Clean Hydrogen Peroxide Synthesis via a Nanocatalyst Process

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ABSTRACT

HTI has developed a nanocatalyst technology that enables the synthesis of H_2O_2 from hydrogen and oxygen. This breakthrough technology eliminates all the hazardous chemicals of the existing process, along with its undesirable byproducts. It produces H_2O_2 more efficiently, cutting both energy use and costs, and generates no toxic-waste.

Keywords: clean synthesis, hydrogen peroxide, nanocatalyst

1 INTRODUCTION

A nanotechnology platform developed at Headwaters Technology Innovation (HTI) has many applications. Several daily-life applications focus on pollution prevention using the trademark NxCat^{TM} nanocatalyst technology. A case study based on direct synthesis of hydrogen peroxide from its element hydrogen and oxygen will be used as an example and discussed.

Hydrogen peroxide (H_2O_2) is a clean, versatile, environmentally friendly oxidant that can substitute for environmentally harmful chlorinated oxidants in many manufacturing operations. However, the current manufacturing process for H_2O_2 is complex, high cost, and energy-intensive. This process uses an anthraquinone working solution, containing several toxic chemicals, which requires additional and complex equipment to control exposure. The solution is reduced by hydrogen in the presence of a catalyst, forming anthrahydroquinone, which then reacts with oxygen to release H_2O_2. The H_2O_2 is removed from the solution with an energy-intensive stripping column and then concentrated by vacuum distillation. While the bulk of the working solution is recycled, the balance is a waste stream of quinone-derived byproducts that requires environmentally acceptable disposal.

Chemical companies thus have been eager for several decades to develop a simpler, large-scale synthesis of H_2O_2 directly from hydrogen and oxygen, for which the only by-product is water.

HTI has produced a robust nanocatalyst technology that enables the synthesis of H_2O_2 directly from hydrogen and oxygen. This breakthrough technology, called NxCat™, is a palladium-platinum catalyst that eliminates all the hazardous reaction conditions and chemicals of the existing process, along with its undesirable byproducts. It produces H_2O_2 more efficiently, cutting both energy use and costs. It uses innocuous, renewable feedstocks and generates no toxic waste. In addition, the technology is expected to reduce capital costs by as much as 50%, generating a greener and competitively priced supply of H_2O_2.

2 CHEMISTRY OF H_2O_2 SYNTHESIS

When hydrogen encounters oxygen, the thermodynamically favored reaction product is water (equation 1). Hydrogen peroxide (H_2O_2) is only an intermediate in this reaction (equations 2 and 3), because hydrogen peroxide is not stable and releases water and oxygen when it decomposes (equation 4). Because hydrogen peroxide is formed midway through the favored reaction, which produces water, it is critical to stop the reaction at equation 2 and not let it proceed to equations 3 and 4.

$$2\,H_2 + O_2 = 2\,H_2O \quad (1)$$
$$H_2 + O_2 = H_2O_2 \quad (2)$$
$$H_2O_2 + H_2 = 2\,H_2O \quad (3)$$
$$2\,H_2O_2 = 2\,H_2O + O_2 \quad (4)$$

3 NXCAT TECHNOLOGY

HTI addressed this challenge by developing a set of proprietary molecular templates that achieve an unprecedented level of control of the catalytic nanoparticles, thereby eliminating unwanted reactions and increasing selection for H_2O_2 to up to 100 percent. The molecular templates are usually made of organic molecules or polymers with many functional groups that have specific effects on the catalyst, a precisely tailored combination of palladium (Pd) and platinum (Pt) in a molar ratio of 50 Pd to 1 Pt. The technology offers many dimensions of selectivity by managing nanoparticle crystal structure, size, composition, dispersion and stability (anchoring), as outlined below.

3.1 Crystal Structure Control

In catalysis Pd surface atoms adsorb molecular hydrogen and oxygen and then speed the exchange of hydrogen and oxygen electrons, because the high electronic conductivity of the metal atoms enhances the electronegative attraction of oxygen atoms to two hydrogen electrons. But a hydrogen peroxide molecule only forms if *two* adjacent Pd atoms adsorb one hydrogen molecule and one oxygen molecule, forming an ionic bond between H_2^{2+} and O_2^{2-} during the electron transfer. But if *three* adjacent Pd atoms adsorb two molecules of hydrogen and one molecule of oxygen, the electron transfer forms two water molecules. Therefore, consistent control of the Pd surface structure is key to managing the outcome.

The schematic diagrams below represent three faces of Pd crystal. Face-111 exposes six adjacent atoms, and face-100 exposes four adjacent atoms. But face-110 exposes only two adjacent atoms, reducing the probability of water formation to one-third of that on face-100, and one-fifth of that on face-111. Thus the reaction selectivity for H_2O_2 is greatly enhanced if the palladium in the catalyst retains the face-110 crystal structure.

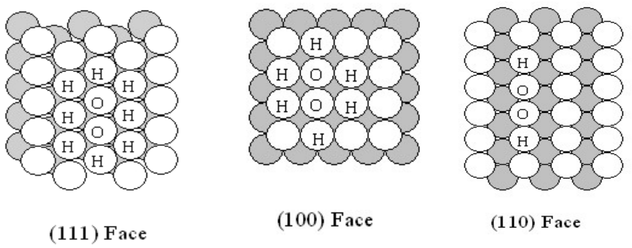

Figure 1: Crystal face-111 makes six Pd atoms available to H and O molecules, while face-100 exposes four Pd atoms. But crystal face-110, which exposes Pd atoms in pairs, favors H_2O_2 formation.

Under the auspices of a 1998 National Science Foundation Small Business Innovation Research grant (#DM 97760555), HTI, which was then called Hydrocarbon Technologies, Inc., conducted pioneering research that uncovered a relationship between the growth rate of each Pd crystal face and the number of sodium polyacrylate polymer molecules surrounding each Pd ion. That allowed the researchers to establish the (proprietary) ideal ratio of the capping polymer to Pd. The polymer, they also found, must have a straight-chain morphology to allow the metal atoms to react with the functional groups along the polymer chain to form the desired crystal face. The resulting face-controlled catalyst selectivity for H_2O_2 improved to about 100 percent, significantly greater than the best results (74 percent) patented by an industry leader using catalysts without controlled Pd exposition under similar reaction conditions[1].

3.2 Particle Size Control

Uniform nanoparticle size is also critical in augmenting the reaction selectivity. HTI researchers observed that a 4-nm particle catalyst produced hydrogen peroxide—but a catalyst containing 2-nm particles created water. In a proprietary process, HTI engineered molecular templates of specific size and concentration that allow the template molecules to wrap around the metal atoms of the catalyst, thus keeping the nanoparticles at the desired size.

3.3 Particle Composition Control

A careful selection of the functional group of the molecular template enables HTI to control the nanoparticle composition, thus minimizing unwanted reactions. For example, to fabricate a catalyst with specific proportions of palladium and platinum HTI selects a template containing two functional groups, one with an affinity to palladium and the other with an affinity to platinum. By precisely adjusting the ratio of the two selected template molecules the research team can achieve the exact formulation of the catalyst composition.

3.4 Particle Dispersion Control

An even dispersion of catalyst particles is one of the most difficult conditions to achieve in nanotechnology because metal nanoparticles have a strong tendency to clump together, minimizing the exposure of particle surface area, and thereby weakening the catalyzing effect on hydrogen-oxygen bonding. HTI overcame this challenge by engineering molecular templates with functional groups that bond closely with the metal atoms, counteracting the tendency of the particles to agglomerate. Thus stabilized, nanoparticles remain evenly dispersed while exposing a large surface area, retaining their powerful reactivity in the catalyst.

3.5 Particle Anchor Control

Catalytic processes usually involve the confinement of the active component of the catalyst to a substrate by physical force, such as by Van de Waals force. But the NxCat approach is to use a molecular template to bind the palladium nanoparticles to a substrate of carbon black, silica or other catalyst supports. The chemical bond is much stronger than physical force and more firmly fixes the nanoparticles to the substrate surface, stabilizing the catalyst so it can withstand severe reaction conditions and last a long time under commercial applications (see diagrams below). A test of more than 3,000 hours by Degussa in 2005 confirmed that the catalyst remained stable even in extremely industrial harsh conditions, such as in the presence of sulfuric acid and hydrogen peroxide. The resulting catalyst has an expected industrial lifespan of more than three years.

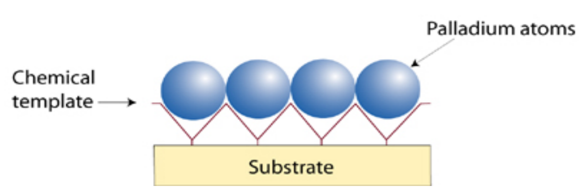

Figure 2: Metal atoms held on a substrate by a molecular template produce a stable, long-lived catalyst.

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4 ADVANTAGES OF NXCAT TECHNOLOGY

The HTI nanocatalyst technology lays out an alternative, "green" pathway for producing hydrogen peroxide. By replacing an industrial method requiring the continual use of large amounts of hazardous chemical reagents with a catalyzed, direct synthesis route that uses only innocuous, renewable feedstocks of hydrogen and oxygen, NxCat cuts the cost of producing a fully effective, product. By providing alternative reaction conditions it reduces the risk of flammability and explosion of conventional production methods while using an aqueous or organic solvent with minimal human health and environmental impacts. Through precise nanoparticle control the catalytic method allows for a far greater range of reaction selectivity without using of the energy-intensive equipment in conventional H2O2 production. NxCat also completely eliminates the toxic quinone-derived byproducts of the conventional process. The only possible byproduct of reaction between hydrogen and oxygen is water.

Finally, NxCat technology delivers the bonus of producing, safely and at lower cost, large amounts of hydrogen peroxide, a clean, safe oxidant that is expected to replace chlorinated oxidants in many industrial processes. By making available a much simpler manufacturing process, it offers the potential of a competitively priced supply of hydrogen peroxide that could do much to increase the market for it, speeding its inclusion in a wider range of industrial processes that now use more environmentally deleterious chemicals.

5 COMMERCIAL DEMONSTRATION AND POTENTIAL APPLICATIONS

HTI has also taken a step unprecedented in the development of catalytic direct-synthesis processes by partnering with an industry leader to test the process at industrial scale. In 2005, with German manufacturer Degussa AG, HTI completed the milestone of pilot testing the technology. HTI and Degussa completed construction of a commercial demonstration plant in 2007, and will jointly perform a full-scale technology demonstration in 2008. HTI and Degussa plan to market the technology worldwide. Several other major manufacturers have expressed interest.

Work is already underway to adapt the flexible catalytic technology to other industrial manufacturing processes. HTI partner Degussa AG has recruited another industry partner to adapt the NxCat technology to the manufacture of propylene oxide. Worldwide, about 55 percent of propylene oxide is produced using a chlorohydrin process that produces large amounts of aqueous waste[2] The direct synthesis of H_2O_2 has the potential to eliminate that waste stream.

NxCat can also be used in the production of various other large-volume chemical products to achieve fewer deleterious environmental impacts, including: caprolactam, epichlorohydrin, adipic acid and phenol. HTI long-term plans include applying it in the fabrication of chemicals, energy, environment, pharmaceuticals and other products. As a breakthrough foundational technology, its potential is virtually limitless.

REFERENCES

[1] Dupont, U.S. Patent 4,832,938.
[2] Lempert et al., "Environmental Technologies."