

Review

# Heterogeneous Gold Catalysis: From Discovery to Applications

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Received: 25 March 2019; Accepted: 22 April 2019; Published: 29 April 2019



**Abstract:** In the present review, the important and current developments of gold catalysts for a wide range of applications are comprehensively summarized. This review also provides a detailed study of the literature data concerning the preparation, characterization, and catalytic applications of gold catalysts. Additionally, the main aspects of using supported gold nanoparticles (AuNPs) as catalysts for oxidation reactions are considered. In particular, the oxidation of benzyl alcohol to benzaldehyde and the production of adipic acid from cyclohexane are discussed in detail. Lastly, the key properties of gold catalysts are described, and an outlook on the application of gold catalysts is presented.

**Keywords:** gold nanoparticles; support effects; oxidation reactions; cyclohexane; adipic acid

## 1. Introduction

The first significant developments of gold catalysts are known since 1965 when the German company Knapsack produced vinyl acetate through the oxidative acetoxylation of ethylene [1]. In 1973, Bond and Sermon conducted the hydrogenation of 1-pentene using gold catalysts [2]. Three decades later, the knowledge of gold catalysts took an enormous step when Haruta [3] and Hutchings [4] groups presented their AuNPs supported on activated carbon for the oxidation of carbon monoxide (CO) and the hydrochlorination of acetylene, respectively. Later, 1998 is certainly one of the most important years in the history of gold catalysts when Prati and Rossi demonstrated the selective oxidation of alcohols using supported AuNPs in the presence of oxygen [5]. Later on, Hutchings and co-workers showed that supported gold could be used for the direct synthesis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) by reacting hydrogen with oxygen under non-explosive conditions [6]. Following such finding, Au catalysts were used for several valuable industrial processes toward sustainable chemistry such as the aerobic oxidation of methanol to the important chemical methylformate and basic raw chemicals for the synthesis of polymers [7,8]. The time has now lastly reached when gold catalysts are beginning to be effective materials for a wide range of applications, particularly in chemical and pharmaceutical industries. Figure 1 summarizes the historical development of gold catalysts over the past five decades.

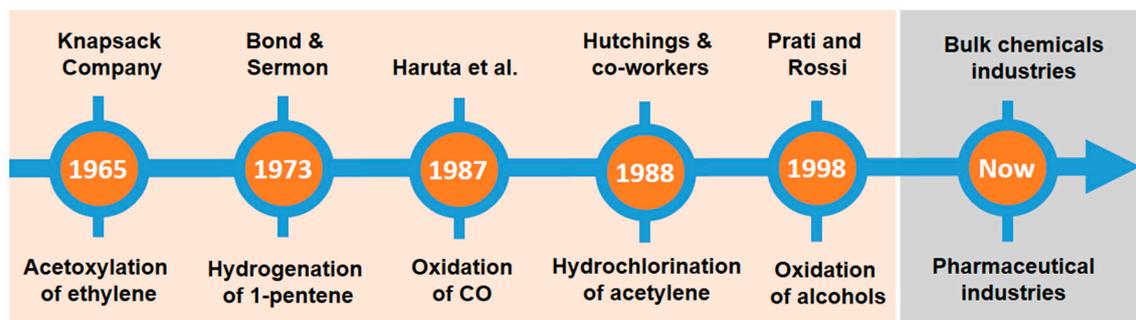


Figure 1. The historical development map of gold catalysts for the last five decades.

In the view of heterogeneous catalysis, supported metal nanoparticles (e.g., Au, Pt, Pd) plays an important role, not only with respect to an economic outlook but also are vital to impact our societal structure [9–11]. In particular, supported AuNPs occupy a substantial niche in the application of gold heterogeneous catalysis in many reactions including selective oxidation [3,12–16], hydrogenation [17–19], water-gas shift reaction [20–22], acetylene hydrochlorination [23,24], C–C coupling reactions [25–27] reduction of NO to N<sub>2</sub> [28,29] direct synthesis of H<sub>2</sub>O<sub>2</sub> [6] and several others [30–33]. The application of supported AuNPs is not limited to these areas. However, gold catalyst can be successfully applied as a potential catalyst for industrial applications including the catalytic combustion of hydrocarbons [19], hydrogen sulphide and sulfur dioxide removal, oxidative decomposition of dioxins [34], oxidative removal of mercury [35], ozone decomposition [36], reduction of NO<sub>x</sub> with propene, carbon monoxide or hydrogen [37], and epoxidation of olefins [38].

The very common question about gold catalysts is why Au particles make remarkably active catalysts? In evaluating the catalytic properties of group VIII metals in terms of the level of d-band vacancy, the group VIII elements gold (Au), silver (Ag), and copper (Cu) have conventionally been regarded as catalytically inert [39]. However, although the d-band is fully occupied in all three metals, Cu and Ag are characterized by relatively low ionization potentials compared to Au. Consequently, Cu and Ag can become catalytically active by losing electrons to generate d-band vacancies. Hence, Cu can be employed in several catalytic applications, such as the synthesis of methanol [40], and Ag can be used in the synthesis of ethylene oxide [41]. By contrast, the relatively high ionization energy of Au affords this metal little molecular attraction [42]. Early experimental research into the surface properties, along with computation of the associated density functions, indicated that dissociative adsorption of O<sub>2</sub> and H<sub>2</sub> onto the surface of Au does not occur at temperatures below 473 K. The catalysis of oxidation and hydrogenation reactions by Au would, therefore, not be anticipated and Au was not previously considered interesting in the field of catalysis [43]. Towards the end of the 1970s, however, Bond et al. [44] obtained promising results for the hydrogenation of alkenes and alkynes in the presence of AuNPs supported on SiO<sub>2</sub>. This prompted further studies in which oxidation in the presence of supported Au catalysts proved successful. Such investigations were the first to indicate the potentially enhanced catalytic activity of Au in the form of small metal nanoparticles, which is less than 5 nm. Haruta et al. [3] and Hutchings co-workers [45] continued this line of study into the 1980s to deliver two discoveries which significantly altered the research approaches to using gold catalysts for different applications. Clearly, these discoveries have shown the tremendous catalytic performance of Au in the hydrochlorination of acetylene [14,15] and the enhanced activity of supported AuNPs in low-temperature CO oxidation [28,46]. Recently discerned properties, such as these, strongly imply that Au might, after all, have a favorable potential in the field of heterogeneous catalysis.

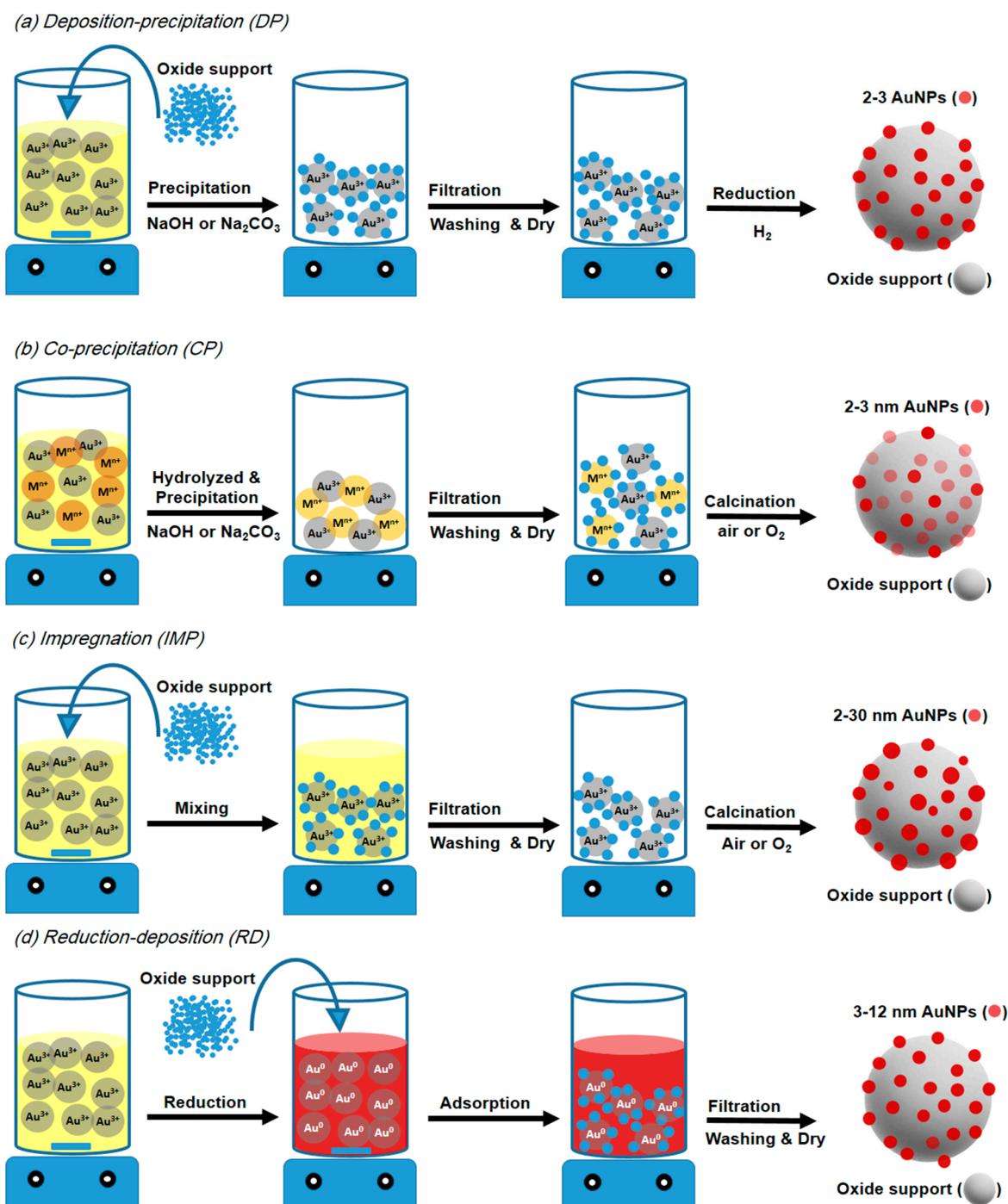
Additionally, the significance and the application of AuNPs in catalysis is further demonstrated by the recent rapid proliferation in academic papers discussing AuNPs. There were less than 100 such papers published during the 1980s, while close to 2500 papers were published during 2018. Since then, the number of new publications has continued unabatedly, thereby demonstrating beyond doubt the great significance of Au in catalysis. In addition, a number of books and comprehensive reviews on this subject have also appeared. Moreover, while few patents were sought prior to the 1990s, this activity has significantly increased to the present steady rate of approximately 4500 patents per year. The present review summarizes the recent advances of gold catalysts, including synthesis methods, properties and analysis methods, and their catalytic performance. Furthermore, the catalytic application is considered in detail to elaborate on the role of such metal in some selected oxidation reactions.

## 2. Synthesis and Stability of Gold Catalysts

### 2.1. Synthesis of Gold Catalysts

As discussed earlier, the size of AuNPs is considered to be a very critical factor for obtaining effective catalysts for several catalytic applications [47,48]. Prior to the right selection of the gold

catalyst composition, it is usually important to make sure, if the progress of reaction is affected by gold particles size. In addition, support is also a characteristic feature to obtain efficient gold catalysts [49–51]. Accordingly, the selection of the preparation method undoubtedly is crucial to the formation of high-performance gold catalysts [52–54]. In general, metal nanoparticles can be prepared using a variety of approaches including physical, chemical, biological, and hybrid techniques. Each method has some specific benefits and also disadvantages. The most common preparation methods of metal oxide supported AuNPs are deposition-precipitation, co-precipitation, impregnation, and reduction-deposition [55–57]. All methods are illustrated in Figure 2 and will be discussed in detail.



**Figure 2.** Schematic illustration of the preparation of gold catalyst via deposition-precipitation (a), co-precipitation (b), impregnation (c), and reduction-deposition (d) methods.

### 2.1.1. Deposition-Precipitation Method

The deposition–precipitation (DP) approach is among the most successful methods for achieving a high dispersion and uniform deposition of AuNPs on the oxide support [58–60]. The central characteristic of this technique is the way to control the pH value. The chosen oxide support is first added to a gold salt, for instance,  $\text{HAuCl}_4$  in aqueous solution, followed by addition of an alkali such as  $\text{Na}_2\text{CO}_3$ , or  $\text{NaOH}$  or urea, to adjust the pH of the solution in the range between 6 and 10. The oxide support adsorbs the resulting Au solution and the mixture is incubated under optimized conditions of temperature, concentration, stirring, and time. The resulting mixture is then subjected to repeated sequences of filtration, washing, and drying to obtain the dry solid material. A flow of  $\text{H}_2$  can be applied in order to convert the  $\text{Au}^{3+}$  ions to AuNPs [61]. The obtained AuNPs are mostly located on the surface of metal oxide carrier with a particle size of 2–3 nm. Since the DP method requires deposition in alkaline solution, it is appropriate for supports, such as  $\text{TiO}_2$ ,  $\text{CeO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , which have a point zero charge at  $\text{pH} \geq 6$ . On the other hand, well-dispersed, small-sized AuNPs cannot be obtained on supports, such as carbon or  $\text{SiO}_2$ , by this approach [62].

### 2.1.2. Co-precipitation Method

Like DP, the facile, single-step co-precipitation (CP) method uses an Au salt in aqueous solution [53,63,64]. The primary difference between CP and DP is the reaction mixture. In CP, the Au salt is mixed with a proper metal nitrate precursor under stirring at a specific temperature, followed by addition of a precipitant to yield a carbonate or hydroxide co-precipitate. The resulting slurry is then filtered, washed and dried prior to calcination of the mixture in air to yield the AuNPs. Although the resulting Au particles are uniformly dispersed, the particle size can increase during calcination, hence the size can be difficult to control. The obtained AuNPs using this method is mostly embedded in the metal hydroxide matrix with an average size of 2–3 nm. Thus, a small percentage of AuNPs will be on the surface of metal oxide. The CP method requires the support precursor compound to be carbonate or hydroxide, which can be precipitated with  $\text{Au}(\text{OH})_3$  at the deposition step [65].

### 2.1.3. Impregnation Method

The impregnation method (IMP) is widely used in catalyst synthesis due to its simplicity and low cost. A simplified version of the DP and CP methods is IMP. In this method, different types of metal oxide supports can be used and there is no need to adjust the pH [66]. The dried support is added into the solution of dissolved Au salts, which is then subjected to filtration, washing and drying at an appropriate temperature prior to calcination of the resulting catalysts in a desired atmosphere (e.g., in a flow of  $\text{O}_2$  or  $\text{H}_2$ ) [67]. The AuNPs obtained from this approach have a wide size distribution ranging between 2 and 30 nm with many residual chlorides. The IMP is noticeably easier than DP or CP and finds wide use in industry, for example, to prepare Au nano-catalysts where the specific mechanical strength is a more important requisite than a high loading of the active component. However, IMP method has a difficulty to produce AuNPs with required size unless the support has a well-defined porous structure. In addition, the low proportion of active components is not favorable to catalytic reaction. Although this problem is frequently linked to the particle size and size distribution, there is evidence to suggest that the low activity of IMP products is due to the absence of any interaction between the AuNPs and the applied support. Moreover, since Au salt solutions generally have very low pH values, this approach is not appropriate for supports, such as  $\text{Al}_2\text{O}_3$  or  $\text{MgO}$ , which can dissolve in strongly acidic solutions [68].

### 2.1.4. Reduction-Deposition Method

The concept of the reduction-deposition method (RD) approach differs from that of the above-mentioned conventional methods. Instead of loading the support with AuNPs via sintering and reduction, an alternative method is first to reduce Au ions to colloidal AuNPs at the start using suitable

methods (e.g., the Brust-Schiffrin or Turkevich-Frens method). The in-situ reduction of Au ions can be conducted individually or in the presence of a metal oxide carrier. This leads to good control of the size of Au particles. The support is then impregnated into the resulting AuNPs, which are completely adsorbed by the support. Finally, the resulting metal oxide supported AuNPs material is subjected to several repeated sequences of filtration, washing, and drying. The crucial aspect of this approach is the adsorption of AuNPs by the support, which requires the support to have a large surface area, strong adsorption capacity, and tolerance towards washing to a sufficient level of cleanliness to prevent the aggregation of the AuNPs.

## 2.2. Stability of Gold Catalysts

Stability of gold catalysts has become a substantial focus of attention because of growing appreciation that the catalytic efficiency of Au particles is significantly dependent upon particle dimensions. Indeed, it was confirmed that as the particle size of Au increases, its catalytic performance decreases substantially for various organic reactions [69] and some others [70]. Nevertheless, the problem is that such small particles tend to increase in size during reactions, and hence, lose their unique properties gradually. In the most common approaches to producing gold catalysts, organic polymers and solid supports are commonly applied to enhance the stability of AuNPs against their aggregation, thus increasing their catalytic activities. Polyvinylpyrrolidone (PVP), polyvinylalcohol (PVA), or cetyltrimethylammonium bromide (CTAB) are the most used organic compounds for the stabilizing the gold particles [71]. Such AuNPs can be applied either directly as catalysts in liquid phase or deposited to the solid supports. For instance, Tsunoyama et al. [72] first claimed that AuNPs stabilized by PVP are found to be very active in the homocoupling reaction of phenylboronic acid in the presence of H<sub>2</sub>O. Alternatively, AuNPs can be obtained using solid supports during the synthesis of catalysts [73]. However, synthesis conditions may lead to the agglomeration of supported AuNPs. In this context, the selection of solid supports provides an excellent platform to disperse and stabilize the AuNPs.

## 3. Factors Affecting the Catalytic Activity of Gold Catalysts

The primary factors influencing the catalytic activity of gold catalysts toward various reactions are discussed in detail and summarised in Figure 3. These factors include particle size and shape of AuNPs, the preparation method, the nature of the metal carrier, the gold–carrier interactions, and the oxidation state of the gold catalyst. These factors are described below.

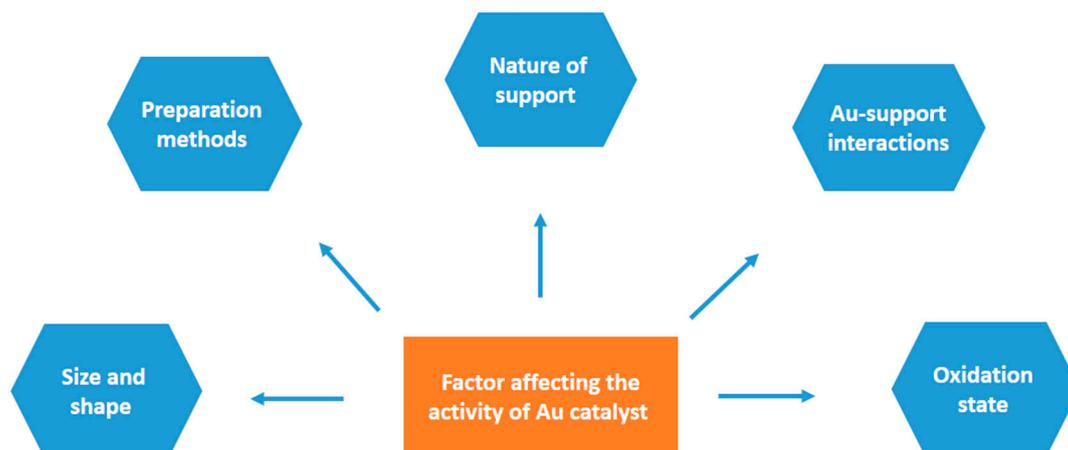


Figure 3. Factors affecting the catalytic activity of gold catalysts.

### 3.1. Effect of Gold Particle Size and Shape

Since the particle size and shape of AuNPs can be tailored to enhance the performance of metal-supported gold nanoparticles, the influence of particle size upon selectivity and catalytic activity has been extensively examined [74,75]. In general, the Au particle size should be below 5 nm in order to obtain an active gold catalyst. Many studies confirmed that the catalytic activity of Au catalyst rises as the average size of the Au particles becomes smaller and smaller [76–78]. Haruta and co-workers [79] made AuNPs supported on  $\text{TiO}_2$ ,  $\alpha\text{-Fe}_2\text{O}_3$ , and  $\text{Co}_3\text{O}_4$  and observed that the catalytic activity was enhanced drastically as the size of Au particle reached below 4 nm. They also further reported that the optimum size of Au particles should be approximately 3 nm in case of using  $\text{TiO}_2$  as support. Moreover, Goodman et al. [80] conducted a series of microscopic investigations and kinetics studies of CO oxidation using AuNPs supported on  $\text{TiO}_2$  (110) single crystal and  $\text{TiO}_2$  (001) thin film, synthesized by vapor-deposition method. They observed that the catalytic activity of such catalyst is linked to the size of Au cluster and the best activity was reported to coincide with the metal-to-nonmetal transition occurring when the size of Au is 3 nm. Hutchings et al. [81] also confirmed that the best catalytic activity of the oxidation of CO was achieved using Au/FeOOH catalyst in the presence of bilayer Au cluster with diameter less than 1 nm, which has about 10 atoms of Au. Nonetheless, ideal particle size for a catalytic system was presented in several studies. For example, Valden et al. [82] obtained AuNPs with Au particle size ranging between 1 and 6 nm supported on single-crystalline  $\text{TiO}_2$  surfaces. The catalytic activity of the CO oxidation was obtained when the size of Au particle was 2–4 nm. Laoufi et al. [83] reported that Au particle with 2.1 nm in size is optimum to have the greatest catalytic activity of CO oxidation. Furthermore, in CO oxidation and the epoxidation of propylene applying supported AuNPs, the size of AuNPs should be below 5 nm in order to enhance the catalytic activity and avoid any byproducts [84]. Various research groups claimed the particle size to be a determining factor in the performance of a catalyst [32]. Furthermore, the catalytic trend of multi-elements supported catalysts is known to extremely rely on the size of the metal particles and on their common interactions [85]. Consequently, Au/FeOx/ $\text{TiO}_2$  catalysts with small AuNPs have been tested toward the oxidation of toluene. Results clearly confirmed that the catalysts were found to be very active with great stability for total oxidation of toluene and highly stable under catalytic conditions.

Besides the size of Au particles, the catalytic efficiency of gold catalysts depends on the particle shapes [86,87]. It is expected that each shape of Au particles has a different configuration leading to different active sites and, therefore, a great influence on catalytic activity is predictable. For instance, Khalavka et al. [88] confirmed that nanorods Au particles exhibited high catalytic activity toward the reduction of p-nitrophenol compared to Au spheres, nanorods, and hollow spheres. Chiu et al. reported [89] that Au particles with anisotropic shape could be altered towards the reduction of para-nitroaniline (4-NA) due to modification in crystal surface. Jiji et al. also showed [90] that gold nanorods have a greater catalytic activity toward the reduction of 4-NA compared to dog bone and spherical AuNPs.

### 3.2. Effect of Gold Preparation Method

As discussed in the previous section, the catalytic activity of supported AuNPs catalysts is extremely dependent on the size of AuNPs. The preparation of supported AuNPs catalysts is certainly considered as a strategic aspect strongly affecting the size of AuNPs [32–34]. Among the various methods for the preparation of Au catalysts, the impregnation approach finds particularly frequent applications. This method involves impregnation of the support with AuNPs generated by the reduction of  $\text{HAuCl}_4$  and can produce an average Au nanoparticle diameter of around 2–30 nm. A major disadvantage of this approach is the presence of chloride ions derived from the Au precursor. Although a gas-phase grafting technique using monodispersed colloidal AuNPs stabilized by a suitable polymer can be used to avoid chloride ion contamination, this leads to AuNP particle size of over 10 nm, which is larger than optimum. Other approaches to generating Au catalysts with high levels

of activity include deposition–precipitation and co-precipitation. Grisel et al. [91] investigated the catalytic activity of AuNPs supported on  $\text{Al}_2\text{O}_3$  towards the total oxidation of  $\text{CH}_4$ . They concluded that catalyst prepared by deposition–precipitation approach showed better activity compared to the one obtained from impregnation approach. Such observation might be due to the presence of small Au particles. In addition, Andreeva et al. [92] studied the activity of vanadium promoted Au/CeO<sub>2</sub> catalysts synthesized through two different deposition–precipitation methods. The first one (DP) deals with the deposition of gold on a calcined CeO<sub>2</sub> and the second one (IMP) over a freshly precipitated cerium hydroxide. They found that catalysts obtained using the DP method are more active compared to the ones obtained by IMP due to the fact that Au remained incorporated into the bulk of CeO<sub>2</sub>. Such behavior leads to lowering the concentration of Au active centers. It can be concluded from previous discussion that the gold preparation method is very important to determine the catalytic behavior of gold catalysts.

### 3.3. Effect of the Nature of Support

One of the important properties of gold catalysis is that its catalytic behavior relies on the size and morphology of the metal particles and, consequently, supports play a vital role in the activity of the catalyst. There are numerous types of supports, such as zeolites, metal oxides, activated carbon, carbon nanotubes (CNT), polymers, metal organic framework (MOFs), that have been used to prevent the agglomeration of metal nanoparticles (e.g., AuNPs) during reactions [93–95]. Several studies have also indicated that the nature of the support and its interactions with the AuNPs influence the catalytic activity [96–98]. The support typically plays multiple roles, such as increasing the thermal stability of the catalyst and decreasing costs, as well as providing an increased surface area and a high level of dispersion of the active component. These characteristics are essential to the production of highly active and selective catalysts. For instance, the type of support used for CO oxidation usually depends on their ability to supply reactive oxygen: reducible materials, such as  $\text{Fe}_2\text{O}_3$ , CeO<sub>2</sub> and non-reducible supports such as  $\text{Al}_2\text{O}_3$ , MgO, and some others. It has been reported that AuNPs over a reducible oxides support shows better catalytic performance towards the oxidation of CO oxidation compared to the ones over non-reducible oxides support [99]. Some reports indicate that no catalytic activity towards CO oxidation at 227 °C was observed using either pure titania or pure AuNPs, however, dispersion of these AuNPs onto a titania support revealed sufficient level of catalytic activity even at 25 °C, which clearly demonstrates the beneficial effects of the support [100]. The specific type of support used has also been shown to influence the catalytic activity of Au nanoparticles. For instance, CO oxidation can be achieved using AuNPs with a range of supports (e.g., TiO<sub>2</sub> or CaO), similar results are not obtained using acidic supports, such as activated carbon or  $\text{Al}_2\text{O}_3$ . At ambient temperatures, the use of an  $\text{Mg}(\text{OH})_2$  support has been shown to be optimal for the oxidation of CO, although the support becomes deactivated after three months. The effect of the support in this example is attributed to the structure of the modified catalyst. Recently, MOFs have emerged as the new interface between heterogeneous catalysts and supramolecules. Tremendous thermal stability of MOFs and narrow pore size make them a great support for the stabilization of metal nanoparticles. The reviews reported by Zhang et al. and Corma et al. comprehensively provide the whole work on MOFs and their applications [101,102]. Additionally, the shape of support plays an important role in the behaviour of catalytic activity of the gold catalyst. Several investigations have suggested that a high concentration of  $\text{Ce}^{3+}$  ions on specific planes effectively improves the catalytic activities in various reactions [103,104]. In addition, the morphology of CeO<sub>2</sub> supports showed an important outcome on the activity of Au/CeO<sub>2</sub> catalysts in the WGS reaction [105]. Carltonbird et al. prepared different shape of CeO<sub>2</sub>, such as rod-, cube-, polyhedral- and octahedral-shapes and coated with AuNPs [106]. It has confirmed that different shapes of CeO<sub>2</sub> displayed different catalytic performance for the oxidation of carbon monoxide. Among all, the AuNPs supported on rod-shaped CeO<sub>2</sub> showed the best CO conversion level of 97.9% at 30 °C, whereas CeO<sub>2</sub> having octahedral shape gave the lowest CO conversion level of 27.7%.

### 3.4. Effect of Gold-Support Interaction

It is known that the metal–support interaction (MSI) is one of the important parameters in describing the catalytic properties of supported metal catalysts [107,108]. MSI was introduced to explain that TiO<sub>2</sub> considerably changed the catalyst properties of the supported metal nanoparticles [109,110]. In addition, the stability of the catalysts is generally influenced by MSI due to changes in the metal–support boundary sites that in turn can have a significant impact on the individual reaction steps, and hence, the overall catalytic activity of the catalysts. In fact, there are different mechanisms (e.g., charge transfer and spill over) that can explain how the MSI can affect the catalytic activity and selectivity. Different research groups have shown the importance and manipulation of MSI by various means. Overbury et al. [111] demonstrated that for equally sized AuNPs supported on SiO<sub>2</sub> and TiO<sub>2</sub>, the catalytic activity of TiO<sub>2</sub> supported AuNPs was higher than Au/SiO<sub>2</sub> which is due to stronger metal–support interaction. Yu et al. have claimed strong dependence of Au size on MSI in Au/TiO<sub>2</sub> catalysts [112]. Furthermore, high catalytic activity towards the water–gas shift reaction was shown for an Au/CeO<sub>x</sub>/TiO<sub>2</sub> catalyst [113]. The high catalytic activity was attributed to the chemical properties of Ce<sub>2</sub>O<sub>3</sub>, which was formed through the interaction with TiO<sub>2</sub> and its effect at the ceria–gold interfaces. Quite recently, Tang et al. confirmed that strong MSI between AuNPs and hydroxyapatite not only improved the sintering resistance of AuNPs upon calcination but also enhanced their selectivity and reusability in liquid phase reaction [114]. Furthermore, Bao et al. prepared highly dispersed Au overlayers supported on molybdenum carbide. Thus, strong interfacial charge transfer between metal and support leads to outstanding activity toward the low-temperature water-gas shift reaction [115]. Zhang et al. [116] demonstrated a new concept of wet-chemistry MSI creates AuNPs on titania. The strategic finding was to employ a redox interaction between Au<sup>δ+</sup> and Ti<sup>3+</sup> precursors in aqueous solution which, accelerates the CO oxidation due to the Au–TiO<sub>x</sub> interface. We believe that despite the significant amount of MSI investigations reported up-to-date, the mechanism and appearance of this effect still needs more discussion. Recently, carbon nanotubes (CNTs) have been applied as catalyst support and promoted noticeably the catalytic performance of catalysts in different applications due to their thermal conductivity, high surface area, and functionalizable surfaces [117,118]. In particular, the unique channels of CNTs are expected to deliver an interesting confinement environment for supported metal nanoparticles, which leads to an effective catalyst. For instance, Liu et al. reported that AuNPs supported on CNTs are photocatalytically active for the oxidation of cyclohexane (X= 14.64%) to high selectivity of 86.88% of cyclohexanol using air at room temperature [119]. Pan et al. [120] also reported that different CNTs could be connected AuNPs through the formation of imide linkage –(C=O) NH– in Au-MWNT conjugates using multiple steps and severe reaction condition.

### 3.5. Effect of Gold Oxidation State

The oxidation state of supported AuNPs, whether it is (Au<sup>0</sup>), Au(I) or Au(III) or, has been suggested to affect its catalytic performance, which is similar to the effect of catalytic properties of cationic Au complexes. Such types of oxidation states of gold remain a matter of great concern [121,122]. The main issue in resolving the oxidation states of the active Au species is linked with the efficiency and complexity of the Au complexes or supported AuNPs in different reactions. The present review delivers a critical discussion of the evidence regarding oxidation states of Au in supported AuNPs catalysts. However, Au complexes were also highlighted in some specific examples. For instance, Fukuda et al. reported [123] that Au<sup>3+</sup> salt was active for the intramolecular addition of an amine to an alkyne under mild conditions. Later on, they also observed that ketones were obtained by the hydration of alkynes using Au<sup>3+</sup> complex [124]. Yang et al. reported the use of Au(I) for the addition of phenols and carboxylic acids to olefins, shown by the conversion of 4-phenyl-1-butene to 4-phenyl-2-butene in toluene solution using Ph<sub>3</sub>PAuOTf catalyst (Ph is phenyl, OTf is trifluoromethanesulfonyloxy) [125]. Their reaction mechanism confirmed that Au(I) binds and activates the olefin for nucleophilic addition by using phenols or carboxylic acids followed by a proton-transfer step that affords the final product and regenerates the Au(I) catalyst.

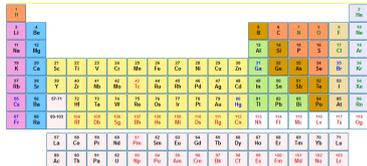
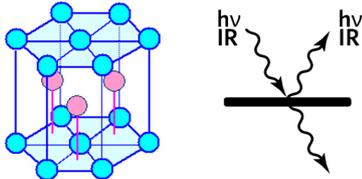
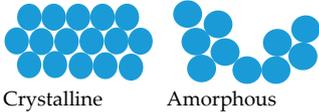
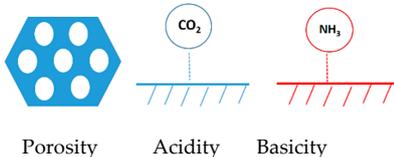
Regarding the oxidation states of supported AuNPs, it is very challenging to realize the exact mechanism involved in such reactions because the type of support also plays a significant role in the catalysis. In early studies, Hutchings et al. [24] showed that the hydrochlorination of acetylene to produce vinyl chloride using supported AuNPs was achieved by the metals capable of forming metastable complexes and Au(I) was the active species in this reaction. Moreover, the Au species can be detected by using X-ray photoelectron spectroscopy (XPS) through the deconvolution of the typical Au 4f<sub>7/2</sub> peak. Norskov and co-workers [126] reported that the Au atoms located on the corners and edges of supported AuNPs are considered to be the active sites. Conversely, the interaction between reversible Ce<sup>4+</sup>/Ce<sup>3+</sup> and Au<sup>3+</sup>/Au<sup>+</sup> reductions is supported by the high catalytic performance of Au/CeO<sub>2</sub>. In addition, it was assumed that the surface of TiO<sub>2</sub> contains Au<sup>+</sup> ions in the case of Au/TiO<sub>2</sub> is the main factor for the CO activation. The synergistic effect between AuNPs and the support plays an important role in obtaining an active gold catalyst, which could be enhanced by the formation of positive Au ions on the surface of nanoparticles. Louis et al. [127] also confirmed that Au species in the oxidic state (III) were obtained during the synthesis of AuNPs supported on TiO<sub>2</sub> using DP approach. They began to transform the Au metal ions to its metallic form under air at 100 and 150 °C using NaOH and urea, respectively, as precipitant. The Au particle size was found to be increased from 1.5 to 3.5 nm after the calcination process. Hence, the catalytic activity of the CO oxidation rose with increasing the fraction of metallic gold and reached the maximum after calcination at 200 °C. In addition, several other studies observed that oxidized Au species (i.e., Au<sup>δ+</sup>, Au<sup>1+</sup>, Au<sup>3+</sup>) is more active compared to Au<sup>0</sup> in case of CO oxidation e.g., [128–130]. In contrast, several literature reports claim that metallic gold (Au<sup>0</sup>) is highly active compared to other Au species. Haruta et al. disputed the role of oxidic Au on the grounds that most XPS findings indicated the presence of metallic gold in the most active gold-based systems [131]. Besides, IR-spectroscopic measurements examining the presence of cationic Au (Au<sup>+</sup>) and zerovalent Au (Au<sup>0</sup>) during CO oxidation indicate that the active site is composed of both species at the outer limit of the junction. Bond and Thompson [132] proposed different intermediate modules showing that both Au<sup>0</sup>, which adsorbs CO, and Au<sup>3+</sup>, which activates surface hydroxy groups for reaction with the adsorbed CO to form adsorbed carboxylate. Delannoy et al. [133] established that the activation of AuNPs supported on CeO<sub>2</sub> by H<sub>2</sub> at 300 °C leads to obtain highly efficient catalyst for the total combustion of propene, compared to the one activated under the mixture of O<sub>2</sub>/He at 500 °C. Zhang and co-workers [134] thoroughly investigated the importance of the presence of mixed gold valence states (i.e., Au<sup>0</sup> and Au<sup>3+</sup>) over Au/macroporous CeO<sub>2</sub>. They concluded that such Au species could be the main feature for the improvement of catalytic activity of these catalysts towards the oxidation of formaldehyde and the combustion of HCHO [134].

#### 4. Characterization Methods of Gold Catalysts

Due to the fact that the catalytic performance of supported AuNPs catalysts can be affected by a range of factors, including surface area, porosity, particle shape, size and morphology, the oxidation state of Au sites, crystallinity, aggregation, oxidation state, reducibility, acidity characteristics, and surface composition, an appropriate and in-depth characterization methods of the gold catalysts is required in order to have a complementary picture on how the above factors affect and control the reaction pathways of the gold catalyst and its reaction mechanism. Table 1 summarizes the broad range of characterization techniques applicable for examination and classification of the gold catalysts. These techniques can be used either in isolation or in combination to identify the characteristics of the gold catalysts. For example, various techniques including energy-dispersive X-ray spectroscopy (EDX), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray fluorescence (XRF) spectrometry can provide information regarding the elemental composition of the obtained catalyst. Meanwhile, techniques, such as vibrational spectroscopy, ultraviolet-visible spectroscopy (UV-vis) and neutron diffraction, can be employed to obtain data regarding the structural characteristics of the catalysts. Moreover, the gold catalyst's shape and size can be effectively characterized via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Finally, techniques, such as

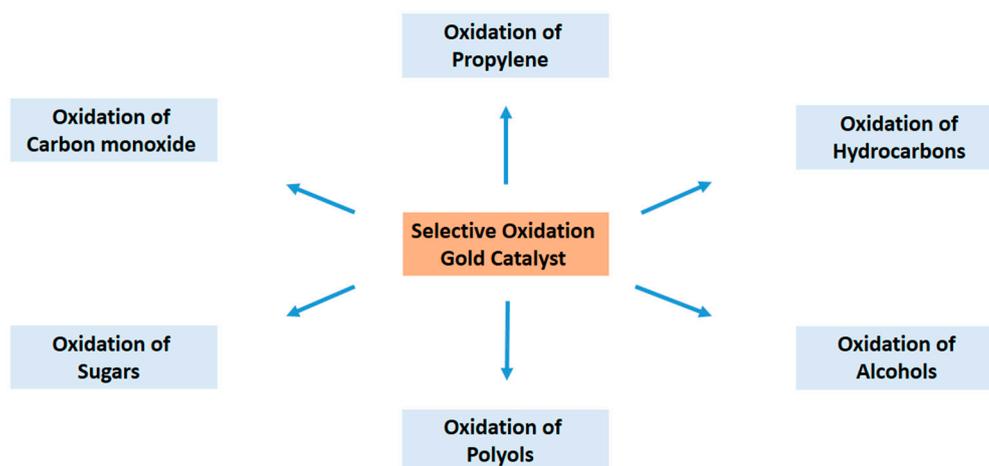
gas adsorption techniques, BET surface area analysis and X-ray photoelectron spectroscopy (XPS), can provide data on surface and textural properties of Au catalysts.

**Table 1.** Summary of some selected characterization techniques of gold catalysts.

Characteristics	Analysis Methods	Delivered Information
Element Composition	<ul style="list-style-type: none"> <li>Inductively coupled plasma (ICP)</li> <li>Energy-dispersive X-ray spectroscopy (EDX)</li> <li>X-ray fluorescent (XRF) &amp; CHNX analyzer</li> </ul>	
Structural Properties	<ul style="list-style-type: none"> <li>Ultraviolet–visible spectroscopy (UV-vis)</li> <li>Vibrational spectroscopy (FTIR + Raman)</li> <li>Neutron diffraction</li> </ul>	
Crystallinity	<ul style="list-style-type: none"> <li>X-ray diffraction</li> <li>Transmission electron microscopy (electron diffraction)</li> </ul>	
Size and Shape	<ul style="list-style-type: none"> <li>Transmission electron microscopy (TEM)</li> <li>Scanning electron microscopy (SEM)</li> <li>Dynamic light scattering</li> </ul>	
Surface & Textural Properties	<ul style="list-style-type: none"> <li>X-ray photoelectron spectroscopy (XPS)</li> <li>Chemisorption analysis</li> <li>BET surface area</li> </ul>	

## 5. Gold Catalysis in the Liquid Phase Application

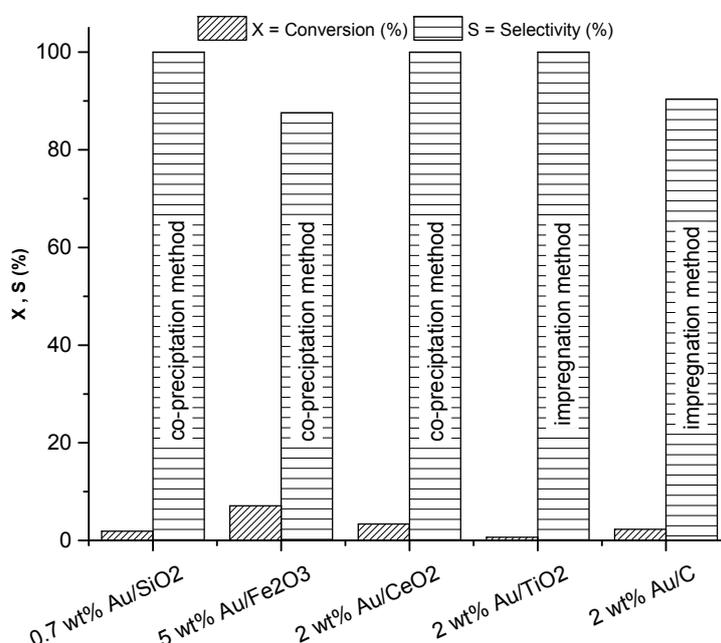
Supported AuNPs find application in a wide range of liquid- and/or gas-phase reactions (Figure 4), including oxidation [4–9], hydrogenation [10–12], the water-gas shift [12,13,15], and coupling reactions [19,20]. Since liquid-phase reactions are among the most important applications in the chemical and pharmaceutical industries [135], the present review will highlight some selected reactions in this aspect of catalysis. Usually, homogeneous catalysis by metal complexes in the presence of stoichiometric reagents has generally been used to achieve such reactions. Solid catalysts, which have various benefits, such as good separability and recyclability, have become favored in the drive towards enhanced sustainability. As noted previously, the catalytic activity and selectivity of the gold catalysts are greatly influenced by the size of gold particles, support, specific surface area and a maximal dispersion of active sites capable of efficiently accomplishing their catalytic tasks. The applications of gold catalysts in the oxidation of alcohols and cyclohexane are discussed in the present section. The effectiveness of these reactions can be evaluated by supporting the AuNPs on various kinds of metal oxide support designed to provide a favorable surface area and to stabilize the small AuNPs, which have intrinsically high levels of dispersion.



**Figure 4.** Some selected examples of the application of Au catalysts.

### 5.1. Oxidation of Alcohols to Benzaldehyde

Catalytic oxidation of alcohols to their corresponding aldehydes, ketones, and carboxylic acids are essential developments not only in energy conversion, but also cover other important areas, such as fine chemical and pharmaceutical industry. In general, different supported metal NPs, such as Pt, Pd, and Au catalysts, have been developed for such application [136]. However, there is still a need to develop new catalysts to facilitate the conversion of the reactants to the target products in order to make the catalytic systems environmentally friendly. Thus, due to their improved resistance to water and oxygen, and greater selectivity when the alcohol reactant contains more than one oxidizable group, the gold catalysts have gradually developed from this type of reaction. Selective oxidation of several alcohols is selected as a model reaction and will be discussed in detail.



**Figure 5.** Solvent-free oxidation of benzyl alcohol to benzaldehyde using Au catalysts. Reaction conditions: 40 ml alcohol, 0.2 g catalyst, 1500 rpm, 100 °C, O<sub>2</sub>=2 bar, 3 h.

The present review has systematically highlighted our previous work in the catalytic oxidation of benzyl alcohol in the liquid phase using supported AuNPs catalyst. Benzyl alcohol (BA) is one of the most considered substrates. Benzaldehyde (BAI) obtained from the selective oxidation of BA

is an industrially useful intermediate molecule in the food industry as a flavoring additive, as well as in the pharmaceutical and perfumery industries [137,138]. Besides, Pt- and Pd-based catalysts, supported AuNPs are also found to be effective catalysts to enhance the BA conversion and the benzaldehyde selectivity using O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>. The first work in this area was done by Prati et al. [139]. They verified for the first time that supported AuNPs can be applied to oxidize alcohols, diols, and polyols in the presence of a base. Several other groups confirmed that the presence of Au catalyst in this application has been shown to control the activity, selectivity, and durability of the catalyst. These studies concluded that the catalytic performance of the gold catalyst is dependent on different factors, such as the size and shape of metal particles and their physicochemical features. In addition, Enache et al. have investigated the solvent-free oxidation of BA to BAl using AuNPs supported on different carriers such as carbon, SiO<sub>2</sub>, CeO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>. They have studied the influence of the type of preparation methods (i.e., DP, CP, and IMP) on the catalytic oxidation of BA to BAl. As shown in Figure 5, AuNPs supported on CeO<sub>2</sub> displayed the highest catalytic activity (conversion = 3.4% and selectivity = 100%) compared to others. However, Au/Fe<sub>2</sub>O<sub>3</sub> showed somewhat higher conversion (7.1%) with low selectivity (87.6%).

**Table 2.** Oxidation of benzyl alcohol over supported AuNPs catalysts.

Catalyst	Au wt. (%)	Oxidant	T (°C)	Time (h)	Solvent	X (%)	Selectivity			Ref.
							BAL	BA	BB	
Au/MgO	7.5	O <sub>2</sub>	130	5	No solvent	51	86	-	14	[140]
Au/Cao	4.7	O <sub>2</sub>	130	5	No solvent	33.3	91.3	-	8.6	[98]
Au/Al <sub>2</sub> O <sub>3</sub>	6.4	O <sub>2</sub>	130	5	No solvent	68.9	56.0	-	35.0	[98]
Au/ZnO	6.6	O <sub>2</sub>	130	5	No solvent	40.5	92.8	-	7.2	[98]
Au/npCeO <sub>2</sub>	0.5	Air	90	2	No solvent	98	99	0	0	[141]
Au/TiO <sub>2</sub>	1.0	O <sub>2</sub>	160	6	No solvent	55	73.7	15.1	-	[142]
Au/TiO <sub>2</sub>	7.8	O <sub>2</sub>	100	8	p-Xylene	12	>99	0	0	[143]
Au/TiO <sub>2</sub>	7.8	O <sub>2</sub>	100	8	water	83	67	10	23	[101]
Au/TiO <sub>2</sub>	7.8	O <sub>2</sub>	100	8	No solvent	15	65	14	11	[101]
Au/MgO	2.6	O <sub>2</sub>	100	3	Methanol	100	8	-	6	[144]
Au <sub>PVA</sub> /TiO <sub>2</sub>	1.7	O <sub>2</sub>	100	1	No solvent	3	100	0	0	[145]
Au/Sr <sub>sup</sub>	2.0	O <sub>2</sub>	120	2.5	No solvent	16.2	73.1	26.9	0	[146]

Alshammari et al. [147] studied the influence of the nature of support (i.e., CaO, MgO, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>) on the catalytic oxidation of BA to BAl using AuNPs. Gold catalysts were evaluated on solvent-free oxidation of BA with oxygen (5 bar) as an oxidant in a Parr autoclave reactor at a reaction temperature of 140 °C. This study showed that the catalytic activity of supported AuNPs is strongly dependant on the nature of used metal oxide carriers. Among all studied catalysts, AuNPs supported on TiO<sub>2</sub> gave the best catalytic performance (X-BA=81% and S-BAl = 94.3%). On the other hand, MgO supported AuNPs was reported to be the least active catalyst (X-BA = 16% and S-BAl = 17%). As confirmed by different spectroscopic and microscopic methods, such high levels of catalytic performance are due to numerous reasons, including high dispersion of AuNPs, smaller Au size, and comparatively greater surface enrichment of Au.

Furthermore, studies have revealed that the activity and selectivity of gold catalyst can be enhanced by the addition of a second metal to Au. Especially, it has been claimed that the addition of Pd to Au lead to a significant enhancement of the catalytic activity, selectivity to BAl and durability of the catalyst in the BA oxidation. Dimitratos et al. [148] revealed that the presence of AuPd alloy supported on activated carbon showed a great selectivity (>94%) to BAl. A similar observation was also observed by Enache et al. using AuPdNPs supported on TiO<sub>2</sub> catalyst [149].

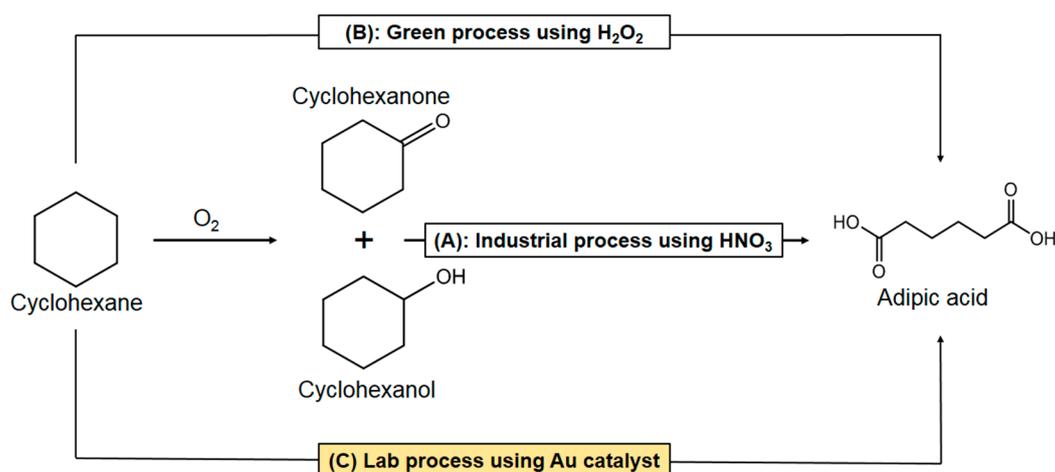
Hutchings et al. also broadly studied the effect of shape on AuNPs supported by TiO<sub>2</sub> towards the oxidation of BA [150]. TOFs values were observed from 14,270 h<sup>-1</sup> to 86,500 h<sup>-1</sup>, with increasing the reaction temperature from 383K to 433K. They concluded that such significant change in the catalytic performance is due to the formation of an Au-rich core/Pd-shell structure, with an electron promotion

effect of Au on Pd. Additionally, previous investigations using supported AuNPs in oxidation benzyl alcohol showed that an excellent selectivity can be achieved under mild conditions, as shown in Table 2.

### 5.2. Oxidation of Cyclohexane to Adipic Acid

Selective oxidation of cyclohexane to adipic acid (Figure 6) is a commercially important reaction in the polymer industry as it is a raw material to produce widely used nylon-6 and nylon-6,6. Furthermore, adipic acid is broadly used as an approved additive in different applications, such as in cosmetics, gelatins, lubricants, fertilizers, and adhesives [151]. The global production of adipic acid is reported to be more than 3.5 million metric tons with an annual growth rate of about 5% [152]. The industrial synthesis of adipic acid involves the following two steps: (i) cyclohexane is oxidised to the ketone (cyclohexanone) and the alcohol (cyclohexanol) and the resulting mixture, referred to as KA-oil, activates a manganese or cobalt catalyst at a temperature of around 150 °C and a pressure of 10–20 bar; (ii) usage of nitric acid as an oxidant generates adipic acid from the KA-oil [153,154]. To ensure an enhanced selectivity towards adipic acid (70–85%), the process is maintained at low conversion rates of 5–10 % and requires the recycling of over 90% unreacted cyclohexane. Although it remains a generally preferred industrial route to adipic acid production, the requisite recycling is costly and the use of nitric acid in the second stage presents unfavourable environmental issues due to the generation NO<sub>x</sub>, which is linked to acid rain, smog and damage to the ozone layer. Consequently, a genuine need for research exists in order to find a green route to adipic acid synthesis, including the development of environmentally friendly applications of supported AuNPs catalysts [155–157]. Although several potential options are available to produce adipic acid, such as oxidation of hexane and hydrogenation of methyl acrylate, the preferred solution in terms of both environmental and commercial practicality is the direct, single-stage oxidation of cyclohexane to adipic acid.

Yuan et al. established [158] a one-pot production of adipic acid by the oxidation of cyclohexane using Fe–porphyrin as a biomimetic catalyst. They produced 21.4% yield of adipic acid at 140 °C using O<sub>2</sub> as an oxidant. Lü et al. reported the production of adipic acid (AA) from cyclohexane using an aerobic catalytic system based on the Anderson-type catalyst with metal molybdenum as the central ion [159]. They recorded 87.1% selectivity for AA with conversion (10.2%) of CH. It also showed that the oxidative mechanism was a free radical process. Iwahama et al. [160] also improved the production of AA from CH using the radical catalyst, N-hydroxyphthalimide (NHPI), with a small amount of a transition metal. For instance, 73% of CH was converted to 73% of AA using atmospheric oxygen (1 atm) in the presence of NHPI (10 mol %) and Mn(acac)<sub>2</sub> (1 mol %) at 100 °C for 20 h.



**Figure 6.** Chemical methods of adipic acid production from cyclohexane. (A) industrial process using HNO<sub>3</sub>, (B) conversion of cyclohexane to adipic acid by using H<sub>2</sub>O<sub>2</sub>, (C) green route process using supported AuNPs catalyst.

Recently, other substrates for the green production of adipic acid have been studied, including cyclohexane [161,162], cyclohexene [163,164], cyclohexanone, and cyclohexanol [165,166]. In addition, Sato et al. [167] obtained adipic acid through the one-pot solventless oxidation of cyclohexene using  $\text{Na}_2\text{WO}_4$  catalyst in the presence of 30%  $\text{H}_2\text{O}_2$ . The overall adipic acid yield (93%) is very high. However, the toxic phase transfer catalyst and the use of a high amount of  $\text{H}_2\text{O}_2$  make this process uneconomical on an industrial scale. Usui et al. were consequently able to produce adipic acid with 78% yield through the oxidation of cyclohexanol using  $\text{H}_2\text{WO}_4$  catalysts in the presence of 30%  $\text{H}_2\text{O}_2$  at 90 °C for 20 h [168]. Nevertheless, this process has several drawbacks such as severe reaction conditions, the demand for phase transfer catalyst and high-energy consumption. Such drawbacks lower their potential to be applied at industrial level. Therefore, there is a need to develop an effective catalyst, eco-friendly, and low energy consumption route to produce adipic acid from cyclohexane.

Lately, Alshammari et al. reported [169] a novel gold catalyst to produce adipic acid in one-step from cyclohexane. In this study, AuNPs supported on different types of oxide carriers, such as CaO, MgO,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$ . The evaluation of this catalyst was conducted in a Parr reactor using acetonitrile as the solvent and TBHP as the initiator. The reaction was conducted at 150 °C and 1 MPa  $\text{O}_2$  for 4 h. The influence of the support upon the catalytic performance of the AuNPs was then evaluated to produce adipic acid with different selectivities. This confirms that the choice of support is a critical factor in catalytic performance, in determining product selectivity and in attaining a suitably enhanced conversion of cyclohexane. While certain minor by-products, including CO,  $\text{CO}_2$ , cyclohexyl hydroperoxide, glutaric acid, and succinic acid, were also produced, the primary by-products generated by this reaction are cyclohexanone and cyclohexanol. The overall selectivity of these two products typically varied in the range from 45% to 70%, depending upon the reaction conditions and the type of support applied. The full range of tests indicated that the optimum performance, with an adipic acid selectivity of 21.6% and a cyclohexane conversion of 16.4%, was obtained using the AuNPs on  $\text{TiO}_2$  support. This is attributed to the presence of the smallest AuNPs and an optimal dispersion, thereby confirming the requirement for small AuNPs and their significant impact upon catalytic performance. On the other hand, the CaO- and MgO-supported catalysts presented poor performance among all catalysts tested, with an overall selectivity of up to 35% and the greatest amounts of undesired by-products, such as CO and  $\text{CO}_2$ . This suggests that CaO and MgO should be regarded as unsuitable supports for this reaction. With respect to selectivity towards adipic acid, the observed catalytic performance decreased in the following order:  $\text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{ZrO}_2 > \text{MgO} > \text{CaO}$ . Furthermore, Yu et al. claimed [170] that AuNPs supported on multiwalled carbon nanotubes (CNTs) gave 45% conversion with 60% AA selectivity using 15 bar of  $\text{O}_2$  as an oxidant for over 8 h at 125 °C. Dai et al. reported [171] that AuNPs supported on carbon was found to be a greatly active catalyst for the cyclohexane oxidation with high conversion (44.9%) of CH and around 54.8% selectivity to AA. Other types of gold catalysts such as Au/ $\text{TiO}_2$ , Au/ $\text{Al}_2\text{O}_3$ , Au/MCM-41 have also been used to convert CH to AA. However, the main products were KA oil with very limited AA.

## 6. Conclusions

The broad and unique applications of gold catalysts in liquid- and gas-phase reactions have recently made this a topic of extreme importance. The performance of the gold catalysts is highly influenced by a wide range of factors including particle size and shape, as well as metal-support interactions. Nevertheless, superior catalytic activity has been demonstrated relative to catalysts based on other noble metals, such as Pd or Pt. Many attempts have been directed at developing an operational gold catalyst with enhanced stability. The present review has focused on various approaches to produce gold catalysts with distinct properties. Additionally, a brief discussion on the most effective tools (including a wide range of microscopic and spectroscopic techniques) for examining and explaining these catalytic properties are emphasized.

The present experimental study demonstrated that the catalytic performance is greatly influenced by the choice of support. For instance, the  $\text{TiO}_2$  (anatase) support exhibited the best performance

of all catalysts tested in the direct oxidation of cyclohexane to adipic acid. This is attributed to the presence of especially small (2–3 nm) AuNPs along with their high level of dispersion on the catalyst surface and significant near-surface enrichment of Au, giving a significant area of active metal over the support, relative to the others.

In general, the logical design of gold catalysts based on a detailed atomic-level conception of surface processes continues to attract significant research interest in heterogeneous catalysis. Further studies may consider the development of bi- or multi-functional catalysts, which could affect present applications or open up new ones. Moreover, logical approaches to sequencing a range of functionalities need to be designed in the near future in order to generate new and appealing environmentally sound nanostructured gold catalysts for a range of applications. In addition, the catalytic systems must be examined under realistic conditions. Since the majority of the examples mentioned herein involved the ex-situ examination of the gold catalysts, it is clear that further efforts should be directed to in-situ studies via methods including in-situ FTIR measurements, in-situ/operando extended X-ray absorption fine structure/X-ray absorption near edge structure (EXAFS/XANES) and environmental TEM.

**Funding:** This research received no external funding.

**Acknowledgments:** The author thanks King Abdulaziz City for Science and Technology (KACST) for support.

**Conflicts of Interest:** The author declares no conflict of interest.

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