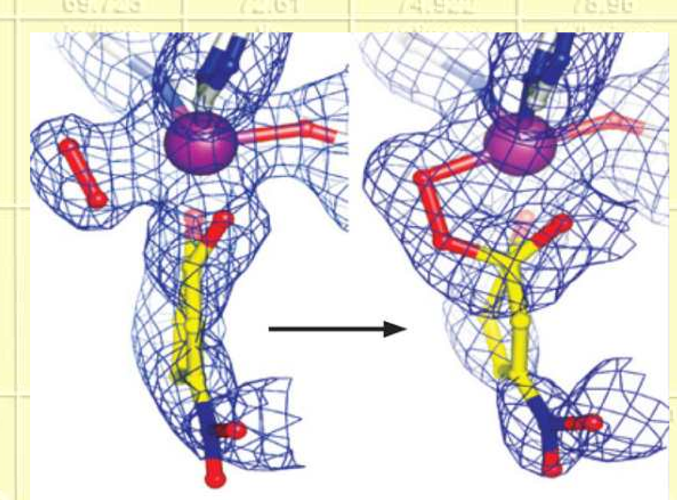
(A) Scheme of electrochemical preparation of THH Pt NCs from nanospheres. (B) Low-magnification SEM image of THH Pt NCs. (C and D) High-magnification SEM images of Pt THH viewed down along different orientations. (E) Geometrical model of an ideal THH. (F) High-magnification SEM image of a THH Pt NC, showing the imperfect vertices as a result of unequal size of the neighboring facets. Scale bars in (C), (D), and (F), 100 nm

Un cristall enciclopèdic

Iron-containing enzymes are major players in activating molecular oxygen for reactions with organic substrates. One of the questions concerning iron enzymes that lack porphyrin-containing heme groups is: How does O_2 interact with the iron and then attack substrates? Biochemistry professor John D. Lipscomb and coworkers have answered this question for one particular nonheme enzyme. In a single crystal of a dioxygenase that cleaves 1,2-dihydroxyaromatic compounds such as catechol, they captured the structures of three intermediates—two of which had not been seen before—that are involved in O_2-activation and -insertion reactions catalyzed by the enzyme (*Science* **2007**, *316*, 453).

On the basis of spectroscopic studies, Lipscomb previously predicted that the enzyme's iron atom binds O_2 and the catechol substrate simultaneously, but observations of the key intermediates specified by the proposed mechanism proved elusive. In the first newly observed intermediate structure, the oxygen molecule binds to the iron in a side-on fashion to give a superoxide ($O_2^{\cdot -}$) ligand, while the two oxygens of the catechol substrate bind to two adjacent ligand sites on the iron. Next, the iron-bound superoxide attacks the catechol moiety to form an alkylperoxo intermediate.

A stroke of luck allowed the researchers to trap the intermediates in a single crystal. They found a new way to crystallize the enzyme so that the four nominally identical active sites experience different packing forces that create slight differences among them. The catalytic cycle has effectively stopped at different points in each subunit.

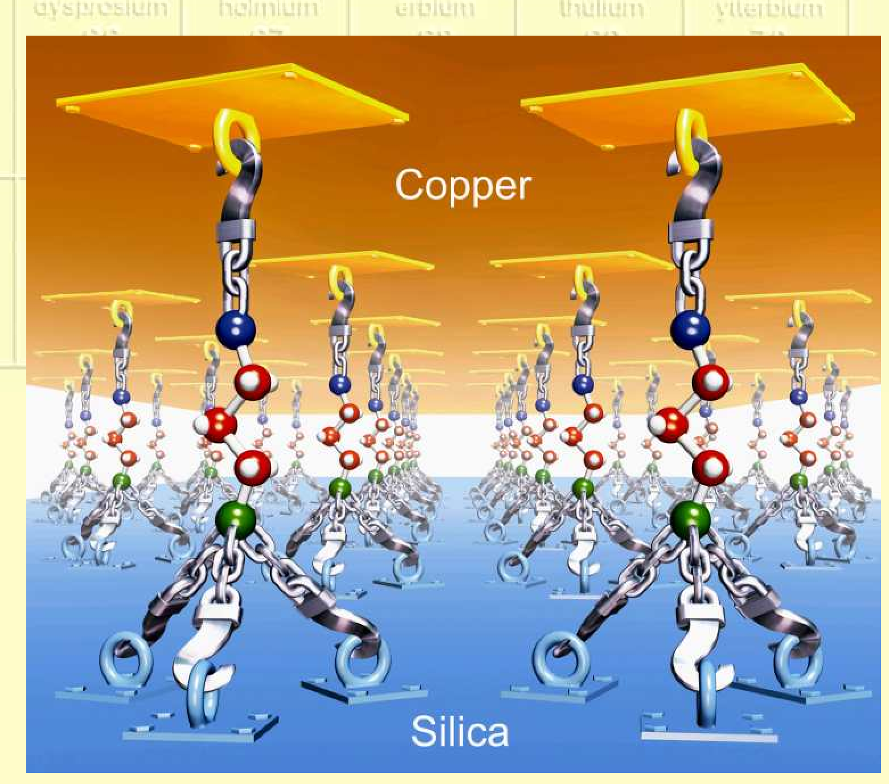


IRONCENTRICITY In the dioxygenase, O_2 interacts with an iron/4-nitrocatechol complex (left) before forming an alkylperoxo intermediate (red = O; yellow = C; blue = N; purple = Fe).

I ara, la nano*cola*

Researchers at Rensselaer Polytechnic Institute (Troy, N. Y.) have developed a new method to bond materials that don't normally stick together. The team's adhesive, which is based on self-assembling nanoscale chains, could impact everything from next-generation computer chip manufacturing to energy production (D. D. Gandhi *et al.*, *Nature* **2007**, *447*, 299).

Less than a nanometer – or one billionth of a meter – thick, the nanoglue is inexpensive to make and can withstand temperatures far higher than what was previously envisioned. In fact, the adhesive's molecular bonds strengthen when exposed to heat. The glue material is already commercially available, but the research team's method of treating the glue to dramatically enhance its "stickiness" and heat resistance is completely new.



Breus

• La *British Library* ha posat en marxa el projecte *Turning the Pages* (http://www.bl.uk/onlinegallery/ttp/ttpbooks.html), que permet fullejar alguns dels seus exemplars més valuosos.

• L'anàlisi dels esquelets dels europeus del Neolític (5800 - 5000 a.C.) demostra que eren intolerants a la lactosa, i per tant no prenien llet (J. Burger *et al.*, *Proc. Natl. Acad. Sci.* **2007**, *104*, 3736).

• Càlculs teòrics indiquen l'estabilitat del ful·lerè de bor B_{80}, el qual té un àtom adicional en el centre de cada hexàgon respecte al C_{60} (N. Gonzalez Szwacki *et al.*, *Phys. Rev. Lett.* **2007**, *98*, 166804).

L'element número **34**, **seleni,** va ser descobert l'any 1817 per J. Berzelius estudiant les impureses en la fabricació de l'àcid sulfúric. El seu nom prové del grec Σεληνη, que vol dir *Lluna*.