

CHAPTER III



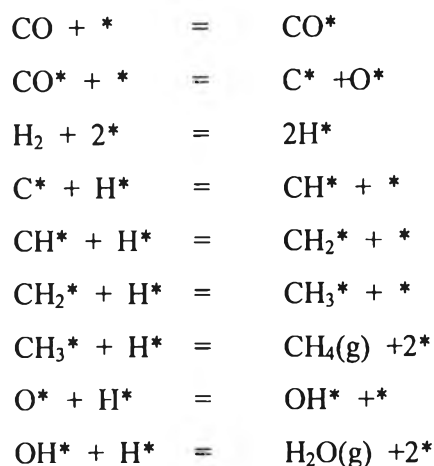
THEORY

3.1 Fischer-Tropsch synthesis (FTS)

Fischer-Tropsch synthesis (FTS) or CO hydrogenation reaction, the production of liquid hydrocarbons from synthesis gases (CO and H₂) is a promising, developing route for environmentally sound production of chemicals and fuels from coal and natural gas. During the past decades, FTS has been developed continuously by many researchers, although the rise and fall in research intensity on this process has been highly related to the demands for liquid fuels and relative economics. This synthesis is basically the reductive polymerization (oligomerization) of carbon monoxide by hydrogen to form organic products containing mainly hydrocarbons and some oxygenated products in lesser amounts. The main reactions of FTS are:



Equations (1) is the formation of methane, the equation (2) is the synthesis of hydrocarbons higher than methane, the equation (3) is the water-gas shift reaction, and the equation (4) is the Boudouard reaction resulting in which results in deposition of carbon. The reaction mechanism of methanation can be described by the following set of mechanism:



Normally, catalysts used for FTS are group VIII metals. By nature, the hydrogenation activity increases in order of $\text{Fe} < \text{Co} < \text{Ni} < \text{Ru}$. Ru is the most active. Ni forms predominantly methane, while Co yields much higher ratios of paraffins to olefins and much less oxygenated products such as alcohols and aldehydes than Fe does.

Commercially, Entrained bed reactors or slurry bubble column reactors are used in FTS since they can remove heat from this exothermic synthesis, allowing better temperature control.

The current main goal in FTS is to obtain high molecular weight, straight chain hydrocarbons. However, methane and other light hydrocarbons are always present as less desirable products from the synthesis. According to the Anderson-Schulz-Flory (ASF) product distribution, typically 10 to 20% of products from the synthesis are usually light hydrocarbon ($\text{C}_1\text{-C}_4$). These light alkanes have low boiling points and exist in the gas phase at room temperature, which is inconvenient for transportation. Many attempts have been made to minimize these by-products and increase the yield of long chain liquid hydrocarbons by improving chain growth probability. It would be more efficient to be able to convert these less desirable products into more useful forms, rather than re-reforming them into syngas and recycling them (Farrauto and Bartholomew, 1997). Depending upon the type of catalyst used, promoters, reaction conditions (pressure, temperature and H_2/CO ratios), and type of reactors, the distribution of the molecular weight of the hydrocarbon products can be noticeably varied.

3.2 Cobalt (Young 1960; Othmer, 1991)

3.2.1 General

Cobalt, a transition series metallic element having atomic number 27, is similar to silver in appearance.

Cobalt and cobalt compounds have expanded from use colorants in glasses and ground coat fits for pottery to drying agents in paints and lacquers, animal and human nutrients, electroplating materials, high temperature alloys, hard facing alloys, high speed tools, magnetic alloys, alloys used for prosthetics, and used in radiology. Cobalt is also as a catalyst for hydrocarbon refining from crude oil for the synthesis of heating fuel.

3.2.2 Physical Properties

The electronic structure of cobalt is $[\text{Ar}] 3d^7 4s^2$. At room temperature the crystalline structure of the α (or ϵ) form, is close-packed hexagonal (cph) and lattice parameters are $a = 0.2501$ nm and $c = 0.4066$ nm. Above approximately 417°C , a face-centered cubic (fcc) allotrope, the γ (or β) form, having a lattice parameter $a = 0.3554$ nm, becomes the stable crystalline form

The scale formed on unalloyed cobalt during exposure to air or oxygen at high temperature is double-layered. In the range of 300 to 900°C , the scale consists of a thin layer of mixed cobalt oxide, Co_3O_4 , on the outside and cobalt (II) oxide, CoO , layer next to metal. Cobalt (III) oxide, Co_2O_3 , may be formed at temperatures below 300°C . Above 900°C , Co_3O_4 decomposes and both layers, although of different appearance, are composed of CoO only. Scales formed below 600°C and above 750°C appear to be stable to cracking on cooling, whereas those produced at 600 - 750°C crack and flake off the surface.

Cobalt forms numerous compounds and complexes of industrial importance. Cobalt, atomic weight 58.933, is one of the first transition series of Group 9 (VIII B). There are thirteen known isotopes, but only three are significant: ^{59}Co is the only stable and naturally occurring isotope; ^{60}Co has a half-life of 5.3 years and is a common source of γ -source for Mössbauer spectroscopy.

Cobalt exists in the +2 or +3 valance states for the major of its compounds and complexes. A multitude of complexes of the cobalt (III) ion exists, but few stable simple salt are know. Octahedral stereochemistries are the most common for cobalt (II) ion as well as for cobalt (III). Cobalt (II) forms numerous simple compounds and complexes, most of which are octahedral or tetrahedral in nature; cobalt (II) forms more tetrahedral complex than other transition-metal ions. Because of the small stability difference between octahedral and tetrahedral complexes of cobalt (II), both can be found equilibrium for a number of complexes. Typically, octahedral cobalt (II) salts and complexes are pink to brownish red; most of the tetrahedral Co (II) species are blue.

Table 3.1 Physical properties of cobalt (Othmer, 1991)

Property	Value
atomic number	27
atomic weight	58.93
transformation temperature, °C	417
heat of transformation, J/g ^a	251
melting point, °C	1493
latent heat of fusion, ΔH_{fus} J/g ^a	395
boiling point, °C	3100
latent heat of vaporization at bp, ΔH_{vap} kJ/g ^a	6276
specific heat, J/(g °C) ^a	
15-100°C	0.442
molten metal	0.560
coefficient of thermalexpansion, °C ⁻¹	
cph at room temperature	12.5
fcc at 417°C	14.2
thermal conductivity at 25 °C, W/(m K)	69.16
thermal neutron absorption, Bohr atom	34.8
resistivity, at 20 °C ^b , 10 ⁻⁸ Ω m	6.24
Curie temperature, °C	1121

Table 3.1 Physical properties of cobalt (cont.)

Property	Value		
saturation induction, $4\pi I_s$, T ^c	1.870		
permeability, μ			
initial	68		
max	245		
residual induction, T ^c	0.490		
coercive force, A/m	708		
Young's modulus, Gpac	211		
Poisson's ratio	0.32		
Hardness ^f , diamond pyramid, of %Co	99.9 99.98 ^e		
At 20 °C	225 253		
At 300 °C	141 145		
At 600 °C	62 43		
At 900 °C	22 17		
strength of 99.99 %cobalt, MPa ^g	as cast	annealed	sintered
tensile	237	588	679
tensile yield	138	193	302
compressive	841	808	
compressive yield	291	387	

^a To convert J to cal, divided by 4.184.

^b conductivity = 27.6 % of International Annealed Copper Standard.

^c To convert T to gauss, multiply by 10^4 .

^d To convert GPa to psi , multiply by 145,000.

^e Zone refined.

^f Vickers.

^g To convert MPa to psi , multiply by 145.

3.2.3 Cobalt Oxides

Cobalt has three well-known oxides:

Cobalt (II) oxide, CoO , is an olive green, cubic crystalline material. Cobalt (II) oxide is the final product formed when the carbonate or the other oxides are calcined to a sufficiently high temperature, preferably in a neutral or slightly reducing atmosphere. Pure cobalt (II) oxide is a difficult substance to prepare, since it readily takes up oxygen even at room temperature to re-form a higher oxide. Above about 850°C , cobalt (II) oxide form is the stable oxide. The product of commerce is usually dark gray and contains 77-78 wt % cobalt. Cobalt (II) oxide is soluble in water, ammonia solution, and organic solvents, but dissolves in strong mineral acids. It is used in glass decorating and coloring and is a precursor for the production of cobalt chemical.

Cobalt (II) oxide, Co_2O_3 , is formed when cobalt compounds are heated at a low temperature in the presence of an excess of air. Some authorities hold that cobalt (III) oxide exists only in the hydrate form. The lower hydrate may be made as a black powder by oxidizing neutral cobalt solutions with substances like sodium hypochlorite. Co_2O_3 or $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is completely converted to Co_3O_4 at temperatures above 265°C . Co_3O_4 will absorb oxygen in a sufficient quantity to correspond to the higher oxide Co_2O_3 .

Cobalt oxide, Co_3O_4 , is formed when cobalt compounds, such as the carbonate or the hydrated sesquioxide, are heated in air at temperatures above approximately 265°C and not exceeding 800°C .

3.3 Co-based catalysts

Supported cobalt (Co) catalysts are the preferred catalysts for the synthesis of heavy hydrocarbons from natural gas based syngas (CO and H_2) because of their high Fischer-Tropsch (FT) activity, high selectivity for linear hydrocarbons, and low activity for the water gas shift reaction. It is known that reduced cobalt metal, rather than its oxides or carbides, is the most active phase for CO hydrogenation in such catalysts. Investigations have been done to determine the nature of cobalt species on various supports such as alumina, silica, titania, magnesia, carbon, and zeolites. The influence of various types of cobalt precursors used was also investigated. It was found that the

used of organic precursors such as Co (III) acetyl acetate resulting in an increase of CO conversion compared to that of cobalt nitrate (Kraum and Baerns, 1999).

3.4 Cobalt-Support Compound Formation (Co-SCF)

Compound formation between cobalt metal and the support can occur under pretreatment and/or reaction conditions, leading to catalyst deactivation. The compound formation of cobalt metal with support materials, however, is difficult to predict because of the lack of sufficient thermodynamic data. Co-support compound formation can be detected evidentially.

3.4.1 Co-Silicate Formation

The formation of cobalt silicates on Co/SiO₂ under hydrothermal conditions has been extensively studied by Kogelbauer *et al.* (1995). Hydrothermal treatment at 200°C led to a catalyst with lower reducibility due to the formation of both reducible and non-reducible (at temperature ≤ 900°C) cobalt silicates. It was found that hydrothermal treatment of the reduced catalyst or hydrothermal treatment of the calcination catalyst in the presence of hydrogen produces cobalt silicates, while hydrothermal treatment of the calcined catalyst in air does not result in their formation. Hydrothermal treatment of the calcined catalyst in inert gas also has little effect.

3.4.2 Co-Aluminate Formation

Interaction of cobalt with its alumina support has been observed by many authors using various techniques including TPR, XRD, EXAFS, and XPS (ESCA). The migration of cobalt ions into alumina lattice sites of octahedral or tetrahedral symmetry is limited to the first few layers of the support under normal calcination conditions. The reaction of Co with γ -Al₂O₃ can form a surface spinel in Co/ γ -Al₂O₃ catalysts. The surface spinel structure can not be observed by X-ray diffraction because it does not have long range, three dimensional order. It has been suggested that cobalt ions occupying surface octahedral site of γ -Al₂O₃ are reducible while cobalt ions occupying tetrahedral sites are non-reducible, at least at temperatures

$\leq 900^{\circ}\text{C}$. At lower calcination temperatures, filling of the octahedral sites is more favorable. Filling of the tetrahedral site of $\gamma\text{-Al}_2\text{O}_3$ may be enhanced by an increase in calcination temperature.

3.5 Silicon dioxide (Patnaik,2002)

3.5.1 General feature of silica

Table 3.2 Physical properties of silica

Properties	
Other names	Silica
Molecular formula	SiO_2
Molar mass	60.1 g/mol
Appearance	white or colourless solid (when pure)
Density and phase	2.6 g/cm^3 , solid
Solubility in water	insoluble
Melting point	1610°C
Boiling point	2230°C

In its many forms, silica has been used in all stages of civilization, from the ancient flints of the Stone Age to the modern silica laboratory ware. Because of its many uses, and of the many varied forms in which it occurs, silica has been called by more names than any other mineral. Many of the older names of flint are now so obsolete that repetition is needless, but many of the present-day names for quartz gems are unknown save to a few jewellers. Then, too, the exact research of the modern laboratory has shown several distinct crystallographic varieties of silica; some of which are closely connected with the temperatures experienced in their life-history.

The many different names, and their different connotations, which are now in use for silica minerals, call for a classification and arrangement in a more ample, yet more concise manner than is to be found in the usual discussion of the varieties of silica. This article is written with the hope of making a scientific classification of these names, so that the use of the different terms will no longer be a cause for tedious searching for definitions.

These varieties are named in the order formed with descending temperatures. Recrystallization changes occur at the temperatures noted when ample time is allowed for the action, often in the laboratory only in the presence of catalysts. Besides the changes at these critical temperatures, there are probably similar changes from unstable forms towards quartz at atmospheric temperatures, especially after long time intervals. With fairly rapid cooling or heating intermediate forms may not occur in their stable zone, but a direct change from one to another without the intermediate product may take place. Most of the recrystallization changes noted are found to occur at both ascending and descending temperatures.

(A) SILICA GLASS - amorphous, a true non-crystalline glass, stable below the melting point and above the "gc" temperature. Quartz Glass, Fused Silica, Fused Quartz, are other names for this supercooled liquid. In most forms at atmospheric temperatures there are traces of cristobalite.

(B) CRISTOBALITE - isometric, or pseudo-isometric, "gc" range is at 1710° where Cristobalite changes to glass as temperatures rise, or glass to cristobalite as they fall. Christobalite, an alternate spelling. Beta Cristobalite, also called High Cristobalite, is the high temperature product, forming in the "gc" range in cooling. It is isometric, and in cooling recrystallizes to Alpha Cristobalite, or Low Cristobalite, at 200-275°, providing cooling through the "ct" and "tq" ranges has been too rapid for recrystallization. It is tetragonal.

(C) TRIDYMITE - hexagonal, bipyramidal. "ct" range is at 1470°, where cristobalite changes to tridymite on cooling. Glass may crystallize as tridymite at 1670° if the cooling was too rapid through the "gc" range. Beta Second Tridymite, or Upper High Tridymite, is the high temperature product, forming in the "ct" range in cooling, and

which recrystallizes to Beta First Tridymite, also called Lower High Tridymite, at 163° if cooling was too rapid for the "tq" transformation. This in turn alters to Alpha Tridymite, or Low Tridymite, at 117°, which is the usual tridymite of nature.

- Asmanite - a meteoric tridymite, related to the above series.
- Vestan - a doubtful silica mineral, probably to be ascribed to tridymite.
- Granuline - a doubtful pulverescent mineral which seems allied to tridymite on optical grounds.

(D) QUARTZ - hexagonal, forms from tridymite in the "tq" range at 870° in cooling. Glass may change to crystalline quartz at about 1400° providing cooling was too rapid for the "gc", "gt" and "ct" transformations. Beta Quartz, or High Quartz, is the high temperature product, forming at the "tq" point. It is hemihedral. On cooling it recrystallizes to Alpha Quartz, also called Low Quartz, at 573°, yielding the stable low temperature mineral. It is tetartohedral, showing polarity along the c axis and is divisible into Right Hand Quartz and Left Hand Quartz

(E) CHALCEDONY - a cryptocrystalline, or very finely fibrous mineral, which has not been successfully located in the thermal equilibrium diagram. Heating to 725-850° usually results in an alteration to tridymite, which thereafter acts as normal tridymite. Chalcedony is usually found as a deposit from solutions, and may be a mixture of glass and quartz, or more probably an intermediate product in the dehydration of the opal colloid. Various subdivisions of chalcedony have been made on optical grounds.

- Chalcedony - biaxial, positive, elongation positive.
 - Chalcedonite - biaxial, negative.
 - Lussatite - biaxial, positive, parallel elongation.
 - Quartzine - biaxial, positive, negative elongation
- pseudochalcedonite, Lutecite.
- Jenzschite - differently soluble, but of same S. G. as chalcedony.
 - Melanophlogite - possibly impure chalcedony.
 - Sulfuricin - probably a chalcedony rich in sulphur.

(F) COLLOIDAL SILICA - is usually hydrous, and is commonly described under opal. Silicon occurs in nature combined with oxygen in various forms of silica and silicates. Silicates have complex structures consisting of SiO_4 tetrahedral structural units incorporated to a number of metals. Silicon is never found in nature in free elemental form. Among all elements silicon forms the third largest number of compounds after hydrogen and carbon. There are well over 1000 natural silicates including clay, mica, feldspar, granite, asbestos, and hornblende. Such natural silicates have structural units containing orthosilicates, SiO_4^{4-} , pyrosilicates $\text{Si}_2\text{O}_7^{6-}$, and other complex structural units, such as, $(\text{SiO}_3)_n^{2n-}$ that have hexagonal rings arranged in chains or pyroxene $(\text{SiO}_3^{2-})_n$ and amphiboles, $(\text{Si}_4\text{O}_{11}^{6-})_n$ in infinite chains. Such natural silicates include common minerals such as tremolite, $\text{Ca}_2\text{Mg}_5(\text{OH})_2\text{Si}_8\text{O}_{22}$; diopside, $\text{CaMg}(\text{SiO}_3)_2$; kaolin, $\text{H}_8\text{Al}_4\text{Si}_4\text{O}_{18}$; montmorillonite, $\text{H}_2\text{Al}_2\text{Si}_4\text{O}_{12}$; tale, $\text{Mg}_3[(\text{OH})_2\text{SiO}_{10}]$; muscovite (a colorless form of mica), $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$; hemimorphite, $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$; beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$; zircon, ZrSiO_4 ; benitoite, $\text{BaTiSi}_3\text{O}_9$; feldspars, KAlSi_3O_8 ; zeolites, $\text{Na}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$; nephrite, $\text{Ca}(\text{Mg},\text{Fe})_3(\text{SiO}_3)_4$; enstatite, $(\text{MgSiO}_3)_n$; serpentine, $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_{10}$; jadeite, $\text{NaAl}(\text{SiO}_3)_2$; topaz, $\text{Al}_2\text{SiO}_4\text{F}_2$; and tourmaline, $(\text{H},\text{Li},\text{K},\text{Na}) \cdot \text{Al}_3(\text{BOH})_2\text{SiO}_{19}$. silica, the other most important class of silicon compounds, exists as sand, quartz, flint, amethyst, agate, opal, jasper, and rock crystal.

3.6 Zirconia

3.6.1 General feature of zirconia

Zirconia exhibits three polymorphs, the monoclinic, tetragonal, and cubic phases. Figure 2.1 shows the typical systems: cubic, tetragonal and monoclinic ones. Crystal structure of cubic, tetragonal and monoclinic zirconia are shown in Figure 2.2 The monoclinic is stable up to $\sim 1170^\circ\text{C}$, at which temperature it transforms into the tetragonal phase, which is stable up to 2370°C (Cormak and Parker, 1990). The stabilization of the tetragonal phase below 1100°C is important in the use of zirconia as a catalyst in some reaction. Above 2370°C , the cubic phase is stable and it exists up to the melting point of 2680°C . Due to the martensitic nature of the transformations, neither the high temperature tetragonal nor cubic phase can be quenched in rapid cooling to room temperature. However, at low temperature, a metastable tetragonal zirconia phase is usually observed when zirconia is prepared by certain methods, for

example by precipitation from aqueous salt solution or by thermal decomposition of zirconium salts. This is not the expected behavior according to the phase diagram of zirconia (i.e., monoclinic phase is the stable phase at low temperatures). The presence of the tetragonal phase at low temperatures can be attributed to several factors such as chemical effects, (the presence of anionic impurities) (Srinivasan et al., 1990 and Tani et al., 1982) structural similarities between the tetragonal phase and the precursor amorphous phase (Osendi et al., 1985; Tani, 1982 and Livage, 1968) as well as particle size effects based on the lower surface energy in the tetragonal phase compared to the monoclinic phase (Garvie, 1978; Osendi et al., 1985 and Tani 1982). The transformation of the metastable tetragonal form into the monoclinic form is generally complete by 650-700 °C.

Table 3.3 Crystal system of zirconia.

Crystal system	Unit cell shape
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$

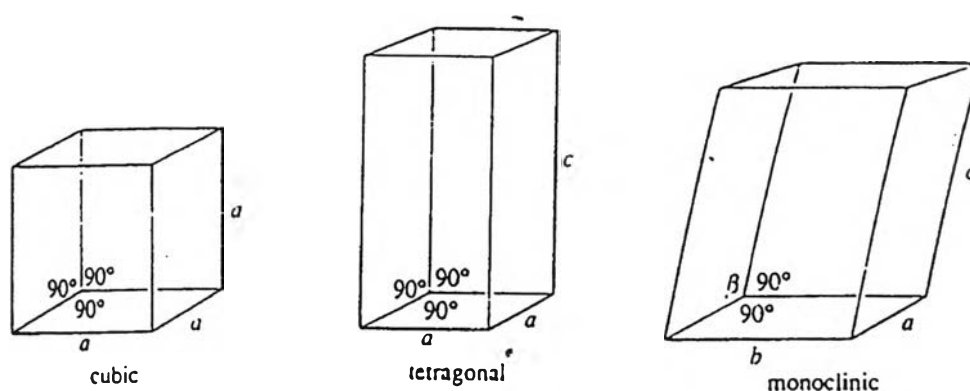


Figure 3.1 The unit cells of the crystal systems. (West, 1997)

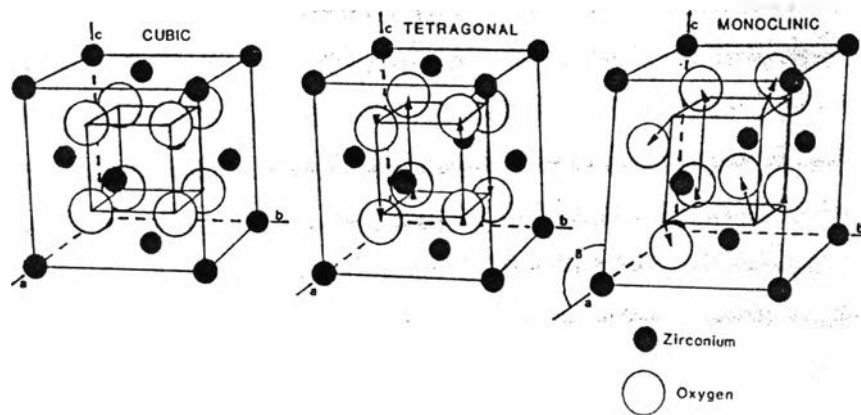


Figure 3.2 Crystal structure of cubic, tetragonal and monoclinic zirconia. (Heuer, 1987)

3.7 Nanotechnology (C.N.R. Rao *et.al*, 2004)

What is the history of nanotechnology?

The scientific community generally attributes the first acknowledgement of the importance of the nanoscale range to the brilliant Nobel Laureate physicist Richard Feynman in his famous 1959 lecture “There's Plenty of Room at the Bottom” in which he first proposed that the properties of materials and devices at the nanometer range would present future opportunities. The term reached greater public awareness in 1986 with the publication of “Engines of Creation: The Coming Era of Nanotechnology” by Eric Drexler.

Nanotechnology is a catch-all phrase for materials and devices that operate at the nanoscale. In the metric system of measurement, “Nano” equals a billionth and therefore a nanometer is one-billionth of a meter. References to nano materials, nanoelectronics, nano devices and nanopowders simply mean the material or activity can be measured in nanometers. To appreciate the size, a human red blood cell is over 2,000 nanometers long, virtually outside the nanoscale range.

Recently, government and private institutions have devoted substantial research into finding potential valuable uses at this scale, as discussed below.

How are nanotechnologies used today?

Despite views that nanotechnology is a far-fetched idea with no near-term applications, nanotechnology has already established a beachhead in several industries. The majority of nanotechnologies commercially used today are based on nano-sized particles. For example, nanoscale ZnO has been used for its UV absorbing properties to create sunscreen. The particles' small size makes them invisible to the naked eye, so the lotion is clear. At American Elements, we produce nanoscale oxides for a wide variety of applications. For example, the small particle size and inherent antimicrobial properties of our Z-MITE™ Zinc Oxide nanoparticles are utilized in bacteria-resistant fabrics and surfaces. For detailed product information on the uses and applications of Z-MITE™.

Nanoparticles have also made a breakthrough in the clothing industry in Eddie Bauer's stain-resistant Nano Care™ khakis. Small whisker-like particles are used to coat the surface fibers of the fabric, creating a stain-repelling surface. Healthcare companies are now marketing antimicrobial bandages coated with silver nanocrystals. Meanwhile, silver nanoparticles on the surfaces of many new refrigerators, air conditioners, and laundry machines act as antibacterial and antifungal agents.

Semiconductor particles, or quantum dots, are currently being manufactured. These fluorescent nanoparticles are being used by biologists to stain and label cellular components. By changing the size of the quantum dot the color emitted can be controlled. With a single light source, one can see the entire range of visible colors, an advantage over traditional organic dyes.

Nanocomposites are also seeing commercial use. Plastic nanocomposites are used for strong, lighter, and rust-proof car components. Toyota recently began using nanocomposites in bumpers that makes them 60% lighter and twice as resistant to denting and scratching. The biomedical field is manufacturing artificial bone composites from nanocrystalline calcium phosphates. These composites are made of the same mineral as natural bone, yet have strength in compression equal to stainless steel.

We have long produced nanoscale materials for certain unique applications, such as those discussed above. For a given amount of material, as particle size decreases, surface area increases. Our nanoscale powders have extremely high surface area, and have found additional uses in applications such as catalysts for automotive catalytic converters, where surface areas on our materials can reach over 100 m² /g

What is the future of nanotechnology?

Nanotechnology is expected to have an impact on nearly every industry. The U.S. National Science Foundation has predicted that the global market for nanotechnologies will reach \$1 trillion or more within 20 years. The research community is actively pursuing hundreds of applications in nanomaterials, nanoelectronics, and bionanotechnology. Most near term (1-5 years) applications of nanotechnology are in the form of nanomaterials. These include materials such as lighter and stronger nanocomposites, antibacterial nanoparticles, and nanostructured catalysts. Nanodevices and nanoelectronics are farther off, perhaps 5-15 years, and will have applications in medical treatments and diagnostics, faster computers, and in sensors.

We are actively involved in pursuing promising research to develop equipment and procedures to manipulate single atoms or molecules with the goal of establishing a new class of man-made atomic structures constructed one molecule at a time. In addition, we support the industrial and academic research efforts by supplying the ultra-pure, advanced materials required to perform nanotechnology research.

What are the safety, hazard and public policy issues with nanotechnology?

Numerous articles have recently been published warning of the dangers presented by unregulated nanotechnologies. The most fantastic of which is the threat of Gray Goo, a hypothesized substance resulting from the runaway dissolution of the earth by self-replicating nanobots. While many of these concerns seem less science than science fiction, the very scale range of these materials do present safety and environmental issues that should be addressed responsibly by industry at least in the

same manner as fine particulate materials are currently handled under existing health and safety guidelines.

The term nanotechnology is employed to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials, with at least one dimension in the nanometer range ($1 \text{ nm} = 10^{-9} \text{ m}$). In Table 2.5.1, we list typical nanomaterials of different dimensions. Properties of materials of nanometric dimensions are significantly different from those of atoms as well as those of bulk materials. Suitable control of the properties of nanometer-scale structures can lead to new science as well as new devices and technologies. The underlying theme of nanotechnology is miniaturization.

Table 3.4 Examples of nanomaterials.

	Size (approx.)	Materials
Nanocrystals and clusters (quantum dots)	diam. 1-10 nm	Metals, semiconductors, magnetic materials
Other nanoparticles	diam. 1-100 nm	Ceramic oxides
Nanowires	diam. 1-100 nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	diam. 1-100 nm	Carbon, layered metal chalcogenides
Nanoporous solids	pore diam. 0.5-10 nm	Zeolites, phosphates etc.
2-Dimensional arrays (of nano particles)	several nm ² - μm^2	Metals, semiconductors, magnetic materials
Surfaces and thin films	thickness 1-1000 nm	A variety of materials
3-Dimensional structures (superlattices)	several nm in the three dimensions	Metals, semiconductors, magnetic materials

There has been an explosive growth of nanoscience and technology in the last few years, primarily because of the availability of new strategies for the synthesis of nanomaterials and new tools for characterization and manipulation.

Table 3.5 Methods of synthesis and investigation of nanomaterials.

Scale (approx.)	Synthetic Method	Structural Tool	Theory and simulation
0.1 to ~ 10 nm	Covalent synthesis	Vibrational spectroscopy NMR Diffraction methods	Electronic structure
<1 to ~ 100 nm	Techniques of self-assembly	Scanning probe microscopies	Molecular dynamics and mechanics
100 nm to ~ 1 μm	Processing, modifications	SEM, TEM	Coarse-grained model etc.