IMPORTANCE & APPLICATIONS OF NANOTECHNOLOGY

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Catalytic Properties of Nanomaterials and Factors Affecting it

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Abstract

This chapter, Nanomaterial, especially metal nanoparticles, have unique catalytic properties and are widely used in the preparation of nanocatalysts; these nanocatalysts are used in many chemical reactions to increase the reaction rate and product efficiency. With the production of nanocatalysts on an industrial scale, we can expect a great change in the country's industries, especially in the oil, petrochemical and pharmaceutical industries. This chapter reviews the catalytic properties of nanomaterials from a new perspective. First, the reasons for the catalytic properties of nanomaterials are investigated and then the effect of factors such as nanoparticle size, nanoparticle shape, distribution, and substrate preparation of nanoparticles on their catalytic properties are explained.

Keywords: Nanomaterial; Petrochemical; Catalytic properties; Nanoparticle size.

Introduction

Today, catalysts are widely used in the production of chemicals, drugs, etc. If we want to show the importance of catalysts, gasoline used in cars is a good example. Gasoline requires at least ten different catalysts in the conversion route from crude oil. Many other products also require the use of catalysts. It is estimated that more than 20% of the GDP of industrialized countries depends on catalysts. Today, nanotechnology has made great efforts to incorporate nanomaterials into catalysts, which has been a successful approach. Due to their importance, nanocatalysts are one of the most important areas of nanotechnology research, especially nanochemistry, and the number of articles and books published about them is increasing (Figure 1). Nanomaterial's have unique catalytic properties. Today, nanomaterials are widely used in the preparation of nanocatalysts [1-8]. Many important reactions are catalyzed by nanomaterials, and these nanocatalysts dramatically increase productivity. These reactions include: Oxidation of carbon monoxide and its conversion to carbon dioxide, decomposition of toxic gases such as nitrogen dioxide, oxidation of methanol and other fuels in fuel cells, and cracking and reactive reactions. Which are very important in the petrochemical industry. At present, many petroleum and chemical processes use economic catalysts to improve selectivity and reduce waste and pollution. For example, the hydrogenation reaction is an important process to produce valuable products in the petrochemical industry, products that are used in everyday life. Using this process, materials with new structure and different chemical and physical properties are created. One of the important uses of the hydrogenation process is to improve the quality of gasoline through the selective hydrogenation of diolphins in various oil fields. The hydrogenation process is exothermic and takes place at low speed even in the absence of a catalyst, even at high temperatures. The use of nanocatalysts containing metal nanoparticles such as palladium on substrates such as carbon nanotubes greatly speeds up this reaction. Methanol as a liquid fuel has a very high energy density and can be produced from living biomass and easily stored in direct methanol fuel cells and used as an available energy source for transportation applications. Metal nanoparticles are used for methanol oxidation due to their very high surface-to-volume ratio and electrocatalytic activity, especially platinum, which has been shown to be very effective in methanol oxidation and significantly increases the electrochemical oxidation of methanol. Research shows that the use of platinum in fuel cells is often necessary and the best option. One of the most common methods is to use platinum as nanoparticles with substrates such as carbon nanotubes (single-walled, multi-walled) or polymers [9-15].

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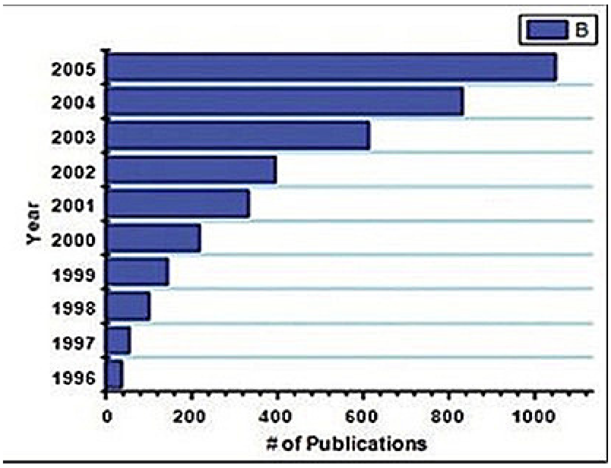

Figure 1: Statistics on the number of publications in the field of nanocatalysts from 1995 to 2005 [1].

The concept of studying the properties of a nanocatalyst

Basically, when we talk about the properties of a nanocatalyst, we mean that either the activity of the catalyst has been studied, or the selectivity of the nanocatalyst has been studied, or research has been done to understand the mechanism of action of the nanocatalyst. Among the mentioned cases, most research has been done on the activity of nanocatalyst. All studies have been performed to enhance the catalytic activity of nanocatalysts [9,16-20].

Reasons for catalytic properties in nanomaterials

When materials are taken to the nanoscale, many of their properties change, such as electrical, optical, magnetic, etc. The emergence of the following three properties is one of these changes: very small size, very high surface-to-volume ratio, and increasing the number of atoms on the surface. These last three factors are the most important reasons for the emergence of catalytic properties in nanomaterials [9,21-24]. Basically, when particles become very small (nanoscale), due to the very high curvature they find, they have many atoms on their surface, which are very weakly bonded to the lattice atoms of the lattice. Therefore, these particles have very high surface energy and are highly active, and it is said that surface atoms are in a state of physical instability and are chemically active, and are prone to perform many chemical reactions. It can be said that the main and determining reason for the emergence of catalytic properties in nanomaterials is their very high surface-to-volume ratio. The higher this ratio, the higher the catalytic properties in nanomaterials due to the increase in surface energy. In principle, the reason for these changes is due to changes in the electronic structure of materials, which can be justified by quantum mechanics. When the particle size becomes too small, the density of the capacitance band states changes and a set of discrete levels is observed. Eventually, as the particles shrink, they become so large that the surface of the particles is spaced by an order of magnitude electron wavelength. In this situation, energy levels can be modeled by the quantum mechanical behavior of a particle in a box. This effect is called the quantum size effect. The emergence of new electron properties can be understood in terms of Heisenberg's uncertainty principle, which states that the more spatially an electron is trapped, the wider its range of motion. In semiconductors, the presence of oxyton has a large effect on the electronic properties. In a massive semiconductor with a photon whose energy is greater than the energy gap of matter, a pair of bound electron-hole pairs called oxytons can be produced. The photon removes the electron from the capacitance band and transfers it to the conduction band. As a result, a hole is created in the capacitance bar that is equivalent to one positive electron or charge. Due to the attraction between the positive hole and the negative electron, a pair of exaction bonds travels across the lattice, which greatly affects the electron and optical properties. If the radius of the nanoparticle is smaller than the electron-hole radius, the range of motion of the exciton is limited. As a result, oxytone uptake is observed and a shift towards lower wavelengths (blue shift, hypochromic effect) is observed. Since the electronic structure of nanoparticles depends on the particle size, their ability to react with other samples also depends on their size [1]. These changes and their effect are very noticeable. For example, one of the metals that behaves very differently in mass and nanoscale is gold. Gold has a very low catalytic properties in the solid state and is one of the most inactive metals, but when taken to the nanoscale it exhibits very high catalytic activity and, interestingly, is one of the most common intermediate metals used in the synthesis of nanocatalysts. In the synthesis of catalysts used for the oxidation reaction of carbon monoxide and its conversion to carbon dioxide [6]. Figures 2 and 3 show the effect of nanoparticle distribution on catalytic properties.

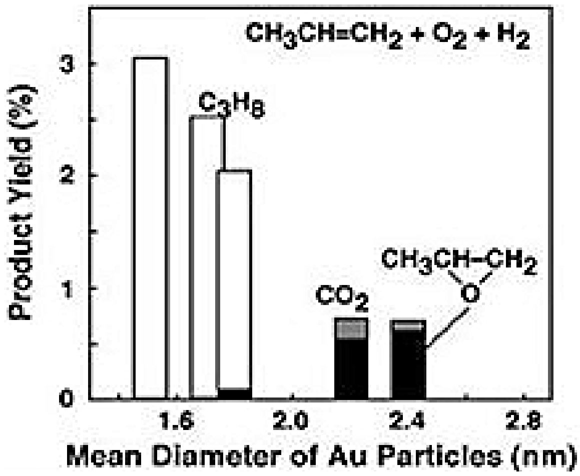

Figure 2: The effect of gold nanoparticle size on catalytic activity in the propene epoxidation reaction has been investigated, which shows that by reducing the size of gold nanoparticles, the yield of the product increases [9].

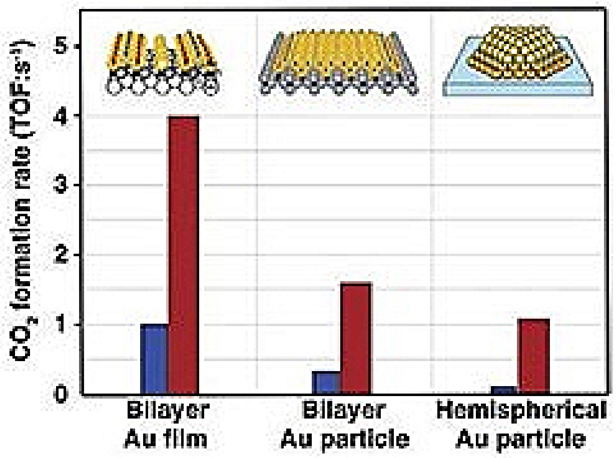

Figure 3: The effect of nanoparticle distribution on the catalytic property in the oxidation reaction of carbon monoxide and its conversion to carbon dioxide (TOF in the vertical part is a standard diagram of catalyst activity) [9].

Factors affecting the catalytic properties of nanomaterial's

Factors affecting the catalytic properties of nanomaterial's are:

1. The size of the nanoparticles.
2. The shape of the nanoparticles.
3. The distribution of the nanoparticles.
4. The preparation medium of the nanoparticles.
5. The reaction conditions [25].

Nanoparticle size

In most cases, the smaller the nanoparticle size, the greater the catalytic properties (Figure 2), but in some cases the catalytic properties do not increase with decreasing nanoparticle size. In the oxidation reaction of carbon monoxide using ruthenium nanoparticles in PVP substrate (PolyN-vinyl-2-pyrolidone), it has been shown that when ruthenium nanoparticles are 6nm in size, their catalytic activity is eight times that of 2nm [4,26-27]. It has also been proven that when gold nanoparticles with dimensions less than 5 nm are used, they show the highest activity and selectivity [2]. Intermediate nanoparticles can have sizes in the range of less than 1 100 nm, but their greatest catalytic activity is observed when their size is around 1-10 nm.

Nanoparticles distributed

The spatial distribution of nanoparticles can also affect their catalytic properties. The higher the spatial distribution of the nanoparticles, the more catalytic properties increase as the number of surface atoms becomes available (Figure 3). In addition, it has been shown that the narrower the nanoparticle size distribution, the greater the catalyst activity.

The shape of nanoparticles

Particles are said to have large curvatures when at the nanoscale, and their surface atoms are unstable. This effect is especially pronounced in non-spherical particles, particles that have many edge and corner locations, such as quadrilaterals, octagons, and cubes. In this case, as the surface-to-volume ratio increases significantly, the nanomaterial's show more catalytic properties (Figure 4); this has been confirmed in most research studies using the X-ray diffraction technique and the observed efficiencies. It is worth mentioning that in the synthesis of colloidal nanoparticles by Bradley method (the most common method of synthesis of colloidal nanoparticles) by controlling the concentration ratio of nanoparticles to stabilizers or using different reluctant depending on the reaction, the desired shape can be synthesized [9,28].

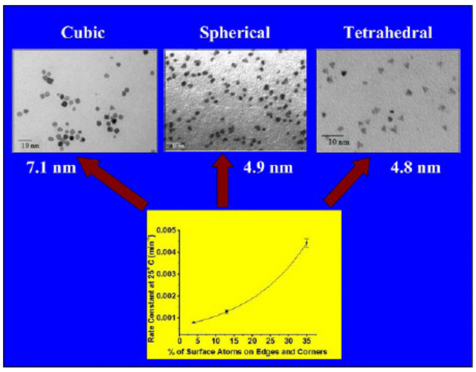

Figure 4: Relationship between angular and lateral surface atom fractions and catalytic activity of Pt nanoparticles in cubic, spherical, and quadrilateral structures [8].

Nanoparticle preparation bed

Materials at the nanoscale have very high surface energy and tend to stick to each other. In most cases, nanoparticles are deposited on a substrate in different ways and then used in the reaction; The reason for this is that the substrate prevents the nanoparticles from accumulating and becoming so-called agglomerated, because when the nanoparticles accumulate, they become out of the nanoparticle state. The substrate traps nanoparticles on its surface through electrostatic and spatial interactions, reduces their surface energy, prevents their accumulation, and also stabilizes them. The effect that the substrate has on the catalytic properties of nanoparticles is different for different nanomaterial's and does not have a specific process and depending on the type of nanomaterial and the type of substrate used, the catalytic properties can be increased or decreased (Figure 5) [9]. It has been shown that when ligand is used as a substrate in the preparation of nanocatalysts, the catalytic property decreases in most cases [5] and when it is used as a substrate, the catalytic property increases in most cases. Various substrates - including polymers, dendrites, metal oxides, carbon nanotubes, and some ligands - are used to make nanomaterial's, but polymer substrates are more common than others. The formation of nanoparticles in polymer substrates has been shown to increase the control of nanoparticles and can determine the state of nanoparticles on the surface, and in most cases increases the catalytic properties of nanomaterial's. Among polymeric substrates, PVP (PolyN-vinyl-2-pyrolidone) is the most commonly used substrate and is an inexpensive, linear polymer on which nanoparticles are uniformly dispersed [9].

Reaction conditions

Daniela de L. Martins et al. Heck reaction (reaction between an aryl halide with an allyl) between iodine benzene and styrene polymer by palladium nanoparticles in a Pt-PVP polyethylene substrate once under normal heating and once using They performed microwaves and observed that catalytic activity as well as selectivity to normal conditions (reflux) improved significantly when the reaction was performed under microwave conditions. The reason for this is that palladium nanoparticles absorb microwave waves and by absorbing these waves, heat transfer is accelerated and catalyst activity is increased [3].

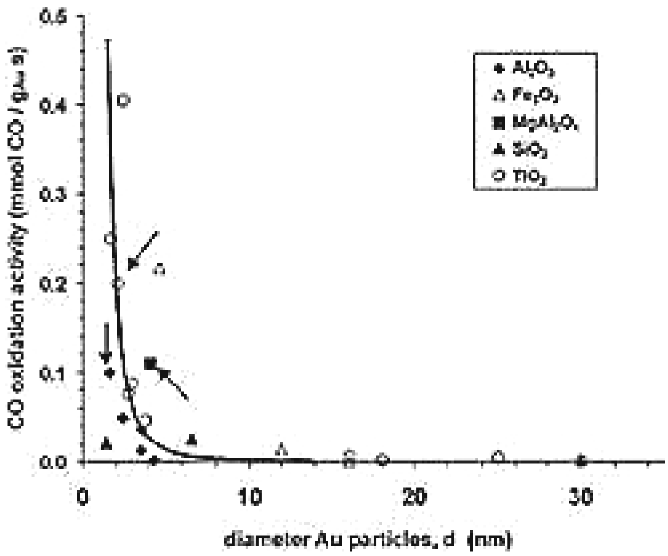

Figure 5: The effect of different oxide substrates on the catalyst activity of gold nanoparticles has been investigated and it is observed that in TiO2 substrate, gold shows the most catalytic properties [9].

Conclusion

In this study, it was shown that the main reason for the catalytic properties of nanomaterials is their high surface-to-volume ratio. This change is due to a change in the electron properties and the fact that reducing the size of nanoparticles does not always increase their catalytic properties, and other factors, such as the shape and substrate used, are very effective. If these nanocatalysts can be produced on an industrial scale, we can see a huge change in industries, especially the oil and petrochemical industries.

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