

Catalysts at the Nanoscale

By Joshua Rolnitzky

During times of war, technology tends to develop at an accelerated pace. World War II was no exception. Using newly invented incendiary devices, Army Rangers from D company of the 2nd Battalion disabled five 155mm guns aimed at the US fleet off of Utah Beach during the invasion of Normandy. These thermite grenades silently fused the guns' elevating and traversing mechanisms by burning at 3000°C. Now, over 60 years later, thermites are receiving a facelift with the help of nanotechnology. And while the military is keenly interested in nanotechnology, hundreds of other organizations are seeking various applications within the nascent field.

The exciting prospect of nanotechnology is its potential use in almost any conceivable domain. Every field from medicine and electronics to manufacturing and fashion stand to benefit from advances in nanotechnology. And while nano-scale technology is multifaceted in its application, the use of nanocrystals as catalysts is perhaps the most intriguing.

In order to understand why nanocrystal catalysts are so promising, one first needs to understand some basic principles of Chemistry. For any chemical reaction to occur, two reactive species must come in contact with each other. The term reactive does not imply unstable; wood is relatively inert unless it is heated. However, if it is warmed to approximately 451° Fahrenheit, the hydrogen and carbon composition of the wood reacts with oxygen in the air to form carbon dioxide and water. While this paper will not address how or why this reaction occurs, it is important to understand that it will cease if the reactive species are not in close proximity to each other. Fire will never originate in the core of burning logs because oxygen is not able to penetrate far beyond the surface. Anyone who has built a campfire knows that the fire only burns on the wood's exterior.

Another key concept to understanding nanocrystal catalysis involves the ratio of surface area and volume. As an object gets larger, its surface area increases less in relation to its volume. A good way to visualize this is to imagine a cube (Figure 1). Volume is measured by multiplying the cube's length, width, and height. Surface area is determined by finding the area of one face of the cube (length times height) and multiplying it by the number of faces: in this case, six.

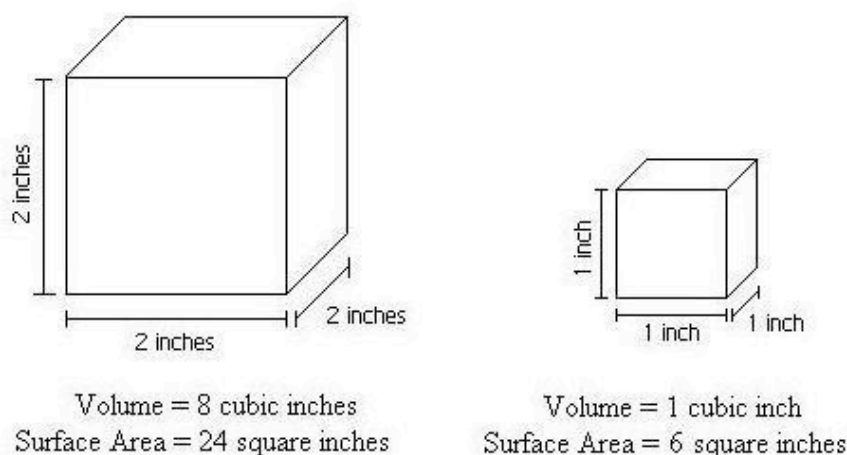


Figure 1: Decreasing the length of a cube's edge reduces the volume (length x width x height) more quickly than its surface area (length x height x number of sides). Smaller objects therefore have a larger surface:volume ratio.

Figure 1 shows that halving the length of each side results in an eightfold decrease in volume, but only a fourfold decrease in surface area. Therefore, smaller objects have more surface area with respect to their volume. This has important implications for chemical reactions. High surface area-to-volume ratios are favorable for chemical reactions. Going back to the campfire example, kindling is used to start the fire. The small pieces of wood have a greater surface area with respect to their volume than larger logs. Lighting the kindling therefore results in a quicker combustion. Additionally, if one throws a handful of sawdust onto a burning fire, a giant flare results. This reaction is chemically identical to ordinary wood burning, but it occurs at a much faster rate.

The general purpose of catalysts is to increase the speed of a given reaction. This is achieved through kinetic means and does not directly affect the thermodynamic properties of a chemical system. Introducing a catalyst increases the speed of a reaction in one of three ways; it can lower the activation energy for the reaction, act as a facilitator and bring the reactive species together more effectively, or create a higher yield of one species when two or more products are formed. Depending on the application, nano-catalysts can be used in all the ways listed above.

Nano-materials are more effective than conventional catalysts for two reasons. First, their extremely small size (typically 10-80 nanometers) yields a tremendous surface area-to-volume ratio. Also, when materials are fabricated on the nanoscale, they achieve properties not found within their macroscopic counterparts. Both of these reasons account for the versatility and effectiveness of nano-catalysts.

Perhaps no one is more interested in studying nano-catalysts than the military. Always looking to gain an edge over other nations, the United States military has invested hundreds of millions of dollars in nanotechnology. One of its more significant discoveries deals with superthermites. Traditionally, thermites are a class of powders that produce metal and an immense amount of heat when reacted. But when thermites are infused with nanometals, specifically nano-aluminum and molybdenum, they produce reactions that progress thousands of times faster than their ordinary analogs [1]. The increased kinetics of the reaction releases heat more quickly, and therefore makes the reaction more intense. Although the military has classified much of the research, it is believed that superthermites will replace conventional organic explosives like TNT for use in a variety of applications [2].

Nanometals also have military applications as propellants. Adding nanoaluminum to missiles, torpedoes, and other munitions can theoretically launch projectiles further and faster than conventional charges. Burn rates with nanoaluminum can be over ten times higher than contemporary propellants [1]. Equipped with nanometals, rockets could potentially reach their targets before any evasive action could be taken.

Every year, military munitions plants crank out hundreds of millions of bullets for armed conflicts and training. In 1997, scientists began to develop alternatives to toxic lead used in standard rounds [1]. Fabricating bullets using nanoaluminum considerably increases their range. In addition, since nanomaterials provide a higher concentration of energy with fewer raw materials, manufacturing munitions with nano-catalysts would actually decrease the overall cost while increasing their effectiveness.

One of the biggest draws of implementing nanotechnology within weapons lies within its control. Varying the mixture of different nanometals yields a wide range of energy release rates [3]. These rates can span from conventional explosives to superthermites. This fine-tuning can also be accomplished by altering the size of the catalysts on the nanoscale.

While the military seeks to destroy the world (or, at least, small parts of it) by utilizing nanotechnology, various groups are hoping nanocatalysts can save it. Several California-based companies are currently developing nanomaterials for improved catalytic converters [4]. With over 500 million cars in existence worldwide [5], improving fuel efficiency can have drastic effects: both environmentally and economically. Improving the rates of catalytic combustion occurs through product

selectivity. In a common automobile, hydrocarbons in the gasoline ignite to create water, carbon dioxide, and the force necessary to drive the engine's pistons. However, impurities in gasoline coupled with inefficient reactions yield harmful byproducts such as carbon monoxide, nitrogen dioxide, and sulfur hexafluoride. These compounds can lead to ozone depletion, acid rain, and other environmental concerns. But nanotech catalysts have the potential to make automobile combustion up to 100% selective and therefore produce little or no toxic byproducts. And since the automobile catalyst market alone is a \$5-7 billion industry, companies stand to save \$4.5 billion annually by implementing nano-catalysts into their converters while saving the environment as well [6].

The limited quantity of fossil fuels on the planet has led researchers towards finding alternative sources of energy. Fuel cells have the ability to generate vast amounts of energy in an environmentally friendly way. Combining oxygen and hydrogen gas within a fuel cell creates enough energy to power a car and other large machines while producing water as the only byproduct. The efficiency of fuel cells is linked to their rate-limiting reaction, or in this case, oxygen reduction. Conventionally, the promotion of the oxidation reaction is accomplished through the use of expensive platinum catalysts. Recently, nano-nickel has been found to promote reactions traditionally catalyzed by platinum [7]. In addition to costing four times less than platinum, nano-nickel has a greater catalytic activity. And newly developed manufacturing processes stand to drop the price on nano-nickel even further while allowing it to be used within large-scale industrial applications.

Physicist Richard Feynman once said that, "at the atomic level, we have new kinds of forces and new kinds of possibilities, new kinds of effects." [8] Contemporary technologies have proved his predictions 45 years after the fact. Nanotechnology exists as an intriguing dichotomy; the fundamental principles of nano-catalysis can be harnessed to destroy the world or to help heal its wounds. It is only a matter of time before the potential of nanocrystal catalysts are realized and implemented on a widespread scale.

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