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Chapter 3

Supported Gold Nanoparticles as Promising Catalysts

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Abstract

In recent times, gold nanoparticles (AuNPs) either in the form of colloids or as supported nanoparticles are being extensively used as efficient redox catalyst materials. Catalysis particularly using supported gold nanoparticles (AuNPs) has attracted immense research interest due to their unique properties and greater potentiality that is directly related to their particle size. The primary objective of this chapter is to provide comprehensive overview about gold metal nanoparticles (AuNPs) and their application as promising catalysts. This chapter contains six sections in total. Section 1 starts with a general introduction, recent progress, and brief summary of the application of supported AuNPs as promising catalysts for different applications. Section 2 briefs the properties and stability of gold nanoparticles. Section 3 reviews the preparation methods of supported AuNPs for a wide range of catalytic applications. Section 4 describes briefly some of the most commonly reported supported AuNPs for different applications. Section 5 concentrates on our own results related to the application of supported AuNPs in heterogeneous catalysis. In this section, the oxidation of cyclohexane (CH) and benzyl alcohol (BA) to adipic acid (AA), benzaldehyde (BAl), and ammoxidation of 2-methylpyrazine to 2-cyanopyrazine are discussed. Finally, Section 6 describes, main points and outlook are summarized.

Keywords: gold nanoparticles, gold catalysts, benzyl alcohol oxidation, cyclohexane oxidation, 2-methylpyrazine ammoxidation

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1. Introduction

Gold (Au) has traditionally been considered to be catalytically inactive, like its other group VIII counterparts, Cu and Ag. The catalytic characteristics of these metals may be determined by the extent of its d-band vacancy [1]; in the cases of Au, Cu, and Ag, is completely occupied. Unlike Au, however, Cu and Ag are characterized by comparatively modest ionization potentials, with the result that Cu and Ag are able to shed electrons, thereby creating d-band holes and, therefore, becoming catalytically active. This means that Cu may, in chemistry applications, be utilized in the synthesis of methanol, while Ag may similarly be utilized in the synthesis of ethylene oxide. Au, on the other hand, is characterized by a comparatively high degree of ionization and, therefore, has low molecular attraction [2]. Early empirical research concerning surface characteristics and associated calculation of density functions shows that, for Au, dissociative adsorption of H_2 and O_2 does not take place at temperatures lower than 473 K, and so it would not be expected to exhibit catalytic activity in respect of hydrogenation and oxidation reactions [3]. This is why heretofore Au has not been of interest in terms of catalysis. Bond et al. [4], however, found in the late 1979s that alkene and alkyne hydrogenation by means of an Au/SiO_2 catalyst delivered results that merited further exploration, which when carried out obtained oxidation utilizing supported Au catalysts. This research suggested for the first time that Au may exhibit enhanced activity when in small (<5 nm) dispersed particulate form. Further research conducted in the 1980s by Hutchings et al. [5] and Haruta et al. [6] yielded two discoveries that significantly changed the opinions of researchers about Au. Such newly discovered characteristics suggest that it may indeed offer good potential in terms of heterogeneous catalytic applications. The specifics of these discoveries concerned the use of Au as a superior catalyst in respect of acetylene hydrochlorination [6], and supported gold nanoparticles (AuNPs) exhibiting enhanced activity in low-temperature CO oxidation conditions [6].

The importance on the usage of gold catalysts is also clearly evidenced from an explosion in the number of academic publications dealing with AuNPs in recent times. In other words, the number of publications appeared in the 1980s is just <100, which is remarkably increased to almost 2000 publications until 2015 (**Figure 1**). In the year 2016 alone (till March), there have been over 800 publications, which undeniably indicate extreme importance of gold in catalysis. In addition, some books and several comprehensive reviews have also been published on this topic. Besides, patents activity was not much before the 1990s but has increased noticeably since then and is now fairly steady at about 500 patents per annum.

Furthermore, conventional knowledge was that Au exhibits the lowest degree of reactivity among other metals, with this opinion, it is acquiring the reputation for being the most "noble" [7]. This very low reactivity arises as a result of its entirely occupied 5d valence shell and its relatively high first ionization potential value. In consequence of this, Au catalysts exhibit poor chemisorption characteristics [8]. Such a conventional perception, however, has not discouraged researchers from further investigating Au in the context of developing new heterogeneous catalysts. Surprisingly, the results achieved from such a research have lately seen exponential growth. The basis for such a recent interest has, however, been largely em-

pirical, centered typically on the oxidation of CO at low temperatures [6]. Consequently, the actual processes that generate the observed effects are a matter of heated debate. To achieve some resolution in this regard, Goodman et al. [9] examined the size of Au clusters in model catalysts, focusing on the influence of quantum size as a means by which the commencement of catalytic activity and the band gap that becomes apparent in the clusters may be explained (**Figure 2(a)**). Subsequent research indicated that the bilayered morphology of the electron-laden Au cluster enables the dissociation of O_2, and that these effects are considered to be determinants of enhanced reactivity [10]. Bokhoven [11] additionally suggested that alteration of the electron structure resulting from Au-Au bond contraction in nanoparticles could also explain the observed enhanced reactivity. Yet more recent research has suggested that correlations may exist between the active site and the low-coordinated Au atoms (**Figure 2(b)**) [12], particularly at corner sites [13]. Varying reactions produced using Au catalysts have also been explored by Mason [14] and Bond [15]; as a result of this, they postulate that the active site is situated at the Au/support edge junction and that cationic Au is present (**Figure 2(c)**). Spectroscopic measurements obtained using IR techniques in respect of cationic Au and zerovalent Au^0 being present during CO oxidation suggest that the active site is made up of Au^0 and Au^+ species at the junction outer limit (**Figure 2(e)**). Additionally, other research suggests that Au nanoparticles lodge themselves within defective areas such as those created by the presence of O_2 holes (F centers), the effect of which is to assign electron density to the AuNPs or atoms (**Figure 2(d)**). The resultant negative charge is said to be responsible for the enhancement of catalytic activity in respect of low-temperature CO oxidation through enabling the adsorption of CO and the dissociation of O_2.

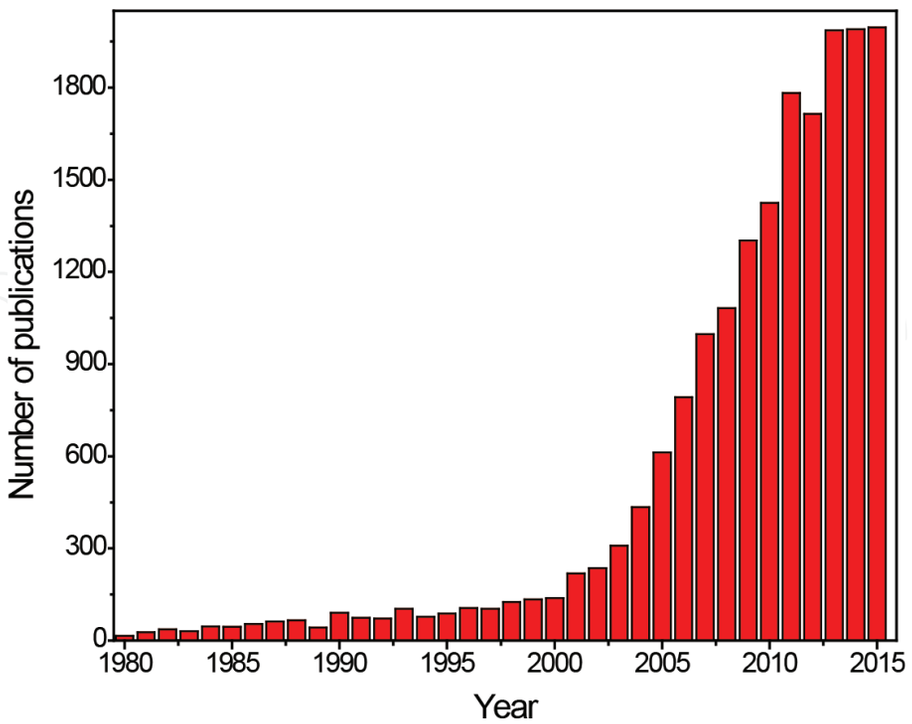


Figure 1. Publications on gold catalysis in the academic literature (source: SciFinder Scholar).

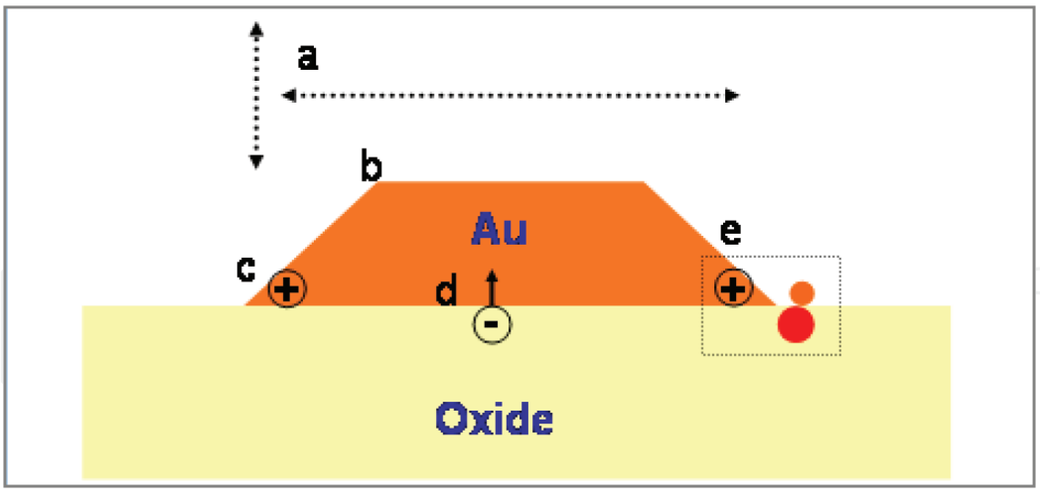


Figure 2. Models proposed for explaining the catalytic activity of Au/oxide catalysts: (a) cluster size effects, (b) low-coordinated Au atoms, (c) cationic gold, (d) electron transfer from F centers of the support to the Au particle, and (e) ensembles of Au^0, Au^+, and support-bound OH groups.

2. Properties and stability of gold nanoparticles

2.1. Physical, chemical, and optical properties of AuNPs

The characteristics of Au in terms of its noncorrosive and nonoxidation properties have made it an attractive – perhaps the most attractive – raw material in the production of jewelry. It is known as a "late transition" metal that belongs to group VIII in the periodic table, together with Cu and Ag. Its atomic mass is 196.97 amu, its M.P. is 1064°C, and its density is 19.6 g/cm^3. The electronic attraction of Au exceeds that of O_2 and the redox potential of the Au^+/Au(0) coupling is +1.5 V. Au's characteristic yellow coloring is the result of optical absorption in the visible portion of the electromagnetic spectrum, which arises as a result of the relatively low band gap apparent between the 5d band and the Fermi level [16]. Au is chemically characterized by a broad variety of oxidation states. Both the +1 and +3 states are usual, although this characteristic differs from other similar metals. Au's +5 state may also be found in $[AuF_6]^-$. There are three monohalides in Au, although fluoride is absent as this ion exhibits electronegativity that is too prominent for stable bonding to take place. The high degree of electronegativity present in Au also produces another feature that is unique to the chemical composition of Au; the presence of the auride anion (Au^-) is also known as the compound CsAu since the late 1970s [17], and for this reason Au does not exhibit direct reactions in relation to other electronegative elements such as O_2 and sulfur, and may only be dissolved by aquaregia (HCl:HNO_3 = 3:1 v/v). AuNPs' optical characteristics are also strongly dependent upon the dimensions and shape of the Au nanoparticles. An unusual characteristic pertaining to colloidal AuNPs is the concentration of their coloring. In large masses, Au is yellow, an effect resulting from reduced reflectivity of blue light in reflected light conditions, whereas Au in thin-film form appears to be blue in color. This blue coloring progressively changes to orange as the particle size reduces; this effect is caused by

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changes occurring in what is known as its surface plasmon resonance (SPR). These characteristics in Au are particularly dependent on the overall oscillation that takes place within the conduction electrons in consequence of the influence exerted by electromagnetic radiation – an effect termed surface plasmon resonance, SPR or localized surface plasmon resonance [18].

2.2. Stability of gold nanoparticles

AuNPs' stability has become a significant focus of attention during the past 20 years as a result of growing appreciation that AuNPs' catalytic activity is significantly dependent upon AuNPs' dimensions. Colloidal nanoparticles are usually thermodynamically unstable, and hence do not possess good long-term stability primarily as a result of agglomeration. This is especially the case with AuNPs due to their inherent particulate attraction, and so establishing and maintaining stability is of particular importance. Long-term agglomeration prevention may be achieved by surface support techniques or through co-ordinating with ligands/anionic species. Two basic approaches are available for achieving stability in colloidal AuNPs through utilization of ligands/anionic species. These are known as steric and electrostatic stabilization [19]. The steric approach is based on the addition of organic moieties to the system to be adsorbed onto the particle surface. It works by ensuring that individual Au nanoparticles are not permitted to come into close proximity. The organic moieties used for this purpose are usually polymers, e.g., polyvinyl alcohol (PVA) [20]. The electrostatic, or charge stabilization, approach makes use of interactivity between anionic species such as halides or polyoxoanions and co-ordinatively unsaturated atoms present at the surface of the metal, the outcome of which is the creation of a scattered dual electrical layer that facilitates coulombic repulsion among the Au nanoparticles. These approaches both have individual advantages and drawbacks: the steric approach is relatively straightforward, requiring the sole addition of polymeric stabilizers; however, in some scenarios stabilizers can be problematic as they exert influence on the dimensions and shape of the created colloidal MNPs. Additionally, the presence of stabilizers may passivate the surfaces of the nanoparticles, thereby engendering

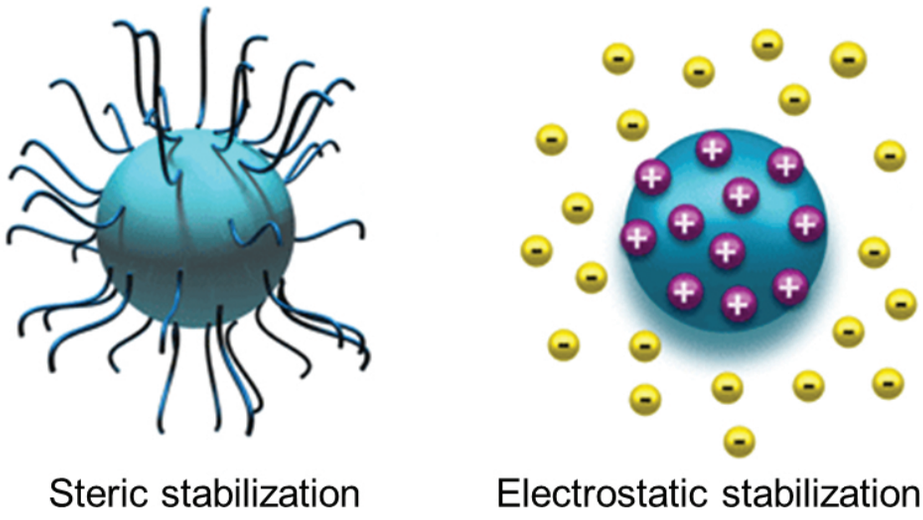


Figure 3. Schematic representation of colloidal AuNPs system stabilization modes.

serious and sudden catalytic inactivity. The electrostatic approach is advantageous in that it can achieve stabilization through simple adjustment of the extent to which ions are concentrated – a technique which is both reversible and economical. The contrasting interactivity achieved by these approaches is illustrated in **Figure 3**.

3. Synthesis and characterization of gold nanoparticles

3.1. Synthesis of gold nanoparticles

AuNPs may be defined according to two broad classifications, known as unsupported particles and supported particles as are illustrated in **Figure 4**. Some selected approaches are explained in detail in the following paragraphs.

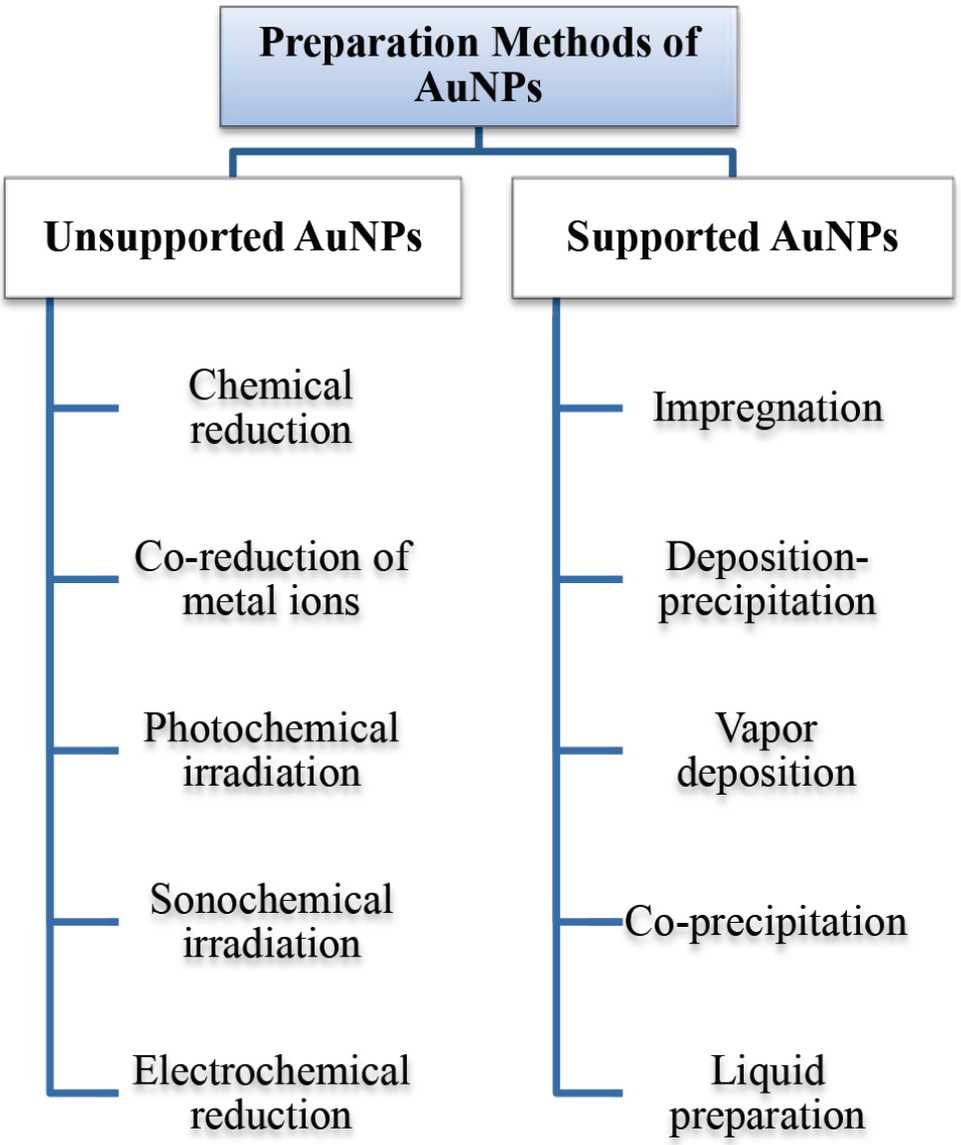


Figure 4. Preparation techniques for unsupported and supported gold nanoparticles.

3.1.1. Unsupported AuNPs

3.1.1.1. Chemical reduction

The production of AuNPs by means of chemical processes involves the reduction of gold ions either by the use of chemical reductants or by the use of externally sourced energy. Turkevich [21] first succeeded in achieving Au suspension through a single-step reduction process of [$AuCl_4^-$] with sodium citrate being used as the reducing agent [22]. It is also possible to use more than one reductant whenever necessary. Other examples of chemical reductants include molecular hydrogen, ascorbic acid, various forms of alcohol, tannic acid, hydrazine, citrate, and so on. Externally sourced energy may be in the forms of photoenergy such as ultraviolet and visible light, electricity, and heat or sonochemical energy. Using these approaches, nanoparticles with closely similar dimensions may be produced and colloidal dispersions may be achieved. However, it is necessary to use a stabilizer, and this is particularly crucial in the case of Au. There are a number of advantages of using chemical reduction techniques to synthesize AuNPs. Some of the most important advantages are as follows.

- Simplicity of process.
- Easy to produce metal colloids that are stable and may be easily isolated in dry powder form.
- The nanoparticles created are of closely similar dimensions.
- Readily applicable to multigram synthesis and scaling-up while delivering reproducible results.

3.1.1.2. Coreduction of mixed ions

This technique bears comparison with the chemical reduction technique, although this coreduction technique is primarily applicable to the production of bimetallic nanoparticles. Colloidal dispersion of bimetallic nanoparticles partially constituted of Au may be achieved by chemical means [23]. By these means, metal ions consisting of more than one metal are typically reduced using a reductant, for instance, citrate [24], with the dimensions of the bimetallic nanoparticles produced however depend upon the composition of the metal. In general, coreduction is the most straightforward means of producing bimetallic nanoparticles.

3.1.2. Supported AuNPs

3.1.2.1. Impregnation method

Impregnation is a widely used preparation method for the synthesis of heterogeneous bimetallic catalysts. The impregnation methodology, where the support is contacted with an aqueous metallic solution (one or more metals), which is then oven dried and calcined under suitable thermal conditions. Two types of impregnation methods can be used: (i) based on the volume of metallic solution with respect to the pore volume of support, namely incipient wetness and (ii) wet impregnation method using excess solvent. In the case of incipient

wetness, the active component solution volume is equal to the total pore volume of the support and in the case of the wet impregnation methodology the volume of solution can be much higher than the total pore volume of the support [25]. Temperature, time of heating, calcination temperature, and supporting material are some of the crucial conditions that control the characteristics of the final catalyst. Chemical reaction between the precursor solution and the metal support may occur during the calcination phase of the period, under particular conditions causing various active phase-support interactions. The advantage of this method is that highly dispersed metal particles loaded on the surface of metal oxides (as supports) can be obtained.

3.1.2.2. Deposition-precipitation method

Deposition-precipitation (DP) technique is one of the most successfully used methods to obtain high dispersion and homogeneous deposition of bimetallic particles on the surface of support. The DP method is used where the solution creates an insoluble form of supported active phase, and this in turn accumulates on the solution connected to the support. Strong precursor-support interactions are expected using this method which enhances the catalyst efficiency and stability of the catalyst. In this method the metal salt precursors are typically carried out of solution in the presence of a suspension of the support by increasing the pH value to obtain immediate precipitation of different metals. For instance, this method is a widely used methodology for creating precursors of highly active supported gold catalysts [26]. Hydroxides or carbonates are created using this methodology and they accumulate on the support [27].

3.1.2.3. Coprecipitation method

Generally metal ions are soluble in acidified aqueous solution and they precipitate as their hydroxides, oxyhydroxides, which upon calcination leads to the formation of suitable metal oxide phases. A mixed oxide in solid-solution form is generated by the coprecipitation of base metal cations. Coprecipitation of bivalent cations in the form of hydroxycarbonate, hydroxyl-chloride, or hydroxyl nitrate is generated by precipitating hydrotalcite of bivalent cations [28]. This process usually produces contamination of the precipitate in the final product and this is restricted through a complex process of washing.

3.1.2.4. Liquid preparation method

This method is the most ancient but widely used chemical method for the synthesis of nanoparticles by the reduction of bimetallic ions in solution. In this method, bimetallic ions are reduced by providing some extra energy and using the different type of chemical reductants. The provided energy is used to decompose the material, and usually, photoenergy, electricity, or thermal energy used. It is most frequent chemical method used for the production of stable bimetallic nanoparticles. The advantage of this method is the ability of controlling the size of the bimetallic nanoparticles. This process is normally operated at low temperature, automatically reducing the production costs of large amounts of bimetallic catalysts [29]. For instance, the synthesis of the colloidal bimetallic nanoparticles containing gold can be achieved

using this method. For instances, metal ions of bi- or trimetals can be reduced by a suitable reductant, e.g., citrate.

3.2. Characterization methods

A comprehensive knowledge of the chemical and physical properties of supported AuNPs as heterogeneous catalysts is needed to understand the nature of active sites, which in turn can help to find and tune the performance. It is essential to realize the catalytic behavior of these materials including deactivation phenomena in such a way that their performance can be further improved. More profound insights on the metal particle structure, size, shape, and catalytic properties of the materials can be gained through a range of methodologies that can be used to categorize them. A range of characterization techniques for identification and characterization of the gold catalysts are illustrated in **Figure 5**. These techniques can be used either individually or collectively applied to understand and analyze the properties of supported AuNPs. The data outlining the structural properties can be given by a range of methods such as X-ray diffraction, UV-vis and vibrational spectroscopies, and neutron and electron diffraction methods. The list of characterization methods and the information that can be obtained from these techniques is illustrated in **Figure 5**. X-ray fluorescence [XRF], atomic absorption spectroscopy [AAS], inductively coupled plasma [ICP], and energy-dispersive X-ray [EDX] are some of the other methods that can provide the elemental composition. The magnitude and morphology of the bimetallic catalysts can be better understood by utilizing a range of different kinds of microscopic methods [e.g., TEM and SEM]. The surface structure and composition of bimetallic catalysts can be achieved using spectroscopic methods [e.g., X-ray photoelectron [XPS], Raman spectroscopy.

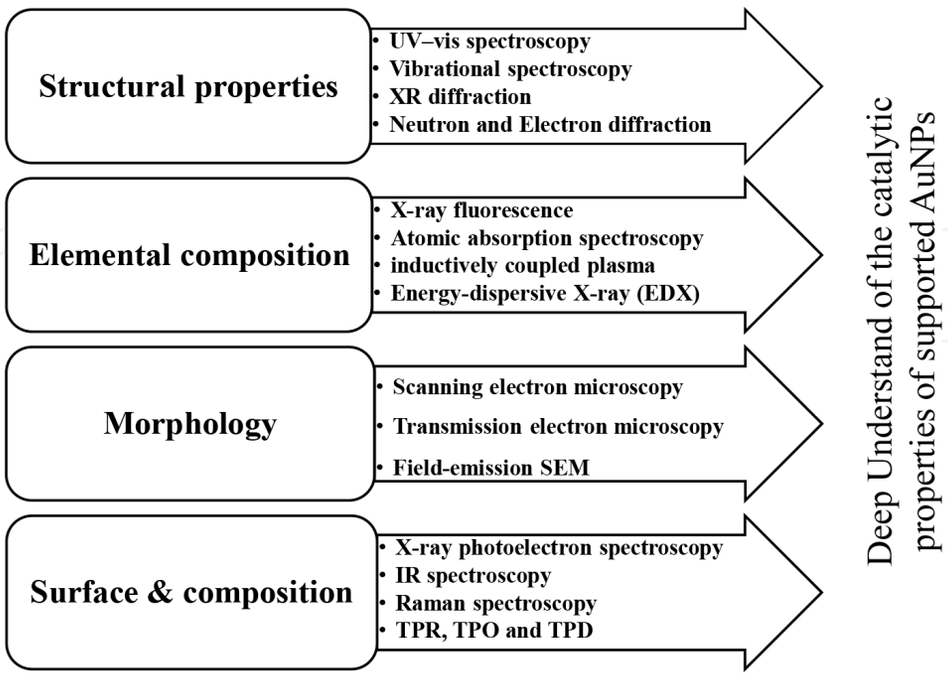


Figure 5. Some selected characterization methods of supported AuNPs' catalysts.

4. Factors affecting the catalytic activity of the gold catalysts

Particle size and shape, structure, composition, surface area, and porosity are found to be among the most important factors that affect the catalytic properties of supported AuNPs in different reactions. **Figure 6** represents the summary of these factors on the catalytic properties. Additionally, the effects of some other selected factors are also discussed in the following section.

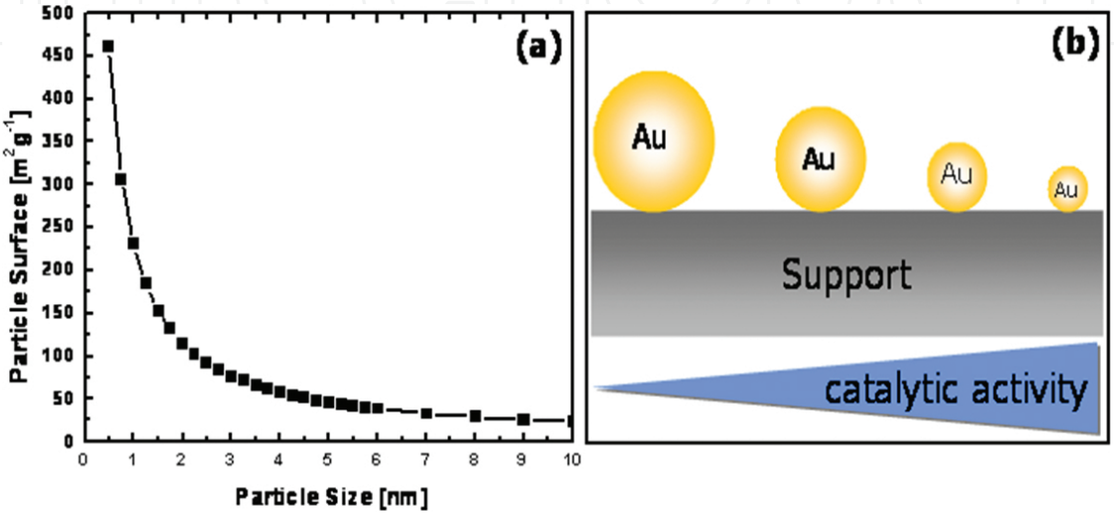


Figure 6. Relation between the size of AuNPs with their surface area (a) and catalytic activity (b).

4.1. Effect of particle size

An increase in the catalytic performance using metallic catalysts can be obtained by tuning the size of the metal particles. The effect of particle size on the catalytic activity and selectivity of supported metal nanoparticles were investigated extensively by Toshima et al. [30]. The surface area will normally increase with decreasing size of metal particles as the total surface area of metal particles is contrariwise proportional to the square of the diameter of nanoparticles. As shown in **Figure 7**, with decreasing size of particles there is an increase in catalytic activity [31]. Slower reactions are caused by continuously decreasing the size of the nanocatalysts whereas increasing the size of the catalyst will decrease the rate of reaction. There is a critical size of metal particle (usually 3 nm) in photochemical hydrogen generation using nanocatalysts of Pt and any size above or below will slow down the chemical reaction [32]. Lopez et al. discovered that particle size is a determining factor of catalyst performance [33].

4.2. Effect of preparation method

Existing research, for example [34], illustrates how the preparation method is influential in terms of the characteristics of supported Au catalysts. This is consequently influential on catalytic activity. A number of approaches [35] concerned with the preparation of Au catalysts have been described elsewhere in this thesis, a most widely used example being impregnation

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[36]. Impregnation involves the reduction of $HAuCl_4$ to AuNPs, after which it is impregnated onto the support. This approach is capable of delivering an Au average nanoparticle diameter in the order of 1–2 nm. This approach has a significant shortcoming in that chloride ions are apparent, having their origin at the Au precursor, for example, $HAuCl_4$. To prevent the chloride ions from becoming contaminated, a gas phase grafting approach that makes use of monodispersed colloidal AuNPs that have been subjected to stabilization by an appropriate polymer may be used [37]. This, however, results in the dimensions of the AuNPs becoming larger than is desirable – something in the order of 10 nm. There are other means of preparing Au catalysts that are characterized by high levels of activity, for instance, deposition-precipitation and coprecipitation being the examples of such a type. In these precipitation techniques, specifying an appropriate pH level is crucial. Au nanoparticle diameters of the order of 1–2 nm may be produced by these means. Whichever approach is adopted for preparing Au catalysts, the application of heat is of significance in respect of catalytic activity [38]. Existing research suggests that Au catalysts are typically calcined at moderate temperatures of 100–200°C (e.g., Au/TiO_2 [39] and Au/Fe_2O_3 [40], to preclude the occurrence of sintering and thereby enhance

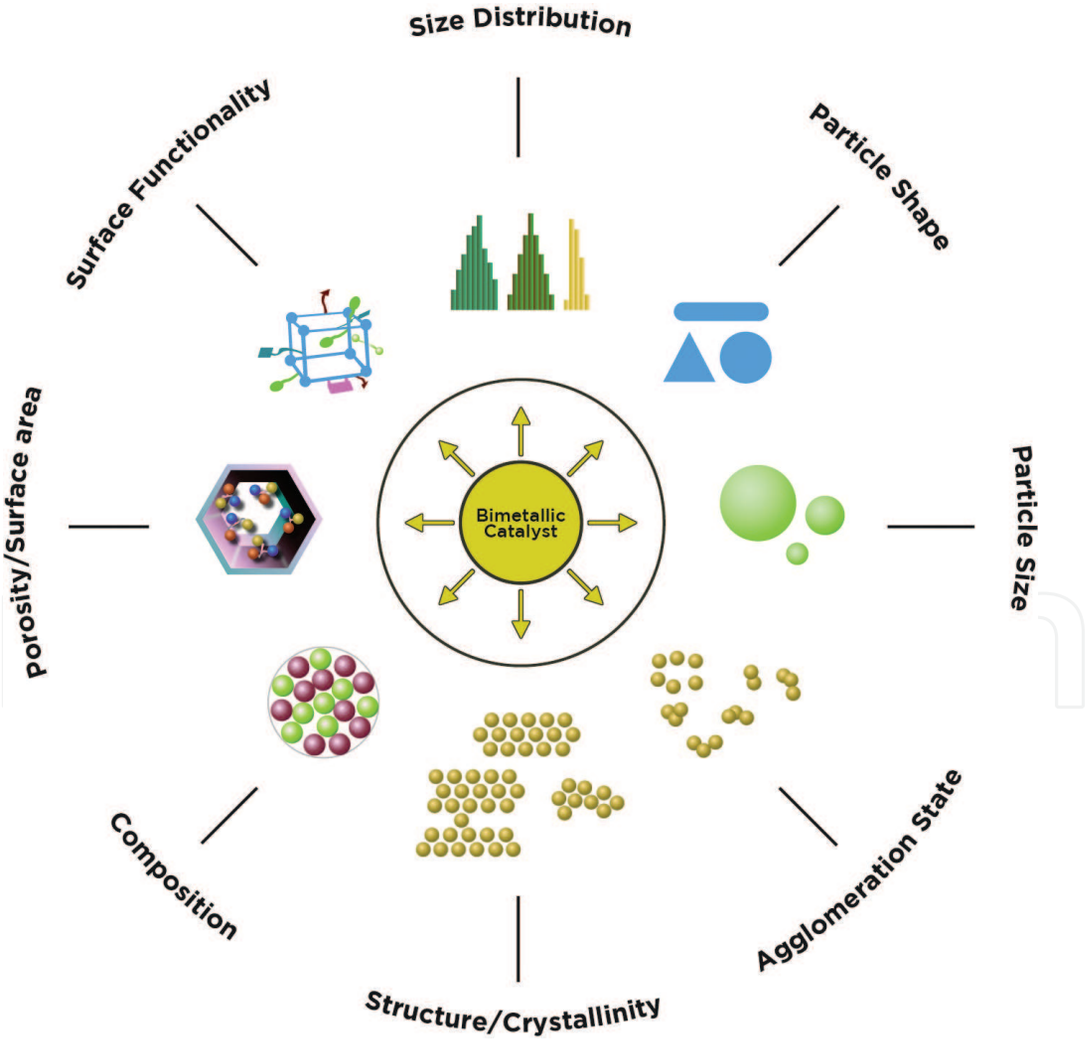


Figure 7. Factors affect the catalytic properties of bimetallic catalysts in different reactions.

the performance of these catalysts with respect to those subjected to higher temperature calcination.

4.3. Effect of support

Support enhances the thermal stability of the catalyst, reducing costs, and provides improved surface area characteristics, high dispersion of active component, etc. All these factors are necessary in the production of catalysts that are characterized by high activity and selectivity. Previous research also indicates that the nature of support and AuNPs' interactivity is influential on catalytic activity [41]. By way of illustration, CO oxidation by means of pure Au particles or pure titania exhibited no catalytic activity at 227°C. When Au nanoparticles are dispersed on a titania support, acceptably high catalytic activity was evident at temperatures as low as 25°C. This fact shows that the support is clearly beneficial [42]. It is also important to note that the type of support used is influential in the nature of reactivity in Au nanoparticle catalyzing reactions. By way of illustration, oxidation of CO may be accomplished using AuNPs in combination with various supports such as TiO_2 and CaO, although acidic supports such as Al_2O_3 and activated carbon do not produce similar results. Research shows that in the cases of CO oxidation, $Mg(OH)_2$ is optimal support for Au at sub-ambient temperatures [43]; however, this undergoes deactivation after 3 months. The influence of the support in this instance is explained in terms of the structure of the modified catalyst.

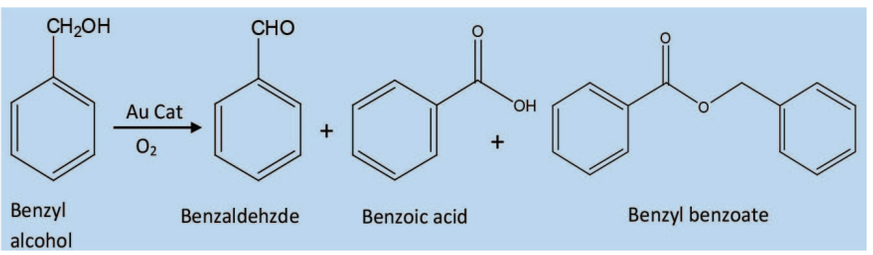
5. Own results

As mentioned elsewhere, support is highly influential on the catalytic activity/selectivity of AuNPs. It is important for the support to exhibit strong metal-support interaction (SMSI), an enhanced surface area, good thermal stability, and high dispersion of active sites that are able to effectively perform their reactive role [44]. This section examines the ways in which supported AuNPs may be used in cyclohexane (CH) to adipic acid (AA) oxidation, and benzyl alcohol (BA) to benzaldehyde (BAl) oxidation, respectively. The success of these reactions may be appraised by situating AuNPs on different types of metal oxide supports. Such supports are designed to deliver beneficial metal surface areas in addition to stabilizing the small AuNPs that have inherently high dispersion degree values [45]. The support material features, type of catalyst preparation, metal loading, and particle size are also important for obtaining enhanced catalytic performance. As a result of this, supported noble metals, for instance gold will exhibit catalytic characteristics that are significantly influenced by the support used [45]. In comparison with the performance of basic supports, acidic ones add to electron shortfalls in noble metals, and good SMSI performance is evident in metals with reducible oxide supports, such as TiO_2 and CeO_2 [44]. When interactivity between metallic components is vigorous, significantly enhanced catalytic activity is exhibited with respect to those catalysts consisting of just one type of metal, contrasting with the situation apparent in relatively inert irreducible oxides such as Al_2O_3 and SiO_2. This section considers five different kinds of supports, bearing in mind benefits resulting from the use of metal oxide supports. Each of these types of support has varying characteristics that include particle size, dispersion, and

performance. In the course of these examinations, benzyl alcohol and cyclohexane oxidation were carried out using five different supports. It should be noted that these reactions were tested in the liquid phase. The results emergent from these tests are set forth in the following paragraphs.

5.1. Oxidation of benzyl alcohol to benzaldehyde

The principles of "green" chemistry put great store by oxidation as the correct means by which chemical intermediates and fine chemicals characterized by enhanced selectivity are to be produced [46]. This is applicable in the context of this research to the oxidation of benzyl alcohol (BA) to produce benzaldehyde (BAl) (**Scheme 1**). The solution produced by this process is often found in pharmaceutical, agrochemical, and perfume-manufacturing applications. The reaction of benzyl alcohol and excessive ammonium permanganate or potassium in aqueous acidic medium may be used to form benzaldehyde (BAl). This process, however, produces appreciable quantities of toxic by-products, and so is problematic in terms of the environment. There have been attempts made to improve the process through the oxidation of benzyl alcohol with a green oxidant (e.g., H_2O_2 or O_2) and an organic solvent, and then applying catalysts such as Pd/C, Pd(II) hydrotalcite, Pd-Ag/pumice, Ru-Co-Al hydrotalcite, and Ni-containing hydrotalcite [47], but all these alternatives still involve the use of solvent, and hence their use is environmentally problematic. It is possible to perform solvent-free oxidation using tert-Butylhydroperoxide (TBHP) over MnO_4^{2-} exchanged hydrotalcite and a transition metal containing layered double hydroxides and/or mixed hydroxides, although this itself is not environmentally friendly as TBHP generates tert-butanol. If the process is to be clean and environmentally friendly, solvent use must be expunged from it and clean and economical molecular oxygen should be used as the oxidant. A process that uses Au/C catalysts to selectively oxidize alcohols and polyols has been developed by Prati et al. [48]. Rossi et al. claimed that gas-phase oxidation of volatile alcohols into aldehydes and ketones may be accomplished by the use of Au catalysts [49, 50]. Schuchardt et al. [51] developed a process that bears comparison with that of Rossi et al. [49] that succeeded in oxidizing glycerol to glyceric acid by the use of Au/graphite catalysts; this was accepted as a viable means that was fully selective in terms of the target output. The precise selectivity of Au/CeO_2 was also confirmed by Abad et al. [47], where benzyl alcohol is to be oxidized to produce benzaldehyde, Prati et al. [48] made use of supported Au on a TiO_2 catalyst [48]. Enache et al. [48] also explored selective oxidation performed by means of Au-Pd alloy particles supported on TiO_2. Ulti-



Scheme 1. Oxidation of benzyl alcohol with O_2 using supported AuNPs' catalysts. Reaction conditions: 30 mL BA, 0.15 g catalyst, 140°C, 5 bar O_2, 4 h.

mately, benzyl alcohol may be oxidized to benzaldehyde in an environmentally friendly and efficient way using molecular oxygen. This process additionally makes use of separable and recyclable supported gold nanoparticles over a variety of metal oxide supports to contribute enhanced end-product selectivity.

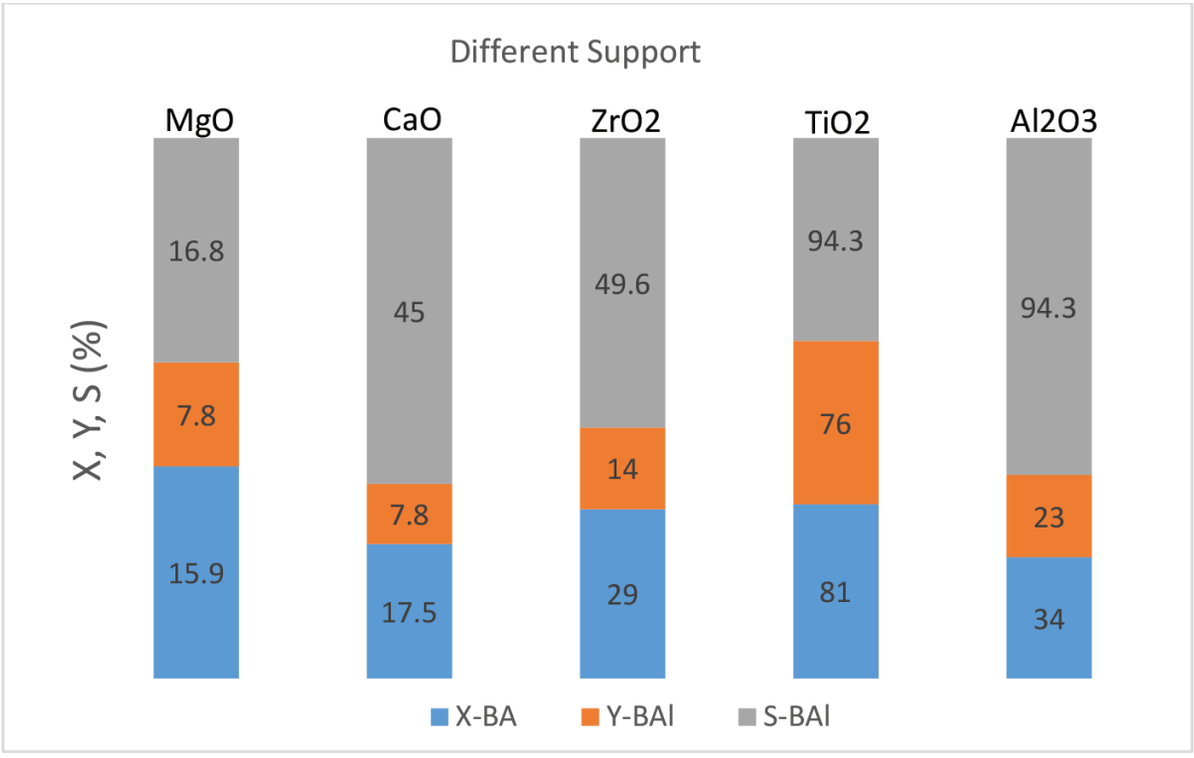


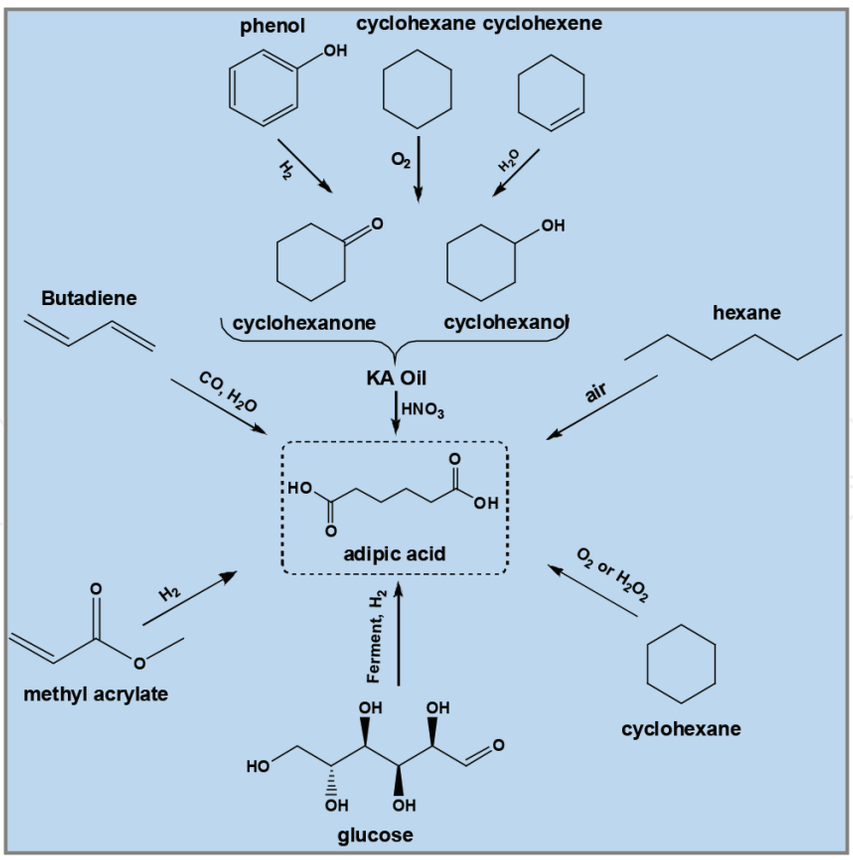
Figure 8. Influence of support on oxidation of benzyl alcohol to benzaldehyde over 1% Au/M catalysts (M = MgO, CaO, ZrO_2, TiO_2, Al_2O_3). Reaction conditions: 30 mL BA, 0.15 g catalyst, 140°C, 5 bar O_2, 4 h (X = conversion; Y = yield; S = selectivity).

Recent research has focused on the oxidation of benzyl alcohol in respect of its reactions to a variety of supported MNPs such as Au nanoparticles on a variety of metal oxide carriers [49]. For this purpose, different oxide supports (MgO, CaO, ZrO_2, TiO_2, Al_2O_3) were used for AuNPs that were prepared using impregnation method [49]. A number of spectroscopic and microscopic methods were used to characterize these catalysts and acquire information concerning their individual characteristics. The catalytic performance of supported AuNPs was appraised using solvent-free oxidation of benzyl alcohol using oxygen (5 bar) as an oxidant in a Parr autoclave reactor set to a reaction temperature of 140°C. It was shown that Au catalyst performance is found to depend significantly on the type of support used, as shown in **Figure 8**. While BAl is the principal product to emerge from this process, at the same time, some by-products were also formed. However, they are estimated to be in small quantities, e.g., benzyl benzoate, benzoic acid, and acetal. The production of benzyl benzoate was the result of additional esterification reactions arising from the presence of benzoic acid and benzyl alcohol. Benzoic acid production is a natural consequence of benzaldehyde overoxidation, and acetal production is a consequence of benzyl alcohol nonreaction and resultant formation as

hemiacetal, which ultimately forms acetal by protonation and deprotonation reactions. The production of acetal in this instance was very small or negligible. In this research the most active catalyst was TiO_2-supported AuNPs (at X-BA = 81%), and the least active catalyst was MgO-supported AuNPs (at X-BA = 16% and S-BAl = 17%) as shown in **Figure 8**. The superior performance of the former is the result of a number of factors including the high dispersion of Au, smaller Au size, and a relatively high surface enrichment of Au. These results were wholly negated in the instance of an inferior catalyst. These results have been subjected to validation by TEM and XPS.

5.2. Oxidation of cyclohexane to adipic acid

The synthesis of dicarboxylic acids from cycloaliphatic hydrocarbons has many applications in industry that include the generation of adipic acid (AA) from cyclohexane (CH) (**Scheme 2**). The production of polyamides, for example, nylon, and others include plasticizers, for example, PVS, and carpets, polyurethane and polyester of various types also make use of this process. It also finds application in the production of agrochemical pest controls [50], the pharmaceutical industry, medicine manufacture, and others. Producing AA commercially is accomplished by means of two stages. The first step involves oxidizing CH to produce cyclohexanone (−One) and cyclohexanol (−Ol), which is achieved by a process using ketone and alcohol, known as "KA-oil", which operationalizes a cobalt or manganese catalyst at a



Scheme 2. Summary of the different pathways for AA production.

pressure between 10 and 20 bar at a temperature of approximately 150°C. The second stage produces AA from the KA-oil of the first stage by the application of nitric acid, as an oxidant [51]. This is the most generally favored means of manufacturing AA commercially, although it involves recycling in excess of 90% of the unreacted cyclohexane. This process operates at low conversion rate of only between 5 and 10%. This conversion rate is kept low to achieve enhanced KA product selectivity of around 70–85%. The aforementioned recycling is expensive and raises questions of environmental unfriendliness with regards to the second stage use of nitric acid and the consequent production of NOx, which is instrumental in respect of undesirable environmental effects that include smog, acid rain, and damage to the atmosphere's ozone layer. Hence there is a real need for research into environmentally friendly way of AA production. An important aspect of this research concerns the discovery of environmentally friendly means of using AuNP catalysts. Keeping this aspect in view, some options are presented here (**Scheme 2**). While a number of potential options are available, the direct, single-stage synthesis of CH to produce AA using O_2 is the desired solution from the perspectives of both the environmental and commercial viability.

This research considers the oxidation of AA from cyclohexane, together with the resultant catalytic activity, as well as the oxidation of benzaldehyde from benzyl alcohol using supported AuNPs. The catalysts used in this process are considered in the following section. Before carrying out the catalytic tests, a number of blank tests were performed under similar conditions to establish whether CH oxidation will take place without a catalyst or TBHP being present, especially in respect of a radical mechanism. These blank tests, conducted without a catalyst but with TBHP, and also without both (a catalyst and TBHP), exhibited negligible instances of CH conversion (merely ~2% after 4 h of reaction) and no AA was discernible within the product output. This outcome shows that (i) no significant reaction occurs in these conditions and (ii) the type of catalyst is significantly influential in terms of performance [50]. Support influence in respect of AuNPs' catalytic performance was initially appraised; **Figure 9** shows the results obtained. These results demonstrate that the type of support used is indeed a key performance indicator in achieving acceptably high CH conversion and product selectivity. It should be noted that small amounts of some by-products such as cyclohexylhydroperoxide, CO and CO_2, glutaric acid, succinic acid were also formed. It was found that from all of the tests performed, AuNPs supported on TiO_2 delivered the best performance in respect of CH conversion and AA production. This was due to the presence of the smallest AuNPs and their enhanced dispersion over this support. In consequence of this result, it is possible to reaffirm the need for small AuNPs and their important influence on AuNPs' catalyst performance. CH conversion and AA selectivity achieved using a TiO_2 supported catalyst were 16.4 and 21.6%, respectively. The resultant by-products from this reaction are cyclohexanone and cyclohexanol, and their overall selectivity varies between 45 and 70%. This selectivity is, however, contingent upon the reaction conditions and the type of catalyst support used. Among all of the catalysts, the MgO and CaO supported solids have shown the poor performance, and the largest quantities of unwanted by-products including CO and CO_2 (total selectivity of up to 35%) were found over these supports. On this basis, MgO and CaO may be considered as inappropriate supports for this reaction. Concerning AA selectivity, performances obtained in decreasing order are as follows: $TiO_2 > Al_2O_3 > ZrO_2 > MgO > CaO$.

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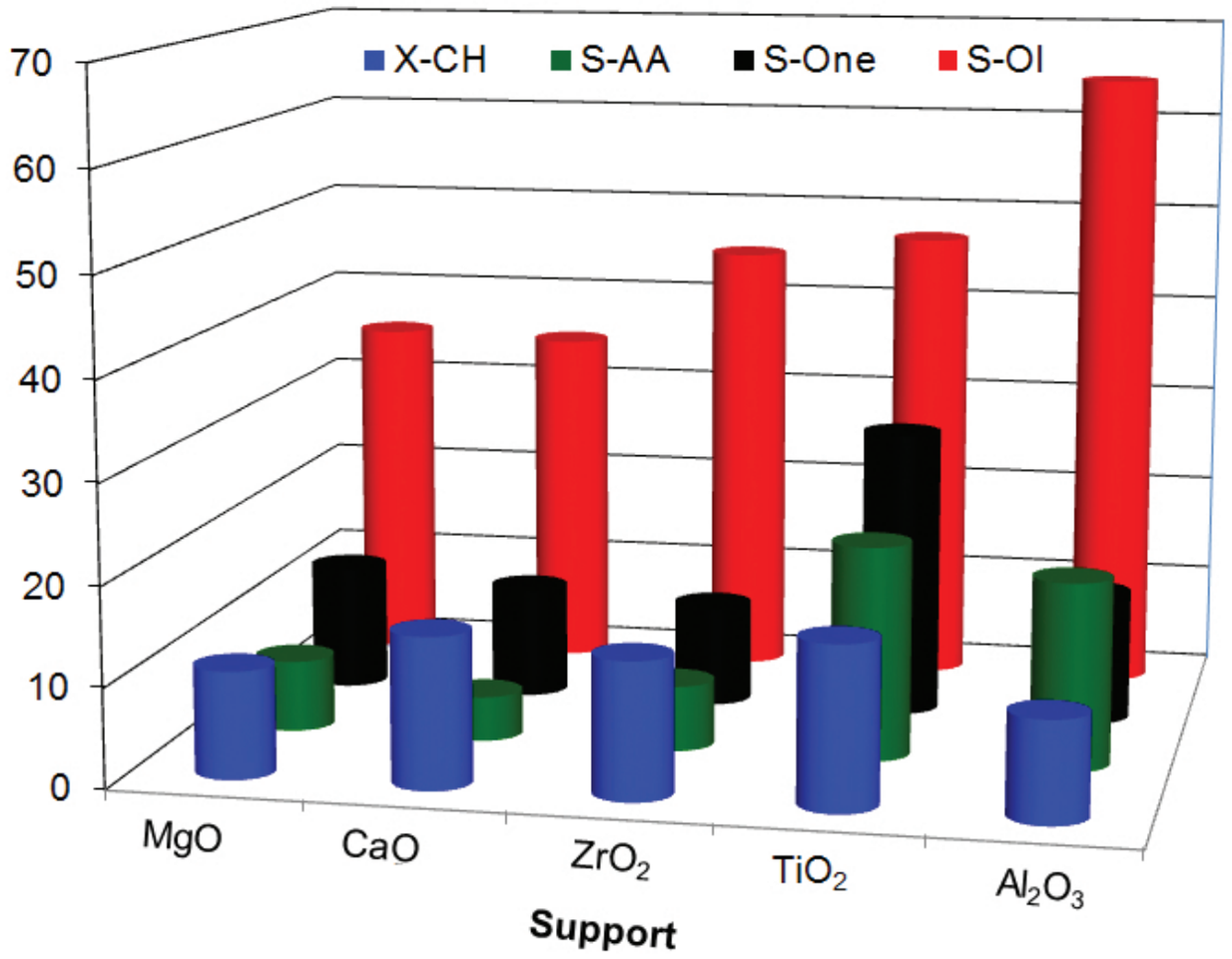


Figure 9. Effect of different oxide support on the oxidation of cyclohexane over Au/X catalysts (X = MgO, CaO, ZrO_2, TiO_2, Al_2O_3). Reaction conditions: (10 ml CH, 20 ml solvent, 0.3 g catalyst, 0.1 g TBHP, pO_2 = 10 bar, *t* = 4 h, 1500 rpm, *T* = 130 °C). X-CH = conversion of cyclohexane; S-AA = selectivity of cyclohexane; S-One = selectivity of cyclohexanone; S-Ol = selectivity of cyclohexanol [50].

The influence of reaction temperature on catalytic performance was examined in this research, and the results are depicted in **Figure 10**. This shows that temperature is positively influential in CH conversion, with an enhancement from 2.4 to 28% as the temperature is increased from 100°C to 170°C. AA selectivity also increased from 6 to 26% as the temperature was increased to 150°C. This then remained mostly constant even when the reaction temperature was further increased to 170°C. Cyclohexanol constituted the primary product at low reaction temperatures (S-Ol = 66.5% at 100°C), suggesting that "-Ol" was the primary reaction product. As the temperature was increased, however, the oxidation process rate increased, which consequently increased the conversion of "-Ol" to "-One" and then to AA. As a result, AA selectivity improved as the temperature rose to 150°C. Increasing the temperature to 170°C caused decline in the production of desired products and enhanced the production of the undesirable ones – primarily those resulting from total oxidation – so it is evident that 150°C is the temperature at which the optimal balance of desired product selectivity and efficient conversion is achieved. In consequence of this, 150°C has been selected as the temperature for further research. In

respect of other influences on the reaction including, catalyst amount, reaction time, stirring speed, and reaction pressure, these were appraised and the resultant findings have been reported elsewhere [50].

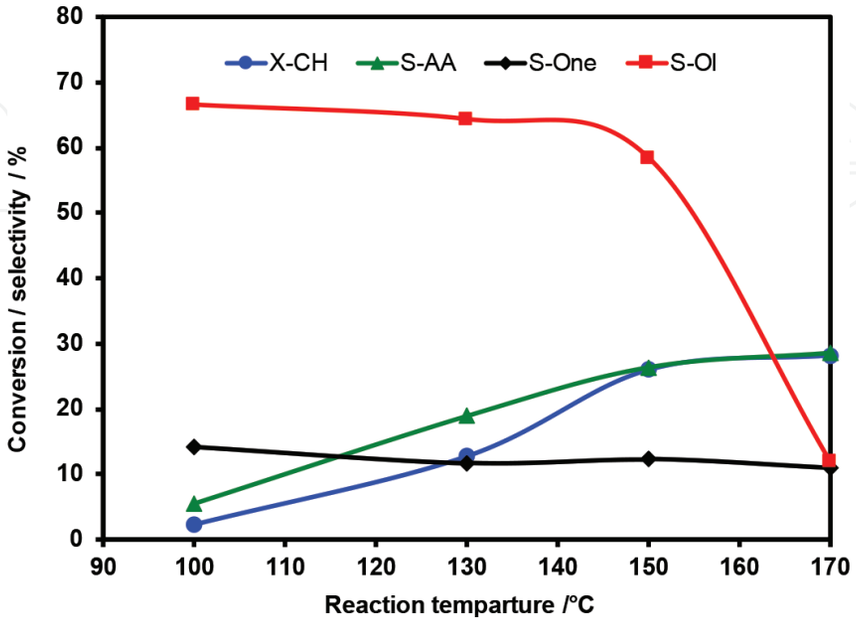


Figure 10. Effect of the reaction temperature on the oxidation of cyclohexane over Au/TiO_2 catalyst; reaction conditions are similar to the ones given in **Figure 9** [50].

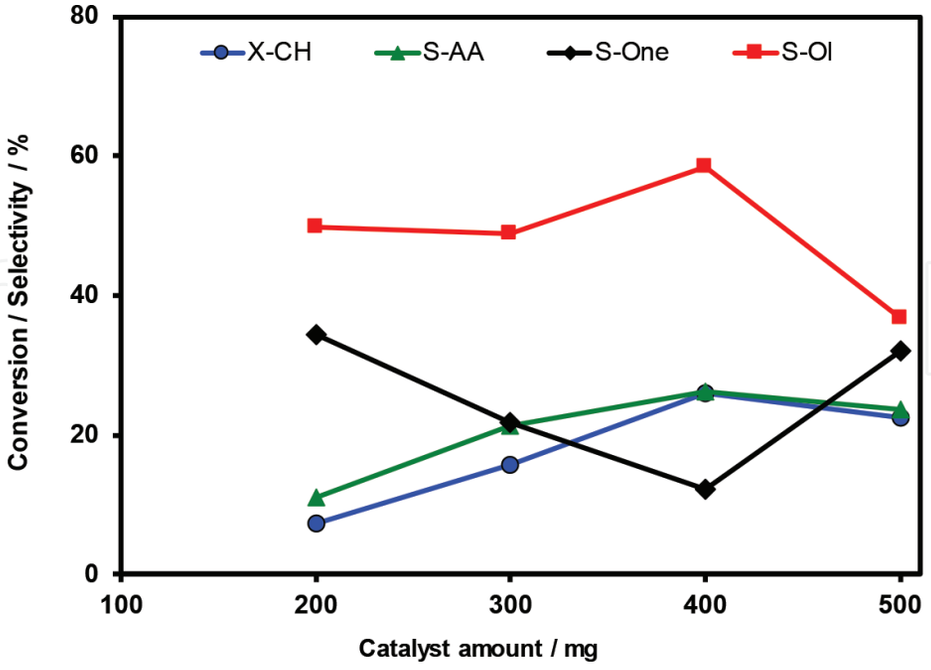


Figure 11. Effect of catalyst amount on the oxidation of cyclohexane over Au/TiO_2 catalyst; reaction conditions are the same as given in **Figure 9** [50].

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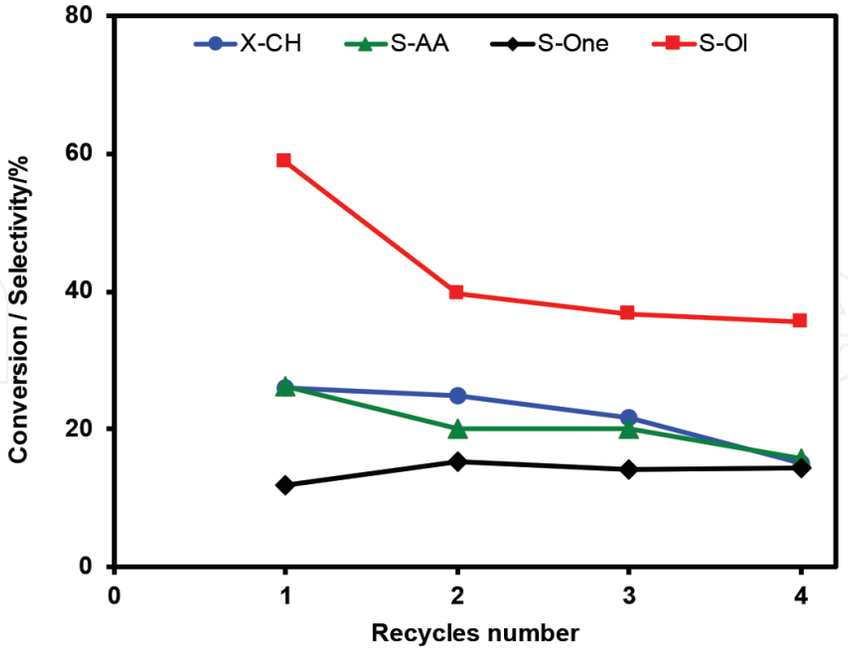


Figure 12. Recycling results of Au/TiO_2 catalyst for the oxidation reaction of cyclohexane; reaction conditions are the same as given in **Figure 9**.

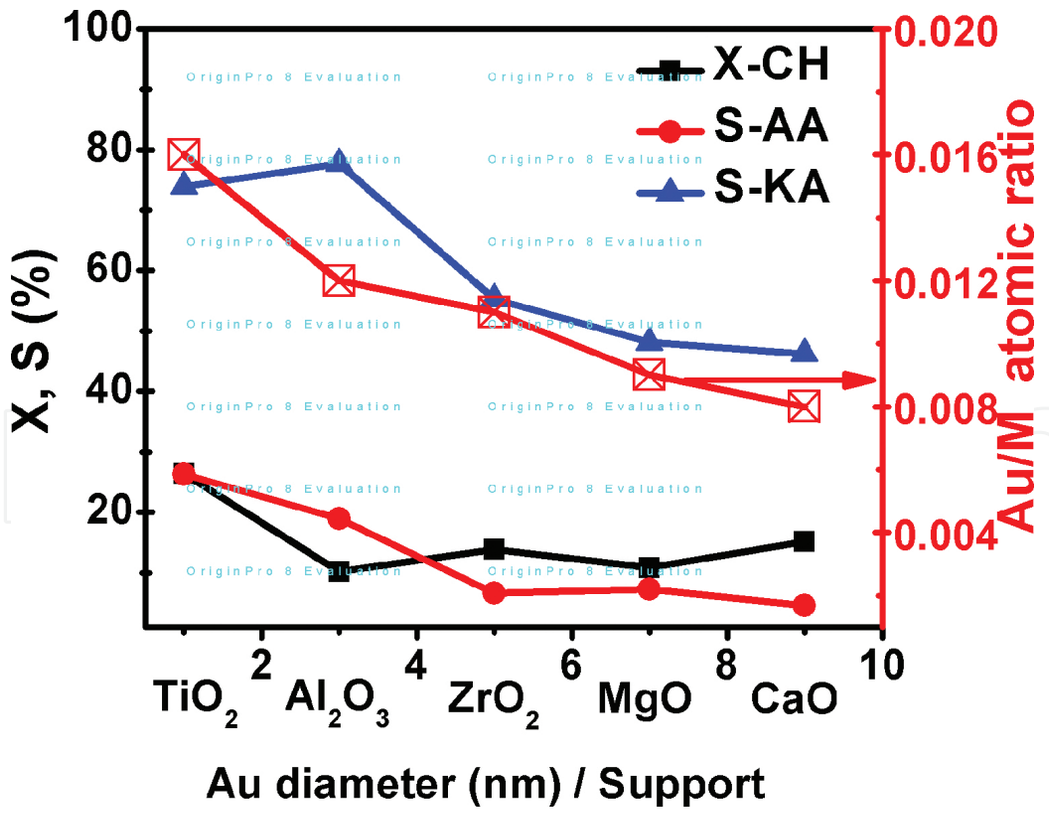


Figure 13. Correlation between cyclohexane conversion (X-CH), selectivity to adipic acid (S-AA) and to KA oil (S-KA) and catalyst properties of supported AuNPs.

This outcome shows that AA production results from cyclohexanone overoxidation. Additionally, "-Ol" selectivity changes between 46 and 58% as the catalyst quantity is increased from 200 to 400 mg (**Figure 11**). Amount of catalyst used has also shown significant influence on the catalytic performance. Usage of relatively high amount of catalyst (500 mg) results in a decrease of "-Ol" selectivity and an increase in "-One" selectivity. "-Ol" oxidation, therefore, produces "-One" by means of a simple oxidation process. It is, however, evident that this relatively high catalyst quantity produced deleterious influence in terms of performance, leading to consequent deterioration in selectivity for the desired products and increased selectivity in respect of unwanted by-products. This research indicates that a catalyst quantity of 400 mg achieves optimal performance.

To establish how stable and reusable the catalyst was, a number of recycling and catalyst washing experiments were conducted using the best catalyst identified from previous tests (i.e., 1% Au/TiO_2). The results of these experiments are shown in **Figure 12**. After the initial experiment, the catalyst was filtered, washed, and dried at 120°C and then a second experiment was conducted using the same reaction conditions. This process was repeated until a total of four such experiments had been completed. A small deterioration in CH conversion was noted for the catalyst that had been subjected to the whole experiment process. It is notable that "-Ol" selectivity decreased for catalyst tested between the first and second experiments; thereafter its performance was more or less constant. In summary, the catalyst's effectiveness deteriorated somewhat as a result of the four experimental cycles, which could be the result of leaching, deactivation, or marginal loss of catalyst arising due to work up process. Between experiments a small loss of catalyst weight was also observed. Analysis by XPS of the pre- and post-experiment cycle catalyst revealed a degree of Au loss, which is believed to be due to leaching. Also, TEM analysis of the post-experiment cycle catalyst suggested that agglomeration had taken place and that the AuNPs' dimensions were inconsistent.

This research also examined whether the superior performance of the TiO_2-supported catalyst could be correlated to that of other materials. Interestingly good correlations were found between AuNPs' dimensions (from TEM), surface Au-to-support atomic ratio (Au/SU) obtained from XPS and catalytic performance, which is illustrated in **Figure 13**. The results obtained correlate significantly with AuNPs' size, and hence CH conversion and AA selectivity vary largely according to AuNPs' dimensions. As expected, the small AuNPs performed better than the larger ones. CH conversion decreased from 26% on TiO_2 supported AuNPs to 9% on CaO-supported AuNPs, while the AuNPs' diameter increased from ca. 2 nm (TiO_2) to 6–8 nm (CaO). The XPS results also indicated that performance is enhanced as Au is enriched at the near-surface area. TiO_2-supported AuNPs exhibited the comparatively highest surface Au/SU atomic ratios (SU = different supports) and therefore exhibited the most superior performance. Also, the superior qualities of TiO_2 are indicated by high Au dispersion and a highly active Au metal area. It is, therefore, clearly indicated that the TiO_2 superior performance is undoubtedly dependent upon small AuNPs' dimensions, high Au enrichment in the near-surface-region, high dispersion, and a higher active metal area. Other influences including, inter alia, surface acidity and reducibility cannot be disregarded. Further research needs to be done yet to ascertain the effect of these influences in a more precise way.

6. Conclusions

Nanoscience and nanotechnology are driven by the ambition of fabricating new materials with improved properties and their further application in different sectors. Metal nanoparticles in particular have been the subject matter of immense interest in recent times due to their unique and extensive applications in various fields including catalysis. The gold nanoparticles (AuNPs) can be applied either in the form of colloidal gold nanoparticles or supported nanoparticles in the form of powdered solid catalysts. Catalytic properties of AuNPs strongly depend on their size, shape, morphology, etc. A comprehensive investigation on the formation mechanism of gold nanoparticles (AuNPs) in colloidal mixture obtained from the reduction of chloroauric acid ($HAuCl_4$) solution using a single reducing agent (e.g., sodium citrate and tannic acid) or a combination of two reducing agents (e.g., sodium citrate plus tannic acid) is possible. It is also possible to monitor the growth steps of AuNPs at different time intervals during synthesis either through in-situ and/or ex-situ methods. Besides the small particle size, atomic flexibility of metal clusters can also play a vital role on the adsorption and catalysis. The measurement of changes in the surface plasmon band position of colloidal AuNPs, along with dynamic light scattering results provide important information on the particle size, shape, and distribution. Besides, the size and morphological changes at different stages during different processes can also be analyzed by transmission electron microscopy. The Au particles exhibit different shapes (spherical and nanowires) with varying particle size and nanowire diameter that depends strongly on the method of preparation and nature of reducing agent applied. In our study, the combination of two reductants surprisingly led to a drastically reduced size (ca. 3 nm) with spherical morphology compared to their parent solutions with either of single reducing agent. This result clearly indicates that the combination of reductants has a significant influence on the particle size, morphology, and formation mechanism.

On the other hand, highly dispersed metal nanoparticles on various catalyst supports are indeed an important class of heterogeneous catalysts that are being extensively used in various fields related to energy, environmental as well as chemical industries. The catalytic performance of nanoparticles in various catalytic reactions depends strongly on their size, shape, and the metal-support interactions. Dopants and surface modifiers can also play a key role on catalytic performance. Own investigations revealed that the nature of support exhibits strong influence on the catalytic performance. From our results on the direct oxidation of cyclohexane to adipic acid, the TiO_2 (anatase) support is found to display the best catalytic performance among other oxide supports applied. The best performance of TiO_2 is attributed to the formation of small AuNPs (2–3 nm), high dispersion of nanoparticles on its surface, high enrichment of Au in the near-surface-region, and high active metal area of Au over the support compared to others. Nonetheless, fully rational design of catalysts based on an atomic-level understanding of surface processes involved still remains highly challenging in the field of heterogeneous catalysis research. Scientists have to yet adopt and utilize surface science techniques to explore the elementary steps involved in heterogeneous catalysis particularly using gold nanoparticles. Furthermore, the discovery and subsequent research efforts should focus on improving the fundamental understanding on the dynamics of formation mechanism

of nanostructured AuNPs and extend their applications into different areas beyond catalysis such as biomedicine, optics, and electronics.

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